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1980 J. Phys. A: Math. Gen. 13 789

(http://iopscience.iop.org/0305-4470/13/3/012)

J. Phys. A: Math. Gen. 13 (1980) 789–794. Printed in Great Britain

The surface susceptibility exponent for the polymer problem

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Received 16 May 1979, in final form 26 June 1979

Abstract. Series analysis methods are used to estimate the surface susceptibility exponent for the polymer analogue of a magnet with a free surface, on the square and simple cubic lattices. Our exponent estimates are slightly larger than the surface scaling predictions for both lattices.

Over the last few years there have been a number of attempts to use scaling arguments to make predictions about surface effects in critical phenomena (Watson 1972, Binder and Hohenberg 1972, 1974, Barber 1973, Fisher 1971, 1973, Bray and Moore 1977). Like all scaling predictions, these results rest on an *ansatz* which can most readily be tested by comparing the predictions with results from an independent approach such as Monte Carlo (Binder 1972) or series expansions (Watson 1972, Binder and Hohenberg 1972, 1974, Ritchie and Fisher 1973, Barber *et al* 1978, Whittington *et al* 1979). We have recently investigated the scaling predictions concerning *local* susceptibilities both for the polymer problem (the zero-spin space-dimension limit of the D vector model) (Barber *et al* 1978) and for the Ising model (Whittington *et al* 1979), with the conclusion that surface scaling is probably valid for both these cases, but that an extension due to Bray and Moore (1977), while consistent with series estimates for the Ising problem in two and three dimensions and with the polymer problem in three dimensions, disagrees with series analysis results for the polymer problem in two dimensions.

Scaling predictions (e.g. Watson 1972) have also appeared for global exponents such as γ_s, which characterises the divergence of the total surface susceptibility, χ_s. These suggest that γ_s can be expressed in terms of the bulk exponents γ and ν by the relation

$$\gamma_s = \gamma + \nu. \tag{1}$$

γ characterises the divergence of the bulk suceptibility (χ) while ν characterises the correlation length or, for the polymer problem, the mean square end-to-end length of the polymer, $\langle R_n^2 \rangle$, as

$$\langle R_n^2 \rangle \sim n^{2\nu}. \tag{2}$$

Equation (1) has been tested, using series analysis techniques, for the Ising problem (e.g. Watson 1972) and for the Heisenberg problem (Ritchie and Fisher 1973). For the

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0305-4470/80/030789+06\$01.00

Ising problem the series are rather short (table I of Watson 1972) but the data are just consistent with equation (1). The discrepancy in the exponents is less than 0·05 in two dimensions and less than 0·1 in three dimensions, but the estimates of γ_s have large associated uncertainties. For the Heisenberg problem (in three dimensions) γ_s appears to exceed $\gamma+\nu$ by about 0·1. One of the aims of the present paper is to test the validity of equation (1) for the polymer problem.

We consider various classes of self-avoiding walks on a lattice, confined to a half-space. For convenience consider the N-dimensional hypercubic lattice whose lattice points are the integer points in E^N. Let $c_n^{(i)}$ be the number, per site of the $(N-1)$-dimensional lattice, of n-edge self-avoiding walks which begin at a point in the $(N-1)$-dimensional hyperplane $z_1=i$, and are confined to $z_1\geqslant 1$, and let c_n be the number, per site of the N-dimensional lattice, of otherwise unrestricted n-edge self-avoiding walks. To emphasise the analogy with the critical phenomena problem we write their generating functions as

$$\chi_i(x)=1+\sum_{n\geqslant 1} c_n^{(i)}x^n \tag{3}$$

and

$$\chi(x)=1+\sum_{n\geqslant 1} c_n x^n. \tag{4}$$

The χ_i are analogous to layer susceptibilities (which measure the response of the magnetisation of the ith layer to a change in the bulk field) and χ is analogous to the bulk susceptibility of the magnetic problem. Clearly

$$\chi_1\leqslant\chi_2\leqslant\ldots\leqslant\chi, \tag{5}$$

and this set of inequalities, coupled with a result obtained previously about the divergence of χ_1 and χ (Whittington 1975) establishes that all their generating functions diverge at the same point, $x=x_c=\mu^{-1}$. The surface susceptibility is defined as

$$\chi_s=1+\sum_{i\geqslant 1}(\chi-\chi_i)=1+\sum_{n\geqslant 1} a_n x^n. \tag{6}$$

