Crossover exponent for polymer adsorption in two dimensions

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In view of conflicting results for the crossover exponent, we extend our earlier transfer-matrix calculations for the adsorption of self-avoiding walks at the boundary of a semi-infinite square lattice. Analyzing strips with both one and two adsorbing edges, we obtain $\exp(\epsilon/kT_a) = 2.041 \pm 0.002$ for the critical temperature and $\phi = 0.500 \pm 0.003$ for the crossover exponent. The latter result is in excellent agreement with the prediction $\phi = \frac{1}{2}$ of conformal invariance.

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We consider the adsorption of a long flexible polymer in two dimensions [1]. The polymer is modeled as a self-avoiding walk on a semi-infinite square lattice with energy

$$E = -\epsilon N_1 \ , \tag{1}$$

where ϵ is a constant and N_1 is the number of steps along the boundary.

This system exhibits an adsorption transition at a critical temperature T_a, with a desorbed phase for $T > T_a$ and an adsorbed phase for $T < T_a$. For $T > T_a$ the average number of steps $\langle N_1 \rangle$ of the walk along the boundary remains finite in the limit $N \to \infty$, where N is the total number of steps of the walk. For $T < T_a$, $\langle N_1 \rangle$ is proportional to N in the large-N limit. At the critical temperature

$$\langle N_1 \rangle \sim N^{\phi} \ , \tag{2}$$

where ϕ is the crossover exponent.

Using the conformal-invariance approach and the equivalence [2–4] of the adsorption transition with the special or multicritical transition of the n-vector model in the limit $n \to 0$, Burkhardt *et al.* [5] have derived the crossover exponent $\phi = \frac{1}{2}$. This value also follows from a geometric picture presented recently by Stella *et al.* [6]. The prediction is in good agreement with two numerical studies. Using the transfer-matrix approach, Guim and Burkhardt [7] found $\phi = 0.501 \pm 0.003$, and Veal *et al.* [8] obtained two estimates, 0.51 ± 0.01 and 0.521 ± 0.001. In earlier work based on exact enumerations, Ishinabe [9] estimated $\phi = 0.53$ and 0.50 without quoting uncertainties. From Ishinabe's data, Kremer [10] obtained $\phi = 0.55 \pm 0.1$, and 0.55 ± 0.15 with real-space renormalization. A Monte Carlo study by Birshtein and Buldyrev [11] gave $\phi = 0.51$.

Recently Meirovitch and Chang [12] estimated ϕ with large-scale Monte Carlo calculations using a new scanning procedure [13]. Considering walks of up to $N = 260$ steps, they obtained $\phi = 0.562 \pm 0.020$, which is significantly larger than the theoretical prediction $\phi = \frac{1}{2}$. This discrepancy prompted us to check the theoretical prediction by extending the transfer-matrix calculations.

In our earlier transfer-matrix study [7] we analyzed strips with two adsorbing edges and with widths L of up to $L = 10$ lattice constants. In this paper we extend the calculations to $L = 11$ and obtain additional independent estimates by considering strips with one adsorbing and one free edge as well as strips with two adsorbing edges. A self-avoiding walk on a narrow strip with two adsorbing edges has a tendency to tunnel between the two edges. This tendency is reduced in strips with one adsorbing and one free edge, and we thought the data with this boundary geometry might be better behaved, i.e., easier to extrapolate to infinite L. This turns out to be the case.

As in [7,14] we work in the grand-canonical ensemble, assigning a surface fugacity K_s to each step along an adsorbing edge and a bulk fugacity K to all other steps. In the equivalent n-vector model [2–4] with $n \to 0$, the fugacities K_s, K represent an enhanced edge coupling J_s/kT and the bulk coupling J/kT, respectively. In terms of the multicritical values K_s^*, K^* of the fugacities corresponding to the special transition [3,4] of the magnetic system, the polymer adsorption temperature is given by

$$\exp\left(\frac{\epsilon}{kT_a}\right) = \frac{K_s^*}{K^*} \ . \tag{3}$$

Following [7,14] we construct exact transfer matrices $T_L^{(i)}(K_s, K)$, $i = 1, 2$, for one and two self-avoiding walks, respectively, on strips of width L. The partition functions for one and two self-avoiding walks correspond [2–4] to the spin-spin and energy-energy correlation functions of the magnetic system, respectively. The correlation length $\xi_L^{(i)}$ is related to the largest eigenvalue $\lambda_L^{(i)}$ of $T_L^{(i)}$ by

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

Using the best available estimate [15]

$$K^* = 0.379\,052\,28 \ \pm 0.000\,000\,14 \tag{5}$$

for the critical bulk fugacity, we calculate $K_s^*(L)$ and $y_s(L)$, which approach exact values for the semi-infinite

