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Transfer-matrix study of the adsorption of a flexible self-avoiding polymer chain in two dimensions

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Abstract. We model the polymer as a self-avoiding walk on a semi-infinite square lattice with an energy contribution $-\varepsilon$ from each step along the lattice boundary. The critical adsorption temperature T_a and the 'ordinary' and 'special' surface exponents of the walk above and at the adsorption temperature, respectively, are estimated with transfer-matrix finite-size scaling methods. For the adsorption temperature we obtain $\exp(\varepsilon/kT_a) = 2.041 \pm 0.002$, and for the crossover and susceptibility exponents of the special transition, $\phi^{sp} = 0.501 \pm 0.003$ and $\gamma_1^{sp} = 1.454 \pm 0.004$.

We consider the self-avoiding walk on a semi-infinite lattice with energy defined by

$$E = -\varepsilon N_1. \quad (1)$$

Here ε is a positive constant, and N_1 is the number of steps that coincide with the edge of the lattice. This is a standard model for a long flexible polymer in a good solvent with an attractive short-range force between the polymer and the container wall (Eisenriegler *et al* 1982, Binder and Kremer 1985 and references therein).

The model exhibits a transition at a critical adsorption temperature T_a , with a desorbed phase for $T > T_a$ and an adsorbed phase for $T < T_a$. Using the correspondence (De Gennes 1979) between this transition and magnetic phase transitions of the semi-infinite n -vector model in the limit $n \rightarrow 0$, Eisenriegler *et al* (1982) have given a comprehensive discussion of the universal exponents that characterise the family of walks of N steps in the large- N limit. We recall the definitions of three surface exponents γ_1^o , γ_1^{sp} , ϕ^{sp} which, together with bulk exponents and scaling relations, determine the other most common surface exponents. The partition function $Z_1(N, T)$ of walks with one end attached to the boundary has the asymptotic form

$$\ln Z_1(N, T) = N \ln q_{\text{eff}} + (\gamma_1^o - 1) \ln N \quad T > T_a \quad (2a)$$

$$\ln Z_1(N, T) = N \ln q_{\text{eff}} + (\gamma_1^{sp} - 1) \ln N \quad T = T_a \quad (2b)$$

as $N \rightarrow \infty$ with fixed T . Here q_{eff} is an effective coordination number or connectivity constant. For $T > T_a$ the average number $\langle N_1 \rangle$ of steps of the walk in contact with the boundary remains finite in the limit $N \rightarrow \infty$. However, at the critical temperature

$$\langle N_1 \rangle \sim N^{\phi^{sp}} \quad T = T_a \quad (3)$$

where ϕ^{sp} is non-zero. The superscripts o and sp of the exponents underline the correspondence with the 'ordinary' and 'special' or 'multicritical' transitions of magnetic systems (Eisenriegler *et al* 1982, Binder 1983).

The bulk and surface exponents of the self-avoiding walk in two and three dimensions have been estimated by a variety of methods including exact enumerations, expansions in $\varepsilon = 4 - d$, and Monte Carlo techniques (see Binder and Kremer 1985 for a recent review). In addition, in two dimensions exact values $\gamma = 43/32$, $\nu = 3/4$ for the bulk exponents have been predicted from Coulomb-gas (Nienhuis 1982, Den Nijs 1983) and conformal invariance (Dotsenko and Fateev 1984, Cardy 1987) arguments. Extending the conformal invariance approach to the half-plane geometry, Cardy (1984a) has derived the result $\gamma_1^0 = 61/64$ for the surface exponent in equation (2a).

Some of the most precise numerical estimates of the scaling indices of the self-avoiding walk in two dimensions have been obtained with transfer-matrix finite-size scaling techniques (Derrida 1981, Saleur and Derrida 1986, Duplantier and Saleur 1986, Saleur 1987a, b). In this paper we use the same approach to calculate the critical adsorption temperature and the surface exponents of the model described above on the square lattice. Our results, like those of Duplantier and Saleur (1986), confirm the predictions of conformal invariance for the high-temperature phase. The main motivation of our work was to study the critical behaviour right at the adsorption temperature. We hoped to improve upon the precision of earlier determinations of T_a and ϕ^{sp} (De'Bell 1979, Ishinabe 1983, Kremer 1983) and to estimate γ_1^{sp} , which, as far as we know, has not been evaluated previously in two dimensions.

