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Some tests of scaling theory for a self-avoiding walk attached to a surface

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Abstract. We have defined analogues of the surface and layer susceptibilities of a semi-infinite magnetic system for the self-avoiding walk model of a polymer attached to a surface. Surface scaling relations between exponents appearing in the magnetic problem, as well as a recent renormalisation group exponent relationship, should apply to the self-avoiding walk case and we have generated extensive series expansions of the analogues of these susceptibilities for the square and simple cubic lattices. Our analyses of these series show that surface scaling holds for the self-avoiding walk problem in both two and three dimensions but that the renormalisation group argument gives incorrect values of the exponents in two dimensions.

1. Introduction

Recent interest in the excluded volume effect in polymer adsorption has resulted in a number of investigations of the properties of self-avoiding walks attached to a plane surface. One of the questions which has attracted attention is how the restriction of being attached to a surface in various ways will affect the asymptotic behaviour of the number of distinct self-avoiding walks. To be specific, consider self-avoiding walks on the cubic lattice confined to a half-space by a surface plane ($z = 0$) which we shall take to be a square lattice. Let $c_n^{(1)}$ be the number (per site of the square lattice) of n-step self-avoiding walks which have their first vertex in this plane, and which have no vertices with negative z coordinate, and $c_n^{(1,1)}$ be the corresponding number which have both vertices of unit degree in this plane and no vertices with negative z coordinate. (These quantities appear in, e.g., Silberberg's (1967) treatment of polymer adsorption.) If c_n is the number (per site of the cubic lattice) of self-avoiding n-step walks on the cubic lattice, Hammersley and Morton (1954) showed that the connective constant

$$\lim_{n\to\infty} n^{-1} \ln c_n = \ln \mu \tag{1.1}$$

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exists. Recently Whittington (1975) showed that

$$\lim_{n\to\infty} n^{-1} \ln c_n^{(1)} = \lim_{n\to\infty} n^{-1} \ln c_n^{(1,1)} = \ln \mu \tag{1.2}$$

so that the lattice has the same effective coordination number (μ) for these restricted walks as for unrestricted self-avoiding walks.

There is very good numerical evidence that

$$c_n \sim n^{\gamma-1}\mu^n \tag{1.3}$$

where γ depends only on the dimensionality of the lattice, and it is reasonable to assume a similar n dependence for $c_n^{(1)}$ and $c_n^{(1,1)}$ so that

$$c_n^{(1)} \sim n^{\gamma_1-1}\mu^n \tag{1.4}$$

and

$$c_n^{(1,1)} \sim n^{\gamma_{11}-1}\mu^n. \tag{1.5}$$

Assuming these asymptotic forms, Middlemiss and Whittington (1976) showed that

$$\gamma_1 \leqslant \tfrac{1}{2}(\gamma+1). \tag{1.6}$$

The value of γ is now well established to be $\frac{4}{3}$ in two dimensions, $\frac{7}{6}$ in three dimensions and 1 in four or higher dimensions (see, e.g., Domb 1970). There have been a number of attempts to estimate γ_1 in three dimensions, with estimates ranging from 0·68 to 0·715 (Lax 1974, Mark *et al* 1975, Middlemiss and Whittington 1976, Ma *et al* 1977) and there is a single estimate of γ_{11} for the tetrahedral lattice (Lax 1974). There do not appear to be any estimates for either exponent in two dimensions.

In this paper we report series for $c_n^{(1)}$ and $c_n^{(1,1)}$ for the square and cubic lattices and form estimates of γ_1 and γ_{11}. By means of the zero-spin-component limit we make contact with a surface scaling relation between these and other exponents and with a recent renormalisation group prediction of Bray and Moore (1977).

2. The zero-component limit for semi-infinite systems

The $D\to 0$ limit of D-component spin systems has been discussed by several authors, since de Gennes (1972) originally observed that the polymer problem could be approached in this way. Of these treatments one of the simplest is that due to Sarma, which appears in an appendix to Daoud *et al* (1975).

