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Adsorption of a self-avoiding walk, a real space renormalisation group study for $d = 2,3$

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Abstract. We present a real space renormalisation group calculation for the adsorption of a single self-avoiding walk in d dimensions at a $(d-1)$-dimensional impenetrable wall. The case $d = 3$ is used to check the method. For $d = 2$ the result for the crossover exponent φ gives $\varphi = 0.55 \pm 0.15$. This, in connection with enumerations of Ishinabe, clearly rules out de Gennes' conjecture $\varphi = 1 - \nu$ also for the case $d = 2$. For $d = 2$ cells up to 6×6 are used, for $d = 3$ cells up to $3 \times 3 \times 3$.

1. Introduction

Real space renormalisation group (RSRG) methods were used to study many different problems of polymers during the last few years. For a detailed introduction we refer to a recent review of Stanley *et al* (1982) and references therein. Usually the exponent ν of the mean square radius of gyration was calculated. On the other hand, the problem of the adsorption of a single polymer chain (SAW) at a hard wall, exerting a short-range attractive force, has found a longstanding interest in the literature during the last twenty years (see Eisenreigler *et al* (1982), Whittington (1982) and references therein). This problem up to now has not been studied by RS methods. Such methods turned out to be very useful for investigations of semi-infinite magnetic systems, which were also examined in great detail during the last few years (see Binder (1983) and references therein). Considering recent developments in the field, it is necessary to study the adsorption especially for $d = 2$ by RS methods. The question we are mainly concerned with here is the validity of de Gennes' (1976) conjecture $\varphi = 1 - \nu$. φ is the crossover exponent, which describes the adsorption transition. Due to the $n \to 0$ theorem (de Gennes 1972, 1977, 1979) the transition point corresponds to the so-called multicritical SB point of the semi-infinite n-vector model in the limit $n \to 0$ (Eisenriegler *et al* 1982). For this model Diehl and Dietrich (1981) found that $\varphi = 1 - \nu$ does not hold in general. In a recent exact enumeration of SAWs on a diamond lattice Ishinabe (1982b) calculated $\varphi_{d=3} = 0.6 \pm 0.1$ instead of 0.41. The best value up to now is due to Eisenriegler *et al* (1982), who found $\varphi_{d=3} = 0.59 \pm 0.02$.

For $d = 2$ Ishinabe (1982a) also found strong deviations from $\varphi = 1 - \nu$ by enumeration of SAWs on a square lattice. He obtained approximately $\varphi = 0.55 \pm 0.1$ (estimated from table III of his paper; he uses $\delta_a = 1/\varphi$). Because enumerations can only deal with very short chains it is necessary to investigate this problem by different techniques. Here we try it by a simple RSRG method. In § 2 we describe the method. In § 3 the

results for $d=3$ are compared with the results of the references mentioned above and the results for $d=2$ are given. Section 4 contains the conclusions.

2. Model and method

In the present work we model the polymer chain at a wall by a single SAW on a d-dimensional simple cubic lattice. The chain is confined to the positive half space $+:=\{(x_1,\ldots,x_d),\ x_1\geqslant 0\}$. Then each bond has a probability k_s if it is situated in the $x_1\equiv 0$ plane and the normal bulk-probability k_B otherwise. To renormalise the bulk couplings we use the simple cell method introduced by de Queiroz and Chaves (1980) for $d=2$ and Family (1981) for $d=3$. This method gives very accurate results for the exponent ν (see below) and is explained in detail in figure 1. This renormalisation

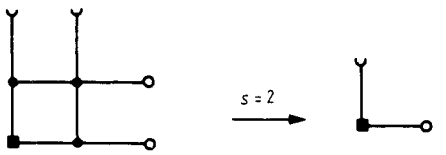

Figure 1. Simple example for the cell renormalisation for scaling factor $s=2$. Each bond has the probability k_B. The walk starts at the origin (■) and 'spans' if it reaches one of the circles (○). For the present example this leads to the renormalisation equation $k'_B=T(k_B)=k_B^2+2k_B^3+k_B^4$. For more details see de Queiroz and Chaves (1980), Family (1981) or Kremer (1983).