In our finite-size scaling analysis, self-avoiding walks on a strip of square lattice with infinite length and a width of L lattice constants are considered. We work in the grand canonical ensemble and assign a surface fugacity K_s to each step along either edge of the strip and a bulk fugacity K to each of the other steps. Generalising the approach of Derrida and Saleur slightly to accommodate the two fugacities K_s and K , we consider transfer matrices $T_L^{(i)}(K_s, K)$, $i = 1, 2$, for one and two self-avoiding walks on the strip, respectively. The largest eigenvalue $\lambda_L^{(i)}$ of $T_L^{(i)}$ determines the characteristic length

$$\xi_L^{(i)}(K_s, K) = -[\ln \lambda_L^{(i)}(K_s, K)]^{-1}. \quad (4)$$

In the $n \rightarrow 0$ limit of the n -vector model equivalent to the polymer model, $K_s = J_s/kT$ and $K = J/kT$ represent the nearest-neighbour surface and bulk couplings of spins. The quantities $\xi_L^{(1)}$, $\xi_L^{(2)}$ are the usual spin-spin and energy-energy correlation lengths, respectively.

The finite-size scaling properties (Barber 1983) of $\xi_L^{(i)}$ follow from standard renormalisation group phenomenology for semi-infinite magnetic systems (see, e.g., Burkhardt and Eisenriegler 1977). For (K_s, K) sufficiently close to the fixed point (K_s^*, K^*) and for L sufficiently large, $\xi_L^{(i)}$ has the form

$$\xi_L^{(i)}(K_s, K) = LF^{(i)}(L^y(K_s - K_s^*), L^y(K - K^*)) \quad (5)$$

where $F^{(i)}$ is a scaling function of two variables. The appropriate fixed points for the polymer problem for $T > T_a$ and $T = T_a$ are the fixed points of the ordinary and special transitions, respectively, of the semi-infinite $n \rightarrow 0$ vector model (Eisenriegler *et al* 1982).

At both the ordinary and special fixed points, $K^* = q_{\text{eff}}^{-1}$ is the bulk critical coupling of the $n \rightarrow 0$ vector model and the reciprocal of the effective coordination number defined in equation (2). For the square lattice K^* has the value

$$K^* = 0.379\,0528 \pm 0.000\,0025 \quad (6)$$

(Derrida 1981, Enting and Guttman 1985).

We analyse our numerical data for $\xi_L^{(i)}(K_s, K)$ in two ways. First we set K equal to the known critical value of equation (6). Then, in accord with equation (5), we

calculate sequences $K_s^*(L), y_s(L), y(L) = \nu(L)^{-1}$ that approach the desired exact values as $L \rightarrow \infty$ from the phenomenological renormalisation group equations (Nightingale 1976, Barber 1983)

$$L^{-1} \xi_L^{(i)}(K_s^*(L), K^*) = (L-1)^{-1} \xi_{L-1}^{(i)}(K_s^*(L), K^*) \tag{7a}$$

$$1 + y_s(L) = \ln[(\partial \xi_L^{(i)} / \partial K_s) / (\partial \xi_{L-1}^{(i)} / \partial K_s)] / \ln[L / (L-1)] \tag{7b}$$

$$1 + y(L) = \ln[(\partial \xi_L^{(i)} / \partial K) / (\partial \xi_{L-1}^{(i)} / \partial K)] / \ln[L / (L-1)]. \tag{7c}$$

The derivatives in equations (7b) and (7c) are all evaluated at $K_s = K_s^*(L), K = K^*$. The estimates obtained in this way from the spin-spin and energy-energy correlation lengths ($i = 1, 2$) with $L = 3, \dots, 10$ are listed in tables 1 and 2, respectively.