Consider a system of D-component spins

$$\boldsymbol{\sigma}_i = (\sigma_i^\alpha ; \alpha = 1, \ldots, D) \tag{2.1}$$

of fixed length

$$\|\boldsymbol{\sigma}_i\| = \left(\sum_{\alpha=1}^{D} (\sigma_i^\alpha)^2\right)^{1/2} = \sqrt{D} \tag{2.2}$$

located on the sites i of a d-dimensional lattice. We take the Hamiltonian to be

$$-\beta H = K \sum_{\langle ij\rangle} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + L \sum_i \sigma_i^1, \tag{2.3}$$

where the first sum runs over all nearest-neighbour bonds of the lattice and the second over all sites. Note that the magnetic field is taken to be in the direction '1' of spin space. Let

$$m(K, L) = \langle \sigma_i^1 \rangle \tag{2.4}$$

be the expectation value of the component of any spin parallel to the magnetic field L, then the zero-field susceptibility

$$\chi_0(K; D) = \lim_{L\to 0} \left(\frac{\partial m(K, L)}{\partial L} \right) = \sum_j \langle \sigma_i^1 \sigma_j^1 \rangle_0, \tag{2.5}$$

where the subscript 0 indicates that the expectation value is to be taken with respect to the Hamiltonian (2.3) with $L = 0$.

Sarma then considered the diagrammatic expansion of $\langle \sigma_i^1 \sigma_j^1 \rangle_0$ in powers of K and showed very directly that in the limit $D \to 0$ the only diagrams which contributed at order K^n are self-avoiding walks of n steps linking sites i and j. Hence he obtained the result that

$$\lim_{D\to 0} \chi(K; D) = C(K) = \sum_{n=0}^{\infty} c_n K^n, \qquad c_0 = 1, \tag{2.6}$$

where $C(K)$ is the generating function for n-step walks. The asymptotic behaviour (1.3) then implies that $C(K)$ has a singularity at $K = K_c = \mu^{-1}$ of the form

$$C(K) \sim A(1 - \mu K)^{-\gamma}, \tag{2.7}$$

analogous to the singularity in the susceptibility.

To discuss the problem of a self-avoiding walk near an interface, we consider the same magnetic model on a d-dimensional half-space bounded by a free surface, and allow an additional magnetic field L_1 (again in the '1' direction of spin space) to couple to spins in the surface layer. Let i denote any surface site and define

$$m_1(K; L, L_1) = \langle \sigma_i^1 \rangle. \tag{2.8}$$

Two different surface susceptibilities can now be defined (Binder and Hohenberg 1972, Barber 1973) by

$$\chi_1(K; D) = \lim_{L\to 0} \left(\frac{\partial m_1(K; L, L_1 = 0)}{\partial L} \right) \tag{2.9}$$

and

$$\chi_{11}(K; D) = \lim_{L_1\to 0} \left(\frac{\partial m_1(K; L = 0, L_1)}{\partial L_1} \right). \tag{2.10}$$

From these definitions, it is straightforward to show that

$$\chi_1(K; D) = \sum_j \langle \sigma_i \sigma_j \rangle_0 \tag{2.11}$$

where the sum runs over all sites of the half-space and

$$\chi_{11}(K; D) = \sum_j{}' \langle \sigma_i \sigma_j \rangle_0, \tag{2.12}$$

where the sum runs *only over surface sites.*

Following Sarma's arguments, we expand both χ_1 and χ_{11} as a diagrammatic expansion in K. In the limit $D \to 0$ we again find that the only diagrams at order K^n which survive are self-avoiding walks of n steps linking sites i and j. Hence we conclude that

$$\lim_{D \to 0} \chi_1(K; D) = C_1(K), \tag{2.13}$$

where $C_1(K)$ is the generating function for $c_n^{(1)}$,

$$C_1(K) = \sum_{n \geq 0} c_n^{(1)} K^n. \tag{2.14}$$

Similarly in the case of the diagrams arising from χ_{11}, which have their last vertex in the surface plane, we have

$$\lim_{D \to 0} \chi_{11}(K; D) = C_{11}(K), \tag{2.15}$$

with $C_{11}(K)$ defined by

$$C_{11}(K) = \sum_{n \geq 0} c_n^{(1,1)} K^n. \tag{2.16}$$

The required indices γ_1 and γ_{11} as defined in (1.4) and (1.5) are now seen, via (2.15) and (2.16), to be analogous to the critical exponents of χ_1 and χ_{11} at the bulk critical temperature K_c. The problem of critical phenomena in semi-infinite systems has, however, been studied in considerable detail in recent years. In particular, this work has established, to a large degree, the validity of the scaling theories of Barber (1973), Fisher (1973) and Binder and Hohenberg (1972).