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geometry in the $L \to \infty$ limit, from the phenomenological renormalization group equations [16,17]

$$L^{-1}\xi_L^{(i)}(K_s^*(L),K^*) = (L-1)^{-1}\xi_{L-1}^{(i)}(K_s^*(L),K^*) \quad (6a)$$

$$1 + y_s(L) = \frac{\ln[(\partial\xi_L^{(i)}/\partial K_s)(\partial\xi_{L-1}^{(i)}/\partial K_s)^{-1}]}{\ln[L(L-1)^{-1}]} . \quad (6b)$$

The derivative in Eq. (6b) is evaluated at $K_s = K_s^*(L)$, $K = K^*$. The crossover exponent ϕ is obtained from y_s using

$$\phi = \frac{y_s}{y} = \frac{3}{4}y_s , \quad (7)$$

where $y = \nu^{-1} = \frac{4}{3}$ is the exact result [1] for the bulk scaling index.

The values of $K_s^*(L)$ and $y_s(L)$ for one and two self-avoiding walks on strips with two adsorbing edges are listed in Tables I and II, respectively. Corresponding data for strips with one adsorbing and one free edge are given in Tables III and IV.

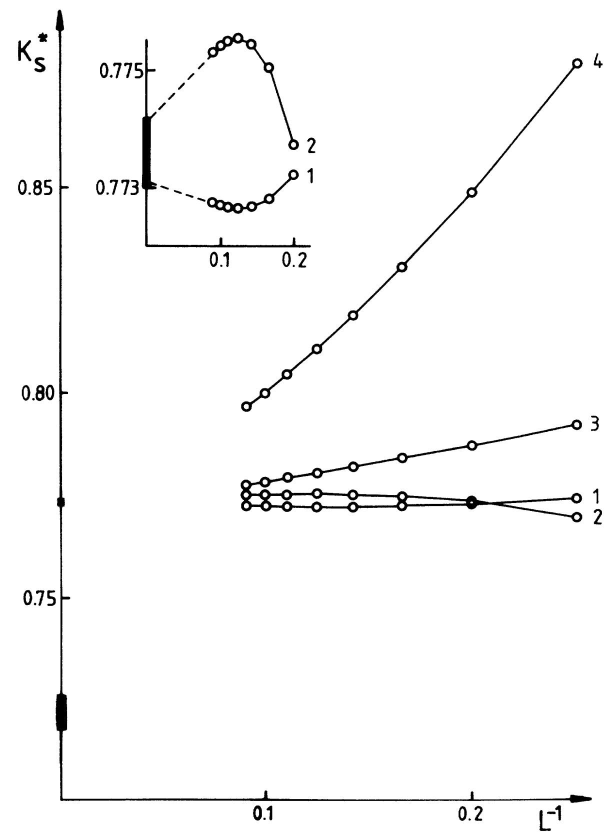

FIG. 1. $K_s^*(L)$ vs L^{-1}. Curves 1 and 2 show data for one and two self-avoiding walks, respectively, on strips with two adsorbing edges. Curves 3 and 4 show data for one and two self-avoiding walks, respectively, on strips with one adsorbing and one free edge. Our estimate of the limiting value is indicated by a solid bar on the vertical axis and the estimate of Meirovitch and Chang by a hatched bar. In the inset linear extrapolations based on $L = 10$ and 11 are shown.

TABLE I. $K_s^*(L)$, $y_s(L)$ for one self-avoiding walk on strips with two adsorbing edges

L	$K_s^*(L)$	$y_s(L)$
3	0.778 688 192	0.676 681 116
4	0.774 528 422	0.682 990 167
5	0.773 232 660	0.684 332 895
6	0.772 813 145	0.684 061 232
7	0.772 681 154	0.683 302 884
8	0.772 655 318	0.682 423 263
9	0.772 671 279	0.681 550 036
10	0.772 703 465	0.680 728 075
11	0.772 740 958	0.679 970 766

TABLE II. $K_s^*(L)$, $y_s(L)$ for two self-avoiding walks on strips with two adsorbing edges.

L	$K_s^*(L)$	$y_s(L)$
3	0.756 242 799	0.705 069 155
4	0.769 952 602	0.686 434 106
5	0.773 762 808	0.681 544 491
6	0.775 039 077	0.679 480 006
7	0.775 461 501	0.678 321 017
8	0.775 554 985	0.677 537 601
9	0.775 513 426	0.676 942 506
10	0.775 416 663	0.676 456 787
11	0.775 299 937	0.676 042 269

TABLE III. $K_s^*(L)$, $y_s(L)$ for one self-avoiding walk on strips with one adsorbing and one free edge.