Table 1. Fixed-point couplings and critical exponents obtained from the one-polymer transfer matrix with equations (6), (7), and (10).

	L	K_s^*	y	y_s	$2x_s^{(1)}$	
Ordinary transition	3	0.274 6752	4.134 7527	-1.175 4341	1.236 0212	
	4	0.271 9838	1.935 4722	-1.067 1939	1.243 7600	
	5	0.270 6985	1.616 6304	-1.036 1482	1.246 4723	
	6	0.269 9783	1.498 8134	-1.022 7016	1.247 6754	
	7	0.269 5275	1.441 5244	-1.015 6387	1.248 2993	
	8	0.269 2197	1.409 2846	-1.011 4651	1.248 6631	
	9	0.268 9945	1.389 3653	-1.008 7927	1.248 8952	
	10	0.268 8210	1.376 2217	-1.007 0173	1.249 0542	
	Exact			4/3	-1	5/4
	Special transition	3	0.778 6861	2.944 9534	0.676 6766	-0.090 7177
4		0.774 5255	2.150 8281	0.682 9858	-0.081 7514	
5		0.773 2291	1.908 0363	0.684 3231	-0.078 3438	
6		0.772 8089	1.786 6341	0.684 0503	-0.077 0568	
7		0.772 6763	1.712 6116	0.683 2882	-0.076 5967	
8		0.772 6498	1.662 2500	0.682 4092	-0.076 4947	
9		0.772 6652	1.625 4964	0.681 5332	-0.076 5598	
10		0.772 6968	1.597 3457	0.680 7112	-0.076 7043	
Exact				4/3		

In the second way of analysing the data we define a two-parameter phenomenological renormalisation $(K_s, K) \rightarrow (K'_s, K')$ under a rescaling of lengths with scale factor $b = L / (L-1)$ according to

$$(L-1)^{-1} \xi_{L-1}^{(1)}(K'_s, K') = L^{-1} \xi_L^{(1)}(K_s, K) \tag{8a}$$

$$(L-1)^{-1} \xi_{L-1}^{(2)}(K'_s, K') = L^{-1} \xi_L^{(2)}(K_s, K). \tag{8b}$$

From the fixed points of (8) one obtains a sequence of estimates $(K_s^*(L), K^*(L))$ for the fixed-point couplings in the semi-infinite case. Linearising the flow equations around the fixed point in the standard manner yields estimates $y_s(L), y(L) = \nu(L)^{-1}$ for the critical exponents. The data obtained in this way are listed in table 3.

Table 2. Fixed-point couplings and critical exponents obtained from the two-polymer transfer matrix with equations (6), (7), and (10).

	L	K_s^*	y	y_s	$2x_s^{(2)}$
Ordinary transition	4	0.248 6936	3.246 3712	-1.709 6323	4.016 5487
	5	0.237 2967	1.868 2705	-1.055 2663	4.085 7424
	6	0.242 8591	1.646 2368	-1.042 9928	4.059 2885
	7	0.246 9462	1.539 7126	-1.029 8724	4.042 9431
	8	0.250 0413	1.479 7257	-1.021 6335	4.032 2397
	9	0.252 4526	1.442 4229	-1.016 3622	4.024 8850
	10	0.254 3756	1.417 6031	-1.012 8307	4.019 6352
Exact			4/3	-1	4
Special transition	4	0.769 9509	2.950 3669	0.686 4312	0.650 4941
	5	0.773 7605	2.334 2868	0.681 5401	0.630 0375
	6	0.775 0363	2.079 7769	0.679 4740	0.622 0777
	7	0.775 4583	1.937 9577	0.678 3135	0.619 0992
	8	0.775 5513	1.846 5519	0.677 5285	0.618 3700
	9	0.775 5094	1.782 2629	0.676 9316	0.618 7301
	10	0.775 4122	1.734 3258	0.676 4441	0.619 6327
Exact			4/3		

Table 3. Fixed-point couplings and critical exponents obtained from the one- and two-polymer transfer matrices with equations (8) and (10).