According to this theory, all surface exponents can be expressed in terms of the bulk exponents and a new surface gap exponent Δ_1 which scales the surface magnetic field. Eliminating Δ_1 yields relations between the surface exponents. In particular, γ_1 and γ_{11} are related through

$$2\gamma_1 - \gamma_{11} = \gamma + \nu \tag{2.17}$$

where γ and ν are the exponents describing the divergence of the bulk susceptibility and correlation length respectively. In the limit $D \to 0$, these exponents correspond (de Gennes 1972) to the exponent γ defined in (1.3) and the exponent (ν) characterising the root-mean-square end-to-end length of a self-avoiding walk

$$R_n = \langle R_n^2 \rangle^{1/2} \sim n^{\nu}. \tag{2.18}$$

Although scaling gives rise to relationships between these exponents, it does not yield independent estimates of either γ_1 or γ_{11}. However, Bray and Moore (1977) have recently given a renormalisation group argument which predicts that

$$\gamma_{11} = \nu - 1. \tag{2.19}$$

Then (2.17) and (2.19) imply that

$$\gamma_1 = \nu + \tfrac{1}{2}(\gamma - 1). \tag{2.20}$$

Using the generally accepted values for γ and ν, that is, in two dimensions $\gamma = \frac{4}{3}$ and $\nu = \frac{3}{4}$ and in three dimensions $\gamma = \frac{7}{6}$ and $\nu = \frac{3}{5}$, these relations given $\gamma_1 = 0{\cdot}916$ and $\gamma_{11} = -0{\cdot}25$ in two dimensions, and $\gamma_1 = 0{\cdot}68\dot{3}$ and $\gamma_{11} = -0{\cdot}4$ in three dimensions.

3. Series analysis

For the square lattice the exact values of $c_n^{(1)}$ and $c_n^{(1,1)}$ which we have obtained are given in table 1. For the cubic lattice, the values of $c_n^{(1)}$ for $n \leqslant 13$ have been given by Middlemiss and Whittington (1976) and we have obtained the next term in this series, as well as the first fourteen terms in the $c_n^{(1,1)}$ series. For completeness we give all the known terms in table 1.

Table 1. Numbers of restricted self-avoiding walks.

	Square lattice		Cubic lattice	
n	$c_n^{(1)}$	$c_n^{(1,1)}$	$c_n^{(1)}$	$c_n^{(1,1)}$
0	1	1	1	1
1	3	2	5	4
2	7	2	21	12
3	19	4	93	40
4	49	8	409	136
5	131	20	1853	528
6	339	40	8333	2032
7	899	100	37965	8344
8	2345	216	172265	33576
9	6199	548	787557	140912
10	16225	1224	3593465	582088
11	42811	3112	16477845	2482240
12	112285	7148	75481105	10451064
13	296051	18228	346960613	45101536
14	777411	42696	1593924045	192563128
15	2049025	109148		
16	5384855	259520		
17	14190509	664868		
18	37313977	1599448		
19	98324565	4105276		
20	258654441	9969396		
21	681552747	25630164		
22		62724196		
23		161490168		