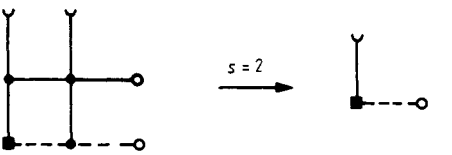

Figure 2. Simple example for the renormalisation of the surface coupling analogously to figure 1. The $\frac{1}{3}$-rule gives $k'_s=T^s(k_B,k_s)=k_s^2+k_sk_B^2$ while the $\frac{1}{4}$-rule would give $k'_s=T^s(k_s)=k_s^2+k_sk_B^2+k_sk_B^3$.

transformation leads to a non-trivial fixed point k_B^*. Near this fixed point one can write for the correlation length $\xi(k_B)$

$$\xi^2(k_B)\propto|k_B-k_B^*|^{-2\nu}. \tag{1}$$

On the other hand for the renormalised lattice one has (s is the renormalisation factor)

$$\xi(k'_B)=s^{-1}\xi(k_B) \qquad \text{with } k'_B=T(k_B) \tag{2}$$

(see e.g. Napiorowski *et al* (1979)).

This transformation has a relevant eigenvalue λ_B which in this simple case is just $\partial T(k_B)/\partial k_B|_{k_B^*}$ and one can write the exponent ν as $\nu=\ln s/\ln\lambda_B$.

The situation now changes if one introduces a different coupling in the plane $x_1=0$. Nakanishi (1981) considered walks in infinite space $-\infty<x_1<\infty$ with a bond probability $k_s(\neq k_B)$ in the 'defect plane' $x_1=0$ and found the value $T_a=\infty$ for the critical temperature T_a of adsorption. But here we are looking for the case of an impenetrable hard wall (walk in +) exerting a short-range attractive force. Using the results of an earlier investigation (de Gennes 1976), a walk in a surface cell is only renormalised to an adsorbed step or walk if a *finite* fraction of the bonds lies in the surface. This fraction can be arbitrarily small, but has to be finite. In the following we use as our minimal values $\frac{1}{3}$, $\frac{1}{4}$, $\frac{1}{5}$ and $\frac{1}{6}$. The corresponding renormalisations are then called after these values as $\frac{1}{3}$-rule etc. Figure 2 gives an example of such a surface cell

renormalisation. For more details we refer to Kremer (1983). We now have a two-parameter RS procedure with

$$(k'_B, k'_s) = \mathcal{T}(k_B, k_s) = (T(k_B), T^s(k_B, k_s)) \tag{3}$$

and

$$\xi(k'_B, k'_s) = s^{-1}\xi(k_B, k_s) \tag{4}$$

has a multicritical fixed point (k_B^*, k_s^*) with two eigenvalues >1.

Linearising the transformation around the multicritical point now results in

$$(k'_B, k'_s) = \begin{pmatrix} \partial_{k_B} T & 0 \\ \partial_{k_B} T^s & \partial_{k_s} T_s \end{pmatrix}\Bigg|_{(k_B^*, k_s^*)} \begin{pmatrix} k_B \\ k_s \end{pmatrix} = \begin{pmatrix} \lambda_B & 0 \\ \partial_{k_B} T_s & \lambda_s \end{pmatrix}\begin{pmatrix} k_B \\ k_s \end{pmatrix} \tag{5}$$

with eigenvalues λ_B and λ_s. This gives $\nu = \ln \lambda_B / \ln s$, while the crossover exponent φ is determined by both eigenvalues (Stanley *et al* 1982) and given by

$$\varphi = \ln \lambda_s / \ln \lambda_B. \tag{6}$$

The generalisation to non-integer values of $s = \frac{3}{2}$ etc is then straightforward (Stanley *et al* 1982).