	L	K^*	K_s^*	y	y_s	$2x_s^{(1)}$	$2x_s^{(2)}$
Ordinary transition	6	0.373 9979	0.199 3406	1.295 9819	-0.953 1863	1.417 0981	4.354 2664
	7	0.376 4184	0.214 4008	1.312 6393	-1.007 2346	1.360 7476	4.236 8078
	8	0.377 5091	0.223 8463	1.319 8180	-1.015 1048	1.329 3343	4.170 8229
	9	0.378 0798	0.230 6195	1.323 7910	-1.015 1587	1.309 4443	4.128 7047
	10	0.378 4062	0.235 7651	1.326 2400	-1.013 6400	1.295 9735	4.099 9900
	Exact			4/3	-1	5/4	4
Special transition	4	0.381 0506	0.763 1403	1.525 0151	0.700 9667	-0.063 1970	0.675 7845
	5	0.378 8458	0.774 6615	1.466 7168	0.674 7587	-0.080 9357	0.626 3708
	6	0.378 2735	0.779 1090	1.432 2688	0.666 6915	-0.089 6168	0.604 0111
	7	0.378 1689	0.780 8091	1.409 9974	0.663 8805	-0.094 2919	0.593 4247
	8	0.378 2073	0.781 3411	1.394 6479	0.662 9691	-0.096 9515	0.588 5426
	9	0.378 2861	0.781 3470	1.383 5415	0.662 8380	-0.098 4975	0.586 6488
	10	0.378 3706	0.781 1121	1.375 2059	0.663 0415	-0.099 3860	0.586 4034
Exact			4/3				

Additional numerical information on surface critical indices follows from the general relation (Cardy 1984b)

$$\lim_{L \rightarrow \infty} L^{-1} \xi_L^{(i)}(K_s^*, K^*) = [\pi x_s^{(i)}]^{-1} \quad (9)$$

between the amplitude of a correlation length and the corresponding surface scaling index. In tables 1-3 sequences of $x_s^{(i)}(L)$ defined by

$$x_s^{(i)}(L) = L[\pi \xi_L^{(i)}(K_s^*(L), K^*(L))]^{-1} \quad (10)$$

are given that approach the limiting value $x_s^{(i)}$ of equation (9) in the large- L limit. Since the one and two-polymer correlation lengths $\xi_L^{(1)}$ and $\xi_L^{(2)}$ correspond to spin-spin and energy-energy correlations in the $n \rightarrow 0$ vector model, the $x_s^{(i)}$ are related to the conventional exponents of surface critical phenomena (Binder 1983) by

$$x_s^{(1)} = \eta_{\parallel}/2 = \beta_1/\nu = [2 + (\gamma - 2\gamma_1)/\nu]/2 \quad (11a)$$

$$x_s^{(2)} = 1 - y_s = 1 - \phi/\nu. \quad (11b)$$

The numerical data in tables 1-3 for the high-temperature desorbed-polymer phase (ordinary transition of the semi-infinite magnetic system) are in excellent agreement with the accepted exact values $y = \nu^{-1} = \frac{4}{3}$ (Nienhuis 1982), $y_s^0 = 1 - x_s^{(2)} = -1$ (Burkhardt and Cardy 1987), and $2x_s^{(1)} = \eta_{\parallel}^0 = \frac{5}{4}$ (Cardy 1984a).

The data in tables 1-3 for critical properties at the polymer adsorption temperature (special transition of the semi-infinite magnetic system) are not nearly so well behaved as the data for the ordinary transition. The estimates for the bulk exponent $y = \nu^{-1}$ are again consistent with the limiting value $\frac{4}{3}$, but the convergence is slower. Also, many of the sequences for surface quantities do not vary monotonically with L but pass through smooth maxima or minima, as seen in figures 1-3. Although such sequences cannot be extrapolated very reliably, we have obtained fairly precise estimates by comparing several different sequences for each of the surface quantities.