We first attempt to form direct estimates of γ_1 and γ_{11} for both lattices. Because of the odd–even alternation in the ratios we have used the Euler transformation $z = 2x/(1+\mu x)$ to map the singularity at $x = -1/\mu$ (see, e.g., Guttmann and Whittington 1978) in the generating function, to infinity, leaving the singularity at $x = 1/\mu$ unchanged. Using the accepted values of μ (2·6386 for the square lattice and 4·6835 for the cubic lattice) we have formed ratio estimates, such as

$$\gamma_{1,n} - 1 = n[(c_n^{(1)}/\mu c_{n-1}^{(1)}) - 1], \tag{3.1}$$

and extrapolated these using standard Neville table methods (see, e.g., Gaunt and Guttmann 1974). Typical results for γ_1 for the square lattice are given in table 2. These suggest

$$\gamma_1 = 0{\cdot}945 \pm 0{\cdot}005 \tag{3.2}$$

Table 2. Ratio estimates of $\gamma_1 - 1$ for the Euler transformed series on the square lattice. α_n are estimates from ratios of adjacent members, $\alpha_n^{(1)}$ are the linear extrapolants $\alpha_n^{(1)} = n\alpha_n - (n-1)\alpha_{n-1}$ and $\alpha_n^{(2)}$ quadratic extrapolants.

n	$\alpha_n \times 10^2$	$\alpha_n^{(1)} \times 10^2$	$\alpha_n^{(2)} \times 10^2$
10	−2·3474	−4·3281	−7·5922
11	−2·5585	−4·6686	−6·2012
12	−2·7393	−4·7286	−5·0284
13	−2·8879	−4·6706	−4·3517
14	−3·0099	−4·5968	−4·1536
15	−3·1129	−4·5540	−4·2760
16	−3·2028	−4·5525	−4·5422
17	−3·2841	−4·5840	−4·8203
18	−3·3591	−4·6347	−5·0414
19	−3·4293	−4·6923	−5·1816
20	−3·4953	−4·7486	−5·2551
21	−3·5574	−4·7995	−5·2829

and are consistent with ratio estimates on the untransformed series and with the results of a Pade analysis.

For γ_{11} on the square lattice, the results of a ratio analysis on the transformed series are given in table 3. The linear extrapolants suggest that $\gamma_{11} \leqslant -0{\cdot}16$ and the quadratic extrapolants suggest $\gamma_{11} \geqslant -0{\cdot}20$. Analysis of the untransformed series suggests a value close to $-0{\cdot}18$ and we take as our final estimate

$$\gamma_{11} = -0{\cdot}19^{+0{\cdot}03}_{-0{\cdot}02}. \tag{3.3}$$

Using these estimates,

$$2\gamma_1 - \gamma_{11} = 2{\cdot}08^{+0{\cdot}03}_{-0{\cdot}04}, \tag{3.4}$$

Table 3. Ratio estimate for $\alpha = \gamma_{11} - 1$ for the square lattice. α_n are direct ratio estimates from the Euler transformed series and $\alpha_n^{(1)}$ and $\alpha_n^{(2)}$ are their linear and quadratic extrapolants. ϵ_n are the successive averages of the linear extrapolants of alternate direct ratio estimates on the untransformed series.

n	α_n	$\alpha_n^{(1)}$	$\alpha_n^{(2)}$	ϵ_n
10	−0·8257	−0·9377	−1·3601	−1·0707
11	−0·8431	−1·0173	−1·3757	−1·2571
12	−0·8617	−1·0663	−1·3110	−1·1461
13	−0·8794	−1·0915	−1·2302	−1·1389
14	−0·8953	−1·1028	−1·1709	−1·1546
15	−0·9095	−1·1084	−1·1442	−1·1741
16	−0·9222	−1·1129	−1·1447	−1·1606
17	−0·9338	−1·1185	−1·1605	−1·1729
18	−0·9443	−1·1254	−1·1802	−1·1685
19	−0·9543	−1·1329	−1·1967	−1·1810
20	−0·9636	−1·1403	−1·2068	−1·1730
21	−0·9724	−1·1470	−1·2107	−1·1824
22	−0·9806	−1·1527	−1·2098	−1·1765
23	−0·9883	−1·1573	−1·2063	−1·1849

while the accepted values of γ and ν and the surface scaling relation (2.17) would give

$$\gamma+\nu=2{\cdot}08\dot{3}. \tag{3.5}$$

Our results are therefore entirely consistent with surface scaling in two dimensions. However, the suggestion of Bray and Moore that $\gamma_{11}=\nu-1$ would give $\gamma_{11}=-0{\cdot}25$. Our results seem to rule out such a value.