3. Results

For this calculation the numbers of spanning SAWs in cells up to $3\times3\times3$ ($d=3$) and up to 6×6 for $d=2$ were enumerated by a computer algorithm. For $k_s = k_B$ the data are the same as earlier results by Family (1981), $d=3$, and Redner and Reynolds (1981), $d=2$. The results of the enumerations are given in the appendix.

Our main interest concerns the case $d=2$. Figure 3 shows the phase diagram, as it is given by the RS flux for $s=2$, $d=2$. The flux diagram reproduces qualitatively for $d=2$ the well known behaviour of semi-infinite magnets. The flow directions along the critical lines are indicated in the figure. The multicritical SB point is completely

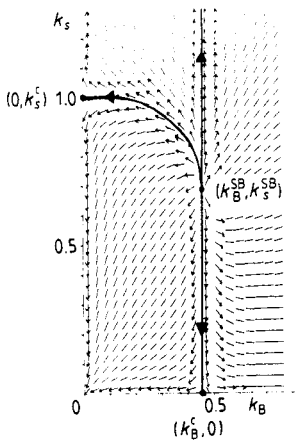

Figure 3. Phase diagram given by the renormalisation flux for renormalisation of a 2×2 cell to a 1×1 cell. The multicritical fixed point (k_B^{SB}, k_s^{SB}) is completely unstable. As is claimed by field theory (Eisenriegler *et al* 1982, Dietrich 1982), k_B^{SB} the critical bulk coupling at the multicritical SB point is the same as for the pure bulk case. For a direct comparison with the magnetic phase diagram we refer to Kremer (1983) or Dietrich (1982).

Table 1. Results of the renormalisation for (*a*) $d=2$ and (*b*) $d=3$. s_1 gives the initial cell size, s_2 the renormalised one. ν is calculated by the usual bulk renormalisation, k_B^* gives the fixed points. For φ and k_s^* all the results of the different rules are given: φ_1, k_{s1}^* corresponds to the $\frac{1}{3}$-rule, φ_2, k_{s2}^* to the $\frac{1}{4}$-rule, φ_3, k_{s3}^* to the $\frac{1}{5}$-rule and φ_4, k_{s4}^* to the $\frac{1}{6}$ rule. For simplicity this is only written in detail in one case. (The approximate error bar in (*a*) for φ is obtained by extrapolating s_1/s_2 to 1 by two series (6/1, 6/2, ... 6/5; 2/1, 3/2, ..., 6/5). Using these values for φ the error is about ±0.150.)

(*a*)

s_2 \ s_1	2		3		4		5		6	
	$\nu=0.715$	$k_B^*=0.466$	$\nu=0.719$	$k_B^*=0.447$	$\nu=0.722$	$k_B^*=0.435$	$\nu=0.724$	$k_B^*=0.426$	$\nu=0.726$	$k_B^*=0.420$
	$\varphi_1=0.597$	$k_{s1}^*=0.783$	$\varphi=0.632$	$k_s^*=0.793$	$\varphi=0.618$	$k_s^*=0.768$	$\varphi=0.626$	$k_s^*=0.770$	$\varphi=0.631$	$k_s^*=0.773$
1	$\varphi_2=0.537$	$k_{s2}^*=0.682$	0.584	0.729	0.587	0.717	0.589	0.719	0.595	0.722
	$\varphi_3=0.537$	$k_{s3}^*=0.682$	0.525	0.663	0.562	0.688	0.561	0.684	0.564	0.686
	$\varphi_4=0.537$	$k_{s4}^*=0.682$	0.507	0.643	0.531	0.659	0.542	0.663	0.540	0.661
			$\nu=0.722$	$k_B^*=0.432$	$\nu=0.726$	$k_B^*=0.423$	$\nu=0.729$	$k_B^*=0.417$	$\nu=0.730$	$k_B^*=0.413$
			$\varphi=0.679$	$k_s^*=0.804$	$\varphi=0.631$	$k_s^*=0.763$	$\varphi=0.639$	$k_s^*=0.769$	$\varphi=0.643$	$k_s^*=0.773$
2			0.638	0.769	0.617	0.734	0.610	0.733	0.613	0.734
			0.495	0.645	0.573	0.695	0.567	0.689	0.567	0.692
			0.444	0.604	0.516	0.654	0.536	0.664	0.532	0.663
					$\nu=0.731$	$k_B^*=0.416$	$\nu=0.733$	$k_B^*=0.411$	$\nu=0.735$	$k_B^*=0.408$
					$\varphi=0.553$	$k_s^*=0.718$	$\varphi=0.604$	$k_s^*=0.751$	$\varphi=0.619$	$k_s^*=0.764$
3					0.591	0.703	0.587	0.716	0.599	0.725
					0.652	0.737	0.607	0.711	0.596	0.709
					0.589	0.697	0.585	0.692	0.564	0.683
							$\nu=0.736$	$k_B^*=0.407$	$\nu=0.737$	$k_B^*=0.404$
							$\varphi=0.659$	$k_s^*=0.780$	$\varphi=0.657$	$k_s^*=0.784$
4							0.583	0.730	0.602	0.735
							0.544	0.683	0.552	0.694
							0.580	0.689	0.547	0.678
									$\nu=0.739$	$k_B^*=0.401$
									$\varphi=0.655$	$k_s^*=0.789$
5	$\varphi=0.55\pm0.15$								0.624	0.741
	$k_s^*=0.65\pm0.05(\simeq T_a=2.\ 3^{+0.5}_{-0.3})$								0.559	0.705
									0.504	0.667