Curves 1-3 in figure 1 depict the data from tables 1-3 for K_s^* at the special transition. We make the plausible assumption that for $L^{-1} < 0.1$ curves 1 and 2 continue to approach the limiting value of K_s^* from below and above, respectively. Then from the last entry in the sequences for K_s^* in tables 1 and 2 we conclude $0.7727 < K_s^* < 0.7754$. These bounds may be improved slightly by noting that curves 1 and 2 have upward and downward curvature, respectively. Thus if one extrapolates each curve to $L^{-1} = 0$ by fitting a straight line through the last two points (see inset, figure 1), the exact K_s^* should lie between the extrapolated values. In this way we obtain our final result $K_s^* = 0.7738 \pm 0.0008$ and $\exp(\varepsilon/kT_a) = K_s^*/K^* = 2.041 \pm 0.002$. The value for $\exp(\varepsilon/kT_a)$ is in good agreement with the results 2.05 and 2.01 of Ishinabe (1983) from two different analyses of exact data for walks with $N \leq 21$. Our value for K_s^* is somewhat larger than the result 0.65 ± 0.05 of Kremer's (1983) real-space renormalisation study.

Unlike conventional magnetic systems on an $L \times \infty$ strip, the n -vector model for $n < 1$ undergoes one-dimensional transitions (Balian and Toulouse 1974). We obtain additional sequences of estimates for K_s^* at the special transition from the critical values $K_s^c(L)$ for which $\xi_L^{(i)}(K_s^c(L), K^*) = \infty$, with K^* given by equation (6). Our results for $K_s^c(L)$ from the one and two-polymer transfer matrices are listed in table 4 and depicted by curves 4a and 4b, respectively, in figure 1. The curves are smooth and monotonic and when extrapolated with standard algorithms (see, e.g., Henkel and Schütz 1988) yield limiting values K_s^* in excellent agreement with our estimates from curves 1 and 2.

We now consider the crossover exponent $\phi^{sp} = y_s^{sp}/y = 3y_s^{sp}/4$ of the special transition. The data for y_s^{sp} from tables 1-3 correspond to the lower three curves in figure 2. The upper two curves show the quantity $1 - x_s^{(2)}$, with $x_s^{(2)}$ taken from tables 2 and 3. According to equation (11b) these two curves should also converge to y_s^{sp} . The lowest two curves in figure 2 yield the most precise bounds on y_s^{sp} . From the last entry in the corresponding sequences we obtain $0.6630 < y_s^{sp} < 0.6764$. Since curve 3 has upward curvature and curve 2 has begun to turn downwards near $L^{-1} = 0.1$, these