For the cubic lattice the results of a ratio analysis on the transformed series are given in table 4. This suggests a value of γ_1 about equal to, or slightly smaller than, 0·7, while Padé estimates of γ_1 suggest a value slightly greater than 0·7. However, these data are not inconsistent with a value as low as 0·683 which is obtained from a combination of surface scaling and the Bray and Moore result, equation (2.20). Our final estimate is $\gamma_1=0{\cdot}70\pm0{\cdot}02$.

Table 4. Ratio estimates of γ_1-1 for the Euler transformed series on the cubic lattice. α_n are estimates from ratios of adjacent members, $\alpha_n^{(1)}$ are the linear extrapolants $\alpha_n^{(1)}=n\alpha_n-(n-1)\alpha_{n-1}$ and $\alpha_n^{(2)}$ quadratic extrapolants.

n	α_n	$\alpha_n^{(1)}$	$\alpha_n^{(2)}$
5	−0·1532	−0·2111	−0·2365
6	−0·1636	−0·2158	−0·2252
7	−0·1732	−0·2174	−0·2214
8	−0·1775	−0·2204	−0·2293
9	−0·1828	−0·2259	−0·2454
10	−0·1879	−0·2337	−0·2647
11	−0·1929	−0·2326	−0·2829
12	−0·1978	−0·2518	−0·2976
13	−0·2026	−0·2604	−0·3079
14	−0·2073	−0·2681	−0·3140

In the case of γ_{11} for the cubic lattice an analysis of the untransformed series suggests a value somewhat less than −0·3 and this is confirmed by the results on the Euler transformed series. Our estimate is $\gamma_{11}=-0{\cdot}35\pm0{\cdot}05$ which just includes the value −0·4 given by (2.19) with $\nu=\frac{3}{5}$.

A difficulty with the analysis given above is that there is some uncertainty in the values of μ and also in the values of γ and ν. This can be circumvented, and a direct test of the surface scaling relation effected, by noticing that

$$e_n=(c_n^{(1)})^2/(c_nc_n^{(1,1)}R_n)\sim n^{2\gamma_1-\gamma_{11}-\gamma-\nu}, \tag{3.6}$$

so that e_n is independent of the value of μ. If we construct the sequence $\{e_n\}$ and assume

$$e_n\sim n^{\phi} \tag{3.7}$$

then ϕ will be zero if surface scaling is obeyed and we can estimate ϕ from the sequence $\{\phi_n\}$, whose elements are defined by

$$\phi_n=\tfrac{1}{2}n[(e_n/e_{n-2})-1] \tag{3.8}$$

and their linear extrapolants

$$\phi_n^{(1)} = \tfrac{1}{2}[n\phi_n - (n-2)\phi_{n-2}]. \tag{3.9†}$$

Values of ϕ_n and $\phi_n^{(1)}$ are given in tables 5 and 6. It appears that, for the square lattice $|\phi| < 0{\cdot}001$, while for the cubic lattice $\phi \simeq -0{\cdot}03$. That is, the evidence in favour of surface scaling is very strong indeed on the square lattice. For the cubic lattice, the series is not sufficiently well behaved for a definite conclusion but our data are not inconsistent with scaling.

Table 5. Direct tests of the scaling relations for the square lattice.

n	ϕ_n	$\phi_n^{(1)} \times 10^2$	$\theta_n \times 10$	$\theta_n^{(1)} \times 10$
13	−0·08916	−1·72538	2·91669	0·84783
14	−0·12835	−0·52944	3·28546	0·45503
15	−0·07605	0·91292	2·59589	0·51069
16	−0·11274	−0·34996	2·93947	0·51756
17	−0·06739	−0·23993	2·36441	0·62829
18	−0·10018	0·02875	2·67029	0·51685
19	−0·06009	0·19380	2·17723	0·58617
20	−0·09008	0·08793	2·45624	0·52984

Table 6. Direct tests of the scaling relations for the cubic lattice.