(*b*)

s_2 \ s_1	2	3
1	$\nu = 0.588$	$\nu = 0.581$
	$\varphi_1 = 0.727$	$\varphi = 0.715$
	$\varphi_2 = 0.675$	0.678
	$\varphi_3 = 0.499$	0.504
2	$\nu = 0.568$	
	$\varphi = 0.691$	
	0.670	
	0.499	

s_2 \ s_1	2	3
1	$k_B^* = 0.297$	$k_B^* = 0.275$
	$k_{s1}^* = 0.383$	$k_s^* = 0.354$
	$k_{s2}^* = 0.357$	0.337
	$k_{s3}^* = 0.578$	0.479
2	$k_B^* = 0.262$	
	$k_s^* = 0.336$	
	0.325	
	0.413	

unstable; the flow direction for $k_s < k_s^{SB}$ points to the bulk fixed point. This fixed point is stable with respect to the critical line to the SB point and unstable with respect to the k_B axis. A similar behaviour is given for the line $(0, k_s^c)$ (k_B^{SB}, k_s^{SB}). The point $(0, k_s^c)$ represents the completely adsorbed chain at $T=0$. For $d=2$ (see figure 3) $k_s^c = 1$ corresponds to the fully stretched chain, which means that the effective coordination number at $T=0$ is equal to one, as expected. In all cases, at the SB point we have $\lambda_B > \lambda_s$. At SB the bulk behaviour dominates and the crossover exponent φ is given by equation (6). Table 1(*b*) shows the results for $d=2$, for the SB point. The other fixed points are then trivial. As shown earlier by other authors, the exponent ν nicely extrapolates for increasing s_1 and $s = s_1/s_2$ approaching 1 to the best value $\nu = 0.75$ $(d=2)$ (Nienhuis 1982). The value of φ is calculated in all cases for the $\frac{1}{3}$-, $\frac{1}{4}$-, $\frac{1}{5}$- and $\frac{1}{6}$-rules. Here a convergent extrapolation to a 'one over infinity' rule for $s \to 1$ is very difficult. We estimate

$$\varphi \approx 0.55 \pm 0.15. \tag{7}$$

This value is in good agreement with Ishinabe's (1982a, b) enumerations. Therefore using both results also for $d=2$ the conjecture $\varphi = 1 - \nu$ can be rejected.

Table 1(*a*) gives the corresponding results for $d=3$. Although here only cells up to $3\times3\times3$ were used, it is clear that the results are in reasonable agreement with the known behaviour and the best value of $\varphi_{d=3} = 0.59$ (Eisenriegler *et al* 1982). Also the renormalisation flux is qualitatively the same as in figure 3.