If we assume that, as $x\to x_c^-$,

$$\chi_s\sim A_s(1-\mu x)^{-\gamma_s}, \tag{7}$$

$$\chi\sim A(1-\mu x)^{-\gamma} \tag{8}$$

and

$$\chi_1\sim A_1(1-\mu x)^{-\gamma_1}, \tag{9}$$

then, since

$$c_n^{(i)}=c_n, \qquad \forall n\leqslant i, \tag{10}$$

we obtain immediately

$$\gamma\leqslant\gamma_s\leqslant\gamma+1. \tag{11}$$

This should be compared with the scaling prediction in equation (1). The graphs contributing to χ_s are self-avoiding walks which start on one side of the surface plane and have at least one vertex on the other side of this plane, which suggests that the exponent will be relevant to the problem of polymer adsorption at the liquid–liquid interface.

We have derived the first fourteen terms in the expansion of χ_s for the cubic lattice and the first twenty-one terms for the square lattice, and the results appear in table 1.

Table 1. Coefficients of the surface susceptibility series.

n	Cubic lattice	Square lattice
1	1	1
2	10	6
3	71	25
4	440	90
5	2561	307
6	14 230	990
7	77 179	3125
8	408 784	9548
9	2137 605	28 887
10	11 017 370	85 602
11	56 339 979	252 215
12	285 324 892	732 596
13	1437 391 977	2119 923
14	7191 076 878	6071 214
15		17 341 455
16		49 143 504
17		138 999 493
18		390 711 254
19		1096 655 313
20		3062 640 096
21		8543 465 975

Using standard ratio methods (Gaunt and Guttmann 1974), we estimate the exponent γ_s by

$$\gamma_{s,n}^{(0)} = 1 + \tfrac{1}{2}n[(a_n/\mu^2 a_{n-2}) - 1], \tag{12}$$

and the linear and quadratic extrapolants

$$\gamma_{s,n}^{(i)} = (1/2i)[n\gamma_{s,n}^{(i-1)} - (n-2i)\gamma_{s,n-2}^{(i-1)}], \tag{13}$$

with $i = 1$ and 2 respectively. As usual, extrapolations based on alternate terms have been used to minimise the oscillations characteristic of loose-packed lattices. The values used for μ were 2·6385 and 4·6835 (Sykes *et al* 1972).

For the cubic lattice (see table 2) the linear extrapolants are increasing smoothly and suggest $\gamma_s > 1{\cdot}795$, while the quadratic extrapolants are decreasing and suggest $\gamma_s < 1{\cdot}825$. Our final estimate is $\gamma_s = 1{\cdot}81 \pm 0{\cdot}02$. A Padé analysis for this series is somewhat erratic but not inconsistent with this estimate.

The Neville table for the square lattice is shown in table 3. Linear extrapolants suggest $\gamma_s > 2{\cdot}095$ and quadratic extrapolants suggest $\gamma_s < 2{\cdot}105$. We formed Padé approximants to $(x_c - x)(d/dx)(\ln \chi_s(x))$ and evaluated these at the critical point, $x_c = \mu^{-1}$. The results are shown in table 4. These results suggest that $\gamma_s < 2{\cdot}11$ and is probably close to 2·10. As our final estimate we take $\gamma_s = 2{\cdot}10 \pm 0{\cdot}01$.

Table 2. Neville table for the cubic lattice.

n	$\gamma_n^{(0)}$	$\gamma_n^{(1)}$	$\gamma_n^{(2)}$
7	2·308 577	1·552 455	2·720 741
8	2·238 512	1·684 574	2·123 318
9	2·181 981	1·738 895	1·971 946
10	2·143 460	1·763 250	1·881 264
11	2·108 621	1·778 503	1·847 816
12	2·083 892	1·786 054	1·831 662
13	2·060 157	1·793 607	1·827 591
14	2·042 874	1·796 766	1·823 545

Table 3. Neville table for the square lattice.

n	$\gamma_n^{(0)}$	$\gamma_n^{(1)}$	$\gamma_n^{(2)}$
11	2·397 901	2·050 162	2·178 670
12	2·375 945	2·060 013	2·120 280
13	2·347 807	2·072 292	2·122 084
14	2·332 875	2·074 450	2·110 542
15	2·312 772	2·085 039	2·120 093
16	2·301 787	2·084 171	2·113 332
17	2·286 613	2·090 423	2·107 922
18	2·278 225	2·089 732	2·109 195
19	2·266 297	2·093 608	2·105 550
20	2·259 675	2·092 724	2·104 694
21	2·250 032	2·095 518	2·103 639

Table 4. Padé approximants to $(x_c - x)\, d(\ln \chi_s(x))/dx|_{x_c=0\cdot379003}$.