n	ϕ_n	$\phi_n^{(1)}$	θ_n	$\theta_n^{(1)}$
6	−0·20263	−0·24459	0·62155	0·33564
7	−0·21088	−0·33106	0·55653	0·44130
8	−0·20724	−0·22109	0·51934	0·21269
9	−0·17748	−0·06058	0·43817	0·02393
10	−0·16988	−0·02043	0·41024	−0·02616
11	−0·14810	−0·01585	0·35988	0·00754
12	−0·14745	−0·03530	0·34744	0·03346
13	−0·13009	−0·03103	0·31181	0·04743
14	−0·13045	−0·02846	0·30375	0·04163

It is also possible to construct a similar test of equation (2.9) by noticing that

$$f_n = n^{\gamma+1} c_n^{(1,1)} / R_n c_n \sim n^{\theta} \tag{3.10}$$

where $\theta = \gamma_{11} - \nu + 1$. Equation (2.19) would imply that $\theta = 0$. If we assume the accepted values of γ($\frac{7}{6}$ in three dimensions and $\frac{4}{3}$ in two dimensions) we can form the sequence $\{f_n\}$ and use estimators θ_n and $\theta_n^{(1)}$ analogous to (3.8) and (3.9). The results (tables 5 and 6) suggest $\theta = 0{\cdot}05 \pm 0{\cdot}01$ for the square lattice. For the cubic lattice, the linear extrapolants are quite erratic but it appears that $|\theta| < 0{\cdot}13$ and is probably as low as $0{\cdot}04$. These data certainly do not allow us to exclude $\theta = 0$.

† The ratios and linear extrapolants of alternate terms have been used in order to reduce the effect of the singularity on the negative real axis (Guttmann and Whittington 1978), as is standard practice (Gaunt and Guttmann 1974).

4. Discussion

There have been several previous estimates of γ_1 for a variety of three-dimensional lattices. From a rather short series on the tetrahedral lattice, Lax (1974) suggested $\gamma_1 = 0{\cdot}68$ in excellent agreement with the value 0·683 obtained from equation (2.20), and a similar result was also obtained for the four-choice cubic lattice (Mark *et al* 1975). Ma *et al* (1977) considered the face-centred cubic and body-centred cubic lattices and estimated $\gamma_1 = 0{\cdot}70$. These results, together with the results presented here, are consistent with equation (2.20) being correct in three dimensions and hence, probably, with both surface scaling and equation (2.19) being correct. The only previous estimate of γ_{11} is also due to Lax (1974) who found $\gamma_{11} = -0{\cdot}56$ for the tetrahedral lattice. This result disagrees with our estimate for the cubic lattice, and also with equation (2.19). The series on which this result was based was both short ($n = 14$) and has alternate terms equal to zero, so that the series has (effectively) only seven available terms. Lax also gives an argument (his appendix A) which leads to $\gamma_{11} \simeq -0{\cdot}57$ in three dimensions. In his notation, it is easy to show that $c_n = C_{n+2}$ for the cubic lattice and except for a constant multiplicative factor, the same result will hold for other lattices. Hence $c(x)$ and $C(x)$ must have singularities at the same point (e.g., $x = 1/\mu$) with the *same* exponent, in contrast to Lax's assertion (see his equation (A.9) and (A.13)), which is that the exponents differ in general. Lax thus derives a scaling relation, $\gamma_{11} = \nu - \gamma$, which we believe to be without foundation.

In two dimensions there are no previous estimates of γ_{11} or γ_1. Our results strongly support the surface scaling relation (2.17) but cast serious doubt on the validity of (2.19).

For magnetic systems, the series expansions of the analogous susceptibilities for the Ising model have been obtained by Binder and Hohenberg (1972, 1974). They obtained 10 terms on the square lattice and 8 terms on the simple cubic lattice, which, as they pointed out, are probably too short for an unequivocal identification of the critical exponents γ_1 and γ_{11}. However, in our case we have more than 20 terms for the square lattice and 14 terms for the simple cubic lattice. The extrapolations show every sign of having settled down to their asymptotic behaviours, and so we do not believe that the results we have obtained, notably the breakdown of the relation $\gamma_{11} = \nu - 1$ for the two-dimensional system, can be ascribed to cross-over effects or other manifestations of 'too short' series. Further, the fact that our independent estimates of γ_1 and γ_{11} satisfy surface scaling also leads us to believe that the estimates of γ_1 and γ_{11} are correct.

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