4. Conclusion

We presented a simple RSRG calculation for the adsorption of a single SAW at a hard wall, which exerts a short-range attractive force. The case $d=3$ was treated to prove the validity of our method. For $d=2$ it was shown that the phase diagram, qualitatively, is the same as for $d=3$. In agreement with a recent enumeration of Ishinabe (1982a, b) the relation $\varphi_{d=2} = 1 - \nu_{d=2} (=0.25)$ is far outside the error bars.

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Appendix. Enumeration results

Here we give the complete enumeration results for spanning walks on cells up to the size 6×6 $(d=2)$ and $3\times3\times3$ $(d=3)$. The first column gives the number of bonds N, while the second gives the total number of spanning SAWs $N_T(N)$ with N bonds. The next columns give the number of SAWs separated due to the amount N_s of surface bonds. The total number of spanning walks is the same as found by Family (1981) $(d=3)$ and Redner and Reynolds (1981) $(d=2)$.

$d=2$ 2×2 cell				
N	$N_T(N)$	$N_s=0$	1	2
2	1	0	0	1
3	2	1	1	0
4	1	0	1	0

$d=2$ 3×3 cell					
N	$N_T(N)$	$N_s=0$	1	2	3
3	1	0	0	0	1
4	3	1	1	1	0
5	9	3	3	3	0
6	5	3	2	0	0
7	9	1	5	3	0
8	2	0	2	0	0
9	4	0	1	3	0

$d=2$ 4×4 cell						
N	$N_T(N)$	$N_s=0$	1	2	3	4
4	1	0	0	0	0	1
5	4	1	1	1	1	0
6	16	4	4	4	4	0
7	34	16	11	6	1	0
8	44	14	15	11	4	0
9	68	29	25	11	3	0
10	77	11	33	24	9	0
11	90	22	40	23	5	0
12	100	4	26	46	24	0
13	84	8	32	35	9	0
14	74	0	9	27	38	0
15	45	0	12	23	10	0
16	12	0	0	5	7	0

$d=2$ 5×5 cell							
N	$N_T(N)$	$N_s=0$	1	2	3	4	5
5	1	0	0	0	0	0	1
6	5	1	1	1	1	1	0
7	25	5	5	5	5	5	0
8	65	25	19	13	7	1	0
9	179	65	51	36	21	6	0
10	243	109	77	40	14	3	0
11	560	187	181	117	57	18	0
12	637	252	223	115	40	7	0
13	1382	328	470	354	174	56	0
14	1372	417	496	322	116	21	0
15	2861	442	837	892	516	174	0
16	2412	486	817	724	325	60	0
17	4767	443	1151	1466	1207	500	0
18	3386	366	1002	1158	702	158	0
19	6053	266	1168	1849	1724	1046	0
20	3333	132	780	1205	959	257	0
21	4991	28	674	1519	1693	1077	0
22	1676	0	291	628	602	155	0
23	1901	0	68	519	804	510	0
24	271	0	0	102	139	30	0
25	248	0	0	26	135	87	0