N	$[N-1/N]$	$[N/N]$	$[N+1/N]$
3	2·1703	2·1541	2·1621
4	2·2958	2·1404	2·1352
5	2·1361	2·1503	2·1219
6	2·1248	2·1128	2·1096
7	2·1099	2·1109	2·1106
8	2·1106	2·1110	2·1072
9	2·1082	2·1144	2·1559

Using the generally accepted values of γ and ν in two and three dimensions ($\gamma = \frac{4}{3}, \frac{7}{6}$, and $\nu = \frac{3}{4}, \frac{3}{5}$ respectively), the scaling predictions for γ_s are $\frac{25}{12} \simeq 2\cdot083$ and $\frac{53}{30} \simeq 1\cdot77$ respectively. The central estimates from the series analysis exceed the predictions by 0·02 and 0·04 respectively, while taking the lowest values consistent with the series results still leaves discrepancies of 0·01 and 0·02 respectively. Notice that the deviation from scaling is in the same direction as for the Ising and Heisenberg models.

Of course, γ and ν are not known exactly and it is conceivable that the generally assumed values might be in error by amounts of the order of 0·01. To circumvent this uncertainty, and to avoid the use of an assumed value for μ, we have formed the series

$$b_n = c_n \langle R_n^2 \rangle^{1/2} / a_n$$

which should behave asymptotically as $b_n \sim n^{\phi}$ with $\phi = \gamma + \nu - \gamma_s$. If scaling is obeyed ϕ should be zero. Estimates of ϕ are given by the sequence $\{\phi_n\}$, where $\phi_n = (n/2)(b_n/b_{n-2} - 1)$. This sequence and linear, quadratic and cubic extrapolants are shown in table 5. From those results we estimate $\phi \gtrsim -0{\cdot}02$ in two dimensions and $\phi = -0{\cdot}05 \pm 0{\cdot}02$ in three dimensions. These results are estimates of the maximum extent of the possible errors in scaling predictions of γ_s. The estimates of ϕ are also completely consistent with our direct estimates of γ_s quoted above, from which it follows that $\phi = -0{\cdot}017 \pm 0{\cdot}01$ and $\phi = -0{\cdot}04 \pm 0{\cdot}02$ in two and three dimensions respectively.

Table 5. Neville table showing estimates of 'breakdown of scaling exponent' ϕ.

Simple cubic lattice					Square lattice			
		Alternate extrapolants					Alternate extrapolants	
n	ϕ_n	linear	quadratic	cubic	n	ϕ_n	linear	quadratic
6	−0·2362	−0·0551			12	−0·1041		
7	−0·2172	−0·0845	−0·9584		13	−0·0984	−0·03916	
8	−0·2019	−0·0992	−0·1433		14	−0·0948	−0·0388	
9	−0·1899	−0·0945	−0·1070	0·3188	15	−0·0902	−0·0366	−0·0294
10	−0·1797	−0·0909	−0·0784	−0·0352	16	−0·0873	−0·0349	−0·0230
11	−0·1707	−0·0842	−0·0663	−0·0323	17	−0·0835	−0·0326	−0·0239
12	−0·1632	−0·0806	−0·0601	−0·0418	18	−0·0811	−0·0320	−0·0219
13	−0·1562	−0·0766	−0·0596	−0·0518	19	−0·0780	−0·0309	−0·0208
14	−0·1505	−0·0741	−0·0577	−0·0545	20	−0·0760	−0·0296	−0·0201

Three possible explanations for this behaviour suggest themselves. One is the breakdown of the scaling relation $\gamma_s = \gamma + \nu$. Another is that the correlation exponent appropriate to the surface problem is different to the correlation function appropriate to the bulk problem. The third possibility is that these results are produced by analysis of series of insufficient length. At present we have no reason to select one of these explanations as being the more likely.

Acknowledgments

A J Guttmann wishes to acknowledge the hospitality of the Chemistry Department at the University of Toronto. This work was financially supported by the National Research Council of Canada.

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