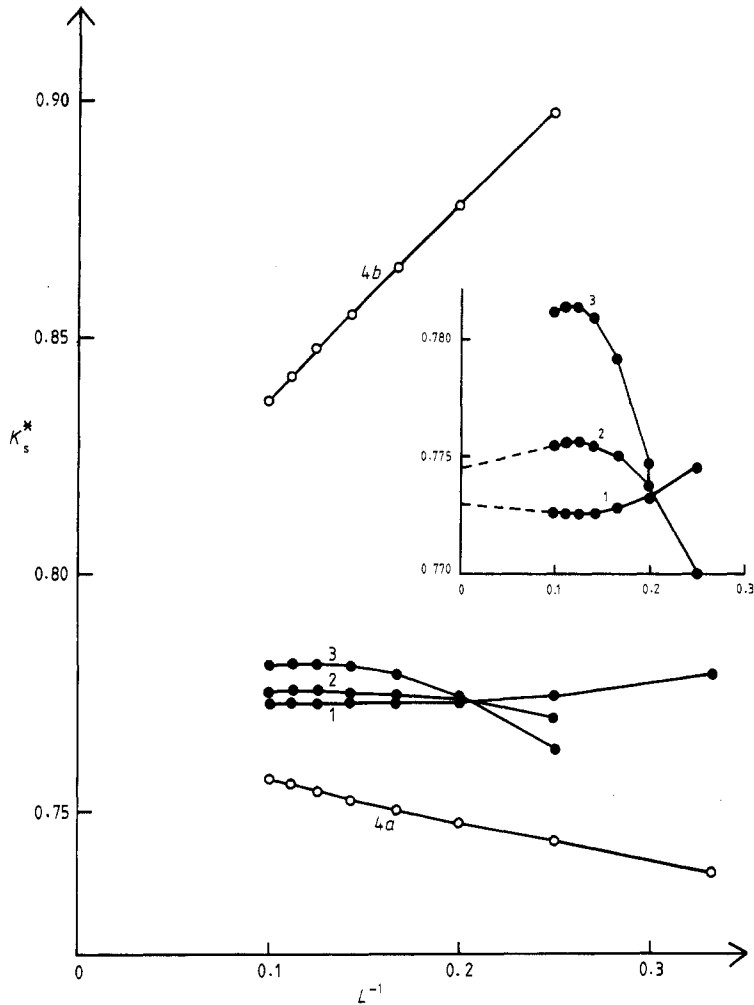


Figure 1. Estimates of the critical surface coupling K_s^* of the special transition from tables 1-4. The broken lines (see inset) show the linear extrapolations on which our stated uncertainties are based.

bounds may also be improved by linear extrapolation (see figure 2) to $L^{-1} = 0$. Our final result is $y_s^{\text{sp}} = 0.668 \pm 0.004$, which corresponds to the crossover exponent $\phi^{\text{sp}} = 0.501 \pm 0.003$. Within our estimated uncertainty y_s^{sp} is consistent with the value $\frac{2}{3}$ and ϕ^{sp} with $\frac{1}{2}$. For ideal polymers without the self-avoiding restriction the exact crossover exponent is also $\phi^{\text{sp}} = \frac{1}{2}$ (DiMarzio and McCrackin 1965, Rubin 1965, Eisenriegler *et al* 1982, Hammersley 1982).

Next we compare our result for the crossover exponent with previous estimates. Ishinabe (1983) finds $(\phi^{\text{sp}})^{-1} = 1.9$ and $\nu/\phi^{\text{sp}} = 1.5$, corresponding to $\phi^{\text{sp}} = 0.53$ and 0.50, respectively, but does not quote an uncertainty. Kremer (1983) estimates $\phi^{\text{sp}} = 0.55 \pm 0.1$ from Ishinabe's table III and obtains 0.55 ± 0.15 from a real-space renormalisation study. Our result 0.501 ± 0.003 is consistent with these estimates and considerably more precise.