$d=2$ N	6×6 cell $N_T(0)$	$N_s=0$	1	2	3	4	5	6
6	1	0	0	0	0	0	0	1
7	6	1	1	1	1	1	1	0
8	36	6	6	6	6	6	6	0
9	111	36	29	22	15	8	1	0
10	356	111	91	70	49	28	7	0
11	826	356	240	139	66	21	4	0
12	1 633	574	471	314	177	76	21	0
13	3 370	1 423	1 043	560	245	82	17	0
14	5 752	1 840	1 770	1 184	628	259	71	0
15	11 035	4 193	3 543	2 052	890	294	63	0
16	17 870	4 690	5 508	4 196	2 283	936	257	0
17	31 410	10 302	10 072	6 703	3 105	1 019	209	0
18	49 817	10 057	14 275	13 064	8 010	3 440	971	0
19	79 163	21 134	24 688	19 068	10 065	3 503	705	0
20	122 682	18 252	31 404	33 170	24 355	11 896	3 605	0
21	177 701	36 169	52 205	46 996	28 602	11 328	2 401	0
22	261 420	27 120	58 418	70 797	58 763	34 347	11 975	0
23	348 760	49 933	93 258	98 431	68 614	31 031	7 493	0
24	468 376	30 737	88 482	125 269	116 538	75 652	31 698	0
25	571 124	50 658	133 483	167 967	133 547	67 657	17 812	0
26	668 111	22 995	100 881	173 533	182 872	129 585	58 245	0
27	722 144	31 358	138 553	216 038	197 297	109 771	29 127	0
28	702 825	8 587	75 238	170 882	210 891	162 769	74 458	0
29	640 132	9 379	88 307	185 460	201 522	123 648	31 816	0
30	507 803	1 121	28 120	104 747	164 454	142 990	66 371	0
31	369 278	1 023	27 826	93 981	130 968	92 383	23 097	0
32	230 029	0	3 732	31 252	74 810	80 965	39 270	0
33	124 655	0	3 216	23 298	46 590	41 332	10 219	0
34	54 159	0	0	3 326	14 026	24 073	12 734	0
35	18 505	0	0	1 949	6 475	7 996	2 085	0
36	3 295	0	0	0	686	1 724	885	0

$d=3$ N	2×2×2 cell $N_T(N)$	$N_s=0$	1	2	3	4
2	1	0	0	1	0	0
3	4	1	1	0	2	0
4	8	2	3	2	0	1
5	12	1	4	6	1	0
6	14	0	5	4	5	0
7	16	0	2	8	6	0
8	10	0	0	5	5	0

$d=3$	$3\times3\times3$ cell									
N	$N_T(0)$	$N_s=0$	1	2	3	4	5	6	7	8	9
3	1	0	0	0	1	0	0	0	0	0	0
4	6	1	1	1	0	3	0	0	0	0	0
5	30	6	6	6	3	0	9	0	0	0	0
6	106	24	24	22	22	9	0	5	0	0	0
7	352	72	79	71	60	56	5	0	9	0	0
8	826	163	199	180	141	85	47	9	0	2	0
9	2 378	341	524	534	451	277	171	74	2	0	4
10	5 086	675	1 074	1 194	1 053	664	299	97	26	4	0
11	13 774	1250	2 380	3 090	2 967	2 295	1 171	445	134	42	0
12	26 426	2086	4 240	6 013	6 241	4 459	2 315	797	239	36	0
13	67 666	3275	8 398	13 695	15 782	13 469	8 038	3 709	1 074	226	0
14	116 734	4537	12 818	23 361	29 565	24 429	14 177	5 876	1 737	234	0
15	278 128	5430	21 362	46 124	65 020	65 851	43 628	21 927	7 296	1 490	0
16	409 188	5317	26 432	64 537	101 142	101 500	68 039	30 969	9 768	1 484	0
17	878 346	4088	33 427	102 477	187 078	230 771	178 481	100 092	34 162	7 770	0
18	1065 878	2298	29 967	109 570	230 128	291 191	233 395	122 352	40 621	6 356	0
19	2013 600	826	24 200	129 293	337 841	533 028	509 208	327 200	123 652	28 352	0
20	1951 424	0	13 005	95 488	307 579	521 237	535 056	335 256	123 678	20 116	0
21	3133 930	0	4 558	70 028	324 309	724 787	915 592	710 447	311 747	72 462	0
22	2295 390	0	0	28 226	186 117	503 485	720 092	565 887	248 203	43 380	0
23	2962 104	0	0	7 893	114 992	463 849	891 025	890 107	479 474	114 764	0
24	1460 748	0	0	0	25 236	180 577	436 512	492 015	276 086	50 322	0
25	1369 060	0	0	0	4 564	83 902	326 316	502 767	362 051	89 460	0
26	340 804	0	0	0	0	6 994	59 320	141 624	111 738	21 128	0
27	170 872	0	0	0	0	528	15 244	65 387	71 489	18 224	0

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