L	$K_s^*(L)$	$y_s(L)$
3	0.801 086 900	0.753 733 390
4	0.792 459 028	0.736 176 262
5	0.787 557 457	0.724 879 078
6	0.784 434 946	0.716 937 343
7	0.782 300 974	0.711 018 734
8	0.780 766 871	0.706 421 646
9	0.779 620 658	0.702 738 814
10	0.778 737 842	0.699 716 543
11	0.778 040 989	0.697 188 072

TABLE IV. $K_s^*(L)$, $y_s(L)$ for two self-avoiding walks on strips with one adsorbing and one free edge.

L	$K_s^*(L)$	$y_s(L)$
3	0.943 538 681	0.925 655 415
4	0.880 318 042	0.847 093 272
5	0.849 040 400	0.807 017 784
6	0.830 717 936	0.782 318 317
7	0.818 865 519	0.765 392 292
8	0.810 658 629	0.753 000 421
9	0.804 686 716	0.743 506 378
10	0.800 173 797	0.735 985 467
11	0.796 660 667	0.729 872 313

In Figs. 1 and 2 the results for $K_s^*(L)$ and $y_s(L)$ are plotted versus L^{-1}. Curves 1 and 2 show the data for one and two self-avoiding walks, respectively, on strips with two adsorbing boundaries, and curves 3 and 4 corresponding data for strips with one adsorbing and one free boundary. Our estimates of the $L \to \infty$ limits are marked on the vertical axis with a solid bar and the Monte Carlo estimates of Meirovitch and Chang with a hatched bar.

In Figs. 1 and 2 the results of the four independent determinations of K_s^* and of y_s appear to converge toward the same value in the limit $L \to \infty$, as expected from ideas of universality. The limiting value of y_s seems close to the prediction $y_s = \frac{4}{3}\phi = \frac{2}{3}$ of conformal invariance. The transfer-matrix estimates of K_s^* and y_s are both inconsistent with the Monte Carlo estimates of Meirovitch and Chang (hatched bars), barring a drastic change in the L-dependence for $L > 11$.

The data for strips with one adsorbing and one free edge (curves 3 and 4 in Figs. 1 and 2) lie farther from the limiting value than the data for strips with two adsorbing edges (curves 1 and 2) but are better behaved. The monotonic approach to the limiting values $K_s^*(\infty)$, $y_s(\infty)$ allows one to extrapolate more reliably.

Applying the van den Broek–Schwartz extrapolation algorithm [18,19] to the data for one and two self-avoiding walks on strips with one adsorbing and one free edge, we generated the sequences shown in Tables V and VI. Note the excellent convergence. After only two iterations of the algorithm most of the ten entries for K_s^* and for y_s agree to three significant figures with each other and with the theoretical prediction $y_s = \frac{4}{3}\phi = \frac{2}{3}$. After four iterations the two sets of data extrapolate to $K_s^* = 0.7734, 0.7739$ and $y_s = 0.666\,63, 0.666\,63$. These values of y_s only differ from the theoretical value $\frac{2}{3}$ in the fifth significant figure.

The data for strips with two adsorbing edges (curves 1

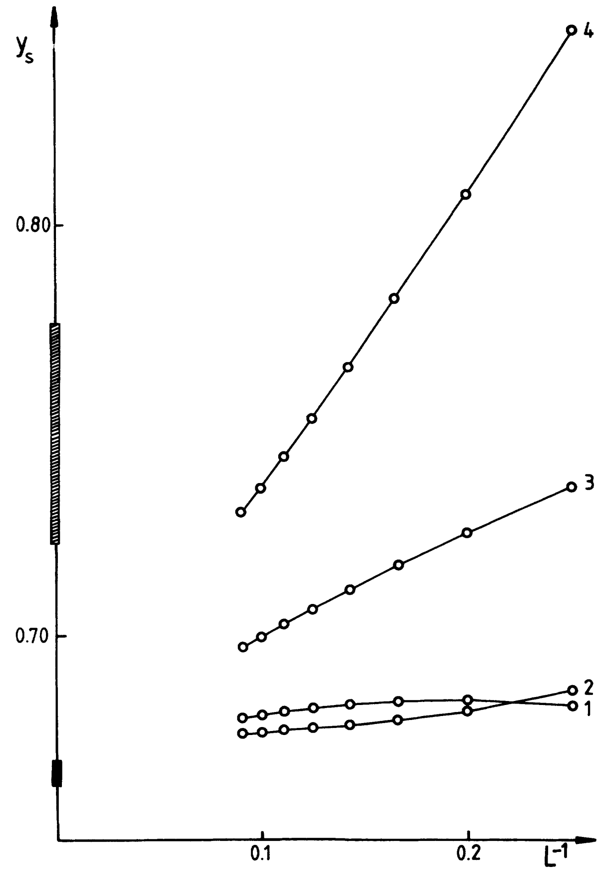

FIG. 2. y_s vs L^{-1}. Curves 1 and 2 show data for one and two self-avoiding walks, respectively, on strips with two adsorbing edges. Curves 3 and 4 show data for one and two self-avoiding walks, respectively, on strips with one adsorbing and one free edge. Our estimate of the limiting value is indicated by a solid bar on the vertical axis and the estimate of Meirovitch and Chang by a hatched bar.