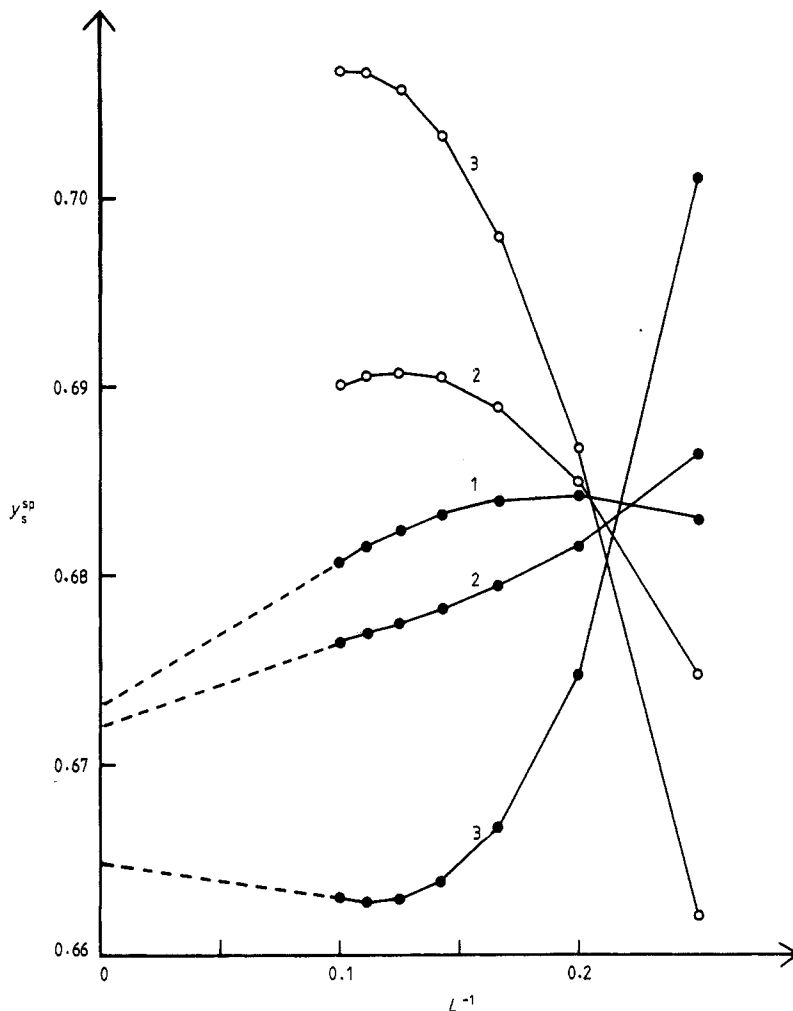


Figure 2. Estimates of y_s (filled points) and of $1 - x_s^{(2)}$ (empty points) at the special transition from tables 1-3. The broken lines show the linear extrapolations on which our stated uncertainties are based.

Finally we consider the exponent $\eta_{\parallel}^{\text{sp}} = 2x_s^{(1)}$ which, as far as we know, has not been estimated previously in two dimensions. Curves 1 and 3 of figure 3 depict the data for $2x_s^{(1)}$ from tables 1 and 3, respectively. Curves *a* and *b* show the quantity $2L[\pi\xi_L^{(1)}(K_s, K^*)]^{-1}$ (see equation (10)) with K^* given by equation (6) and with $K_s = 0.7730$ and 0.7745 , respectively. According to our above analysis the exact K_s^* lies between these two numbers. Values of K_s between the two numbers yield curves between *a* and *b*. On the basis of curves *a* and *b* (see figure 3) we conclude $\eta_{\parallel}^{\text{sp}} = -0.087 \pm 0.008$. The phenomenon of a negative exponent η , corresponding to critical spin-spin correlations that grow rather than decrease with increasing spin separation, has been encountered previously in the $n \rightarrow 0$ vector model (Saleur 1987b and references therein). Combining equation (11a), the exact bulk exponents $\nu = \frac{3}{4}$, $\gamma = \frac{43}{32}$, and our estimate for $\eta_{\parallel}^{\text{sp}}$, we find $\gamma_1^{\text{sp}} = 1.454 \pm 0.004$.

