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Monte Carlo Renormalization of Hard Sphere Polymer Chains in Two to Five Dimensions

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A renormalization group for polymer chains with hard-core interaction is considered, where a chain of N_0 links of length l_0 and hard-core diameter h_0 is mapped onto a chain of $N_1 = N_0/s$ links of length l_1 and hard-core diameter h_1. The length l_1 is defined in terms of suitable interior distances of the original chain, and h_1 is found from the condition that the end-to-end distance is left invariant. This renormalization group procedure is carried through by various Monte-Carlo methods (simple sampling is found advantageous for short enough chains or high dimensionalities, while dynamic methods involving "kink-jumps" or "reptation" are used else). Particular attention is paid to investigate systematic errors of the method by checking the dependence of the results on both N_0 and s. It is found that for dimensionalities $d=2$, 3 only the nontrivial fixed-point is stable, where upon iteration the ratio $\delta_k = h_k/l_k$ tends to nonzero fixed-point value δ^*, while for $d=4,5$ the method converges to the gaussian fixed point with $\delta^*=0$. Taking both statistical and systematic errors into account, we estimate the exponent ν as $\nu = 0.74 \pm 0.01$ ($d=2$) and $\nu = 0.59 \pm 0.01$ ($d=3$). The results are consistent with the expected crossover exponents $\phi = 1/2$ ($d=3$) and $\phi = 1$ ($d=2$), respectively.

I. Introduction

The properties of long flexible polymer chains in dilute solution have attracted much theoretical attention (for reviews, see [1-5]). Concepts like scaling and universality [3-5] have been successfully taken over from the theory of critical phenomena [6] to elucidate the asymptotic behavior of very long chains. Field-theoretic renormalization group methods [7] have already yielded the exponent ν, which describes the asymptotic behavior of the end-to-end distance of $\langle R_N^2 \rangle$ of chains containing N links, $\langle R_N^2 \rangle \propto N^{2\nu}$, with very good accuracy ($\nu = 0.588 \pm 0.001$ [7]). However, these methods cannot explicitly relate the (nonuniversal) prefactor in this relation to the potential describing interactions between the links of a particular polymer chain. In addition, there is also interest in studying the behavior of shorter chains, where this asymptotic law is not yet valid. There one still expects a universal behavior described by a crossover from the behavior of gaussian chains, $\langle R_N^2 \rangle \propto N$, to the above law [8, 9]. Much effort has been devoted in determining this function in terms of a suitably scaled second virial coefficient of the interlink-interaction [2] see also, e.g., [10-15]), but still this problem has not been solved with the same accuracy as estimating the exponent ν. In addition, considering the probability distribution of arbitrary interlink distances even involves other exponents which are not yet known with very high precision [16, 17]. Much less accurate information is known when one considers chains with partially attractive interactions, where collapse transitions [18, 19] and glass transitions [20] can occur,

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or when one considers not so dilute polymer solutions, where interactions among different chains, entanglements [5] etc. become important.

Thus there is interest in developing additional theoretical methods by which some of these questions can be addressed. Although Monte-Carlo simulation methods [11, 19–21] have important applications, their straightforward application to the study of power-laws describing the true asymptotic behavior of very long chains is rather cumbersome. For other phase transition problems, the combination of real space renormalization with Monte Carlo methods seems to become a powerful tool [22–28]. In the present paper we hence propose and investigate a Monte Carlo renormalization group (MCRG) procedure for polymers [29]. Section II contains a brief description of the Monte Carlo techniques used here. Results both on end-to-end distances and on internal distances are shown in detail and discussed in terms of scaling hypotheses. These scaling hypotheses are the basis for the renormalization group analysis which is presented in Sect. III, while Sect. IV contains our conclusions.

II. Monte-Carlo-Results on End-to-End and Internal Distances

1. Polymer Model and Simulation Methods

The model for a polymer chain being studied her is a chain of N links of rigid length l freely joint together in d-dimensional space, for dimensionalities $d=2$, 3, 4 and 5. It is assumed that the $(N+1)$ molecular units (represented by the end-points of the links) interact with an excluded-volume potential, i.e., one has a chain of $(N+1)$ hard spheres, the hard-sphere diameter being denoted as h_0 in the following. Denoting the endpoints of the links by $\mathbf{r}_i$, $i=1,\ldots,N+1$, the quantities of interest here are the mean-square end-to-end distance $\langle R_N^2\rangle$,

$$\langle R_N^2\rangle = \langle(\mathbf{r}_1-\mathbf{r}_{N+1})^2\rangle, \tag{1}$$

as well as mean square internal distances $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle$, where the brackets denote an average over the configurations of the polymer chains which are allowed by the hard-core potential. These quantities are obtained for several values of N (typically $4\leqq N\leqq 60$) as well as several values of the interaction parameter $\delta=h/l$.

It turns out that it is most advantageous to use different kinds of Monte Carlo simulation methods in different regimes of the three parameters N, δ and d. For $d\geqq 4$ the "simple Monte Carlo sampling" is preferable for all N and δ studied. By the "simple sampling" method one uses random numbers to generate