TABLE V. Sequences $K_s^*(M,L)$ generated from Tables III and IV by M applications of the van den Broek–Schwartz algorithm with parameter α.

L	$K_s^*(0,L)$	$K_s^*(1,L)$	$K_s^*(2,L)$	$K_s^*(3,L)$	$K_s^*(4,L)$
			$\alpha = -0.9$		
3	0.801 0869				
4	0.792 4590	0.781 2544			
5	0.787 5575	0.779 0382	0.774 4301		
6	0.784 4349	0.777 7461	0.773 6311	0.773 4368	
7	0.782 3010	0.776 8776	0.773 4800	0.773 4485	0.773 4385
8	0.780 7669	0.776 2572	0.773 4541	0.773 4252	
9	0.779 6207	0.775 7959	0.773 4405		
10	0.778 7378	0.775 4423			
11	0.778 0410				
			$\alpha = -0.85$		
3	0.943 5387				
4	0.880 3180	0.821 9057			
5	0.849 0404	0.806 6805	0.776 4865		
6	0.830 7179	0.798 2677	0.774 0651	0.773 8945	
7	0.818 8655	0.792 9022	0.773 9066	0.773 9134	0.773 9121
8	0.810 6586	0.789 2225	0.773 9137	0.773 9117	
9	0.804 6867	0.786 5681	0.773 9109		
10	0.800 1738	0.784 5787			
11	0.796 6607				

TABLE VI. Sequences $y_s(M,L)$ generated from Tables III and IV by M applications of the van den Broek–Schwartz algorithm with parameter α.

L	$y_s(0,L)$	$y_s(1,L)$	$y_s(2,L)$	$y_s(3,L)$	$y_s(4,L)$
			$\alpha = -0.95$		
3	0.753 7334				
4	0.736 1763	0.705 7359			
5	0.724 8791	0.699 0460	0.664 4327		
6	0.716 9373	0.694 3979	0.666 1475	0.666 2665	
7	0.711 0187	0.690 9813	0.666 2592	0.666 8979	0.666 6324
8	0.706 4216	0.688 3535	0.666 3546	0.665 4592	
9	0.702 7388	0.686 2640	0.666 4619		
10	0.699 7165	0.684 5597			
11	0.697 1881				
			$\alpha = -0.95$		
3	0.925 6554				
4	0.847 0933	0.772 1623			
5	0.807 0178	0.747 1769	0.639 4118		
6	0.782 3183	0.731 8343	0.661 1521	0.666 0651	
7	0.765 3923	0.721 6452	0.665 3876	0.666 7246	0.666 6302
8	0.753 0004	0.714 3796	0.666 4216	0.666 6051	
9	0.743 5064	0.708 9176	0.666 5779		
10	0.735 9855	0.704 6472			
11	0.729 8723				

and 2 in Figs. 1 and 2) are not monotonic, and the standard extrapolation schemes are not very useful. Observing that the one- and two-polymer data for $K_s^*(L)$ appear to approach the limiting value from opposite sides, we obtain crude bounds by making linear extrapolations (see the inset of Fig. 1) using the data points for $L = 10$ and 11. This yields $0.7731 < K_s^* < 0.7741$. The van den Broek–Schwartz extrapolations $K_s^* = 0.7734$ and 0.7739 for strips with one adsorbing and one free edge are within these bounds.

In Fig. 2 curves 1 and 2 appear to curve downwards toward the limiting value of y_s. Making a linear extrapolation through the data points for $L = 10$ and 11, we obtain $y_s < 0.672$ for both curves. The van den Broek–Schwartz extrapolations $y_s = 0.666\,63$ and 0.666 63 for strips with one adsorbing and one free edge are consistent with this bound.

Comparing these extrapolations and bounds, we arrive at the final estimates $K_s^* = 0.7736 \pm 0.0006$ and $y_s = 0.667 \pm 0.004$. From Eqs. (3) and (7) we conclude $\exp(\epsilon/kT_a) = 2.041 \pm 0.002$ and $\phi = 0.500 \pm 0.003$.

In summary we have made four independent determinations of T_a and ϕ from numerically exact transfer-matrix data for infinitely long self-avoiding walks on strips with widths up to $L = 11$. The four determinations are in excellent agreement with each other and the theoretical prediction $\phi = \frac{1}{2}$. In our opinion the theoretical prediction is exact and thus provides a useful test of the reliability of numerical simulations of polymers.

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