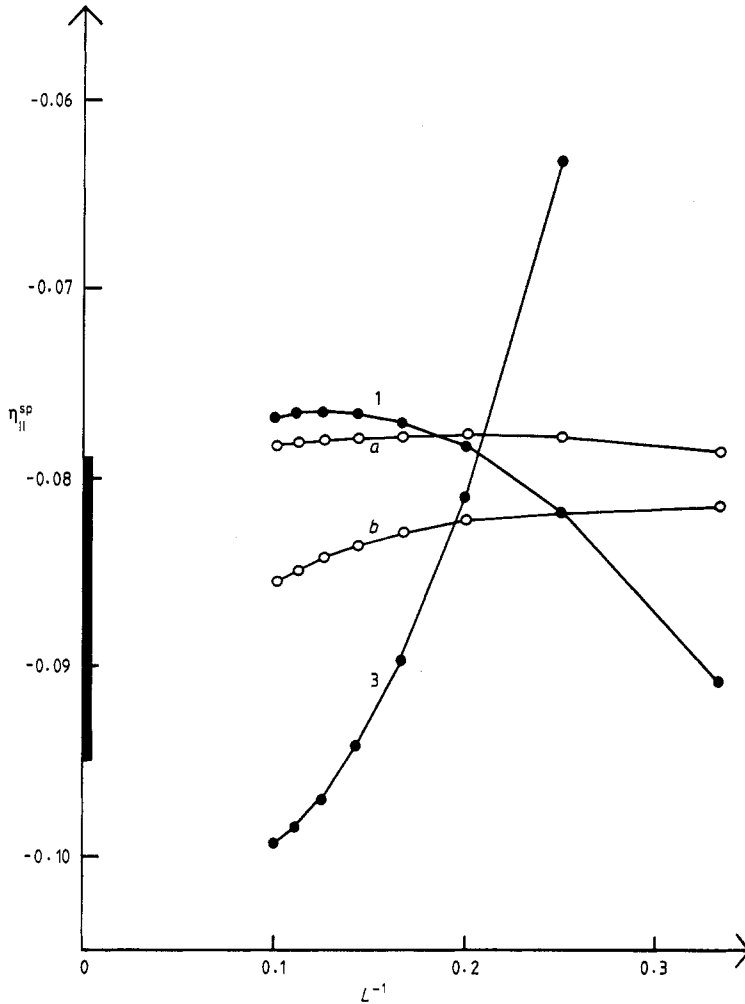


Figure 3. Curves 1 and 3 show estimates for $\eta_{||}^{sp} = 2x_s^{(1)}$ at the special transition from tables 1 and 3. Curves *a* and *b* show the quantity $2L[\pi\xi_L^{(1)}(K_s, K^*)]^{-1}$ with $K_s = 0.7730$ and 0.7745 , respectively, and with K^* given by equation (6). Our estimate of the exact value is indicated by a heavy vertical bar.

Duplantier and Saleur (1986) have proposed the relation $x_s^{(i)} = h_{i+1,1}$ for the surface scaling dimension of *i*-polymer vertices in the desorbed phase. Here $h_{r,s}$ is defined by the Kac formula $h_{r,s} = [(3r - 2s)^2 - 1]/24$. This conjecture reproduces the exact results $x_s^{(1)} = \frac{5}{8}$, $x_s^{(2)} = 2$ for the ordinary transition discussed above and is consistent with numerical evidence for $i > 2$. We note that an analogous relation $x_s^{(i)} = h_{i+1,3}$ is compatible with our results for the special transition, yielding $x_s^{(1)} = -\frac{1}{24}$, i.e. $\eta_{||}^{sp} = -\frac{1}{12}$, $\gamma_1^{sp} = \frac{93}{64}$, and $x_s^{(2)} = \frac{1}{3}$, i.e. $y_s^{sp} = \frac{2}{3}$, $\phi^{sp} = \frac{1}{2}$.

In summary, with transfer-matrix finite-size scaling methods we have studied a model for polymer adsorption in two dimensions equivalent to the $n \rightarrow 0$ vector model on a semi-infinite square lattice. For the desorbed polymer phase (ordinary transition of the magnetic system) our results confirm the accepted exact values of several bulk and surface critical exponents. The adsorption temperature and the critical exponents

Table 4. Critical values K_s^c for which the correlation length $\xi_L^{(t)}(K_s^c, K^*)$ diverges, with K^* given by equation (6).

One polymer		Two polymers	
L	K_s^c	L	K_s^c
2	0.725 1354		
3	0.737 2544	3	0.929 9088
4	0.743 6243	4	0.897 4993
5	0.747 6726	5	0.878 0769
6	0.750 5321	6	0.864 8723
7	0.752 6871	7	0.855 1933
8	0.754 3837	8	0.847 7333
9	0.755 7624	9	0.841 7731
10	0.756 9101	10	0.836 8815

ϕ^{sp} , γ_1^{sp} of the special transition were evaluated with a considerable reduction in the uncertainty of earlier estimates.

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Note added in proof. The exact result $\phi^{sp} = \frac{1}{2}$ has recently been derived with conformal invariance methods (Burkhardt *et al* 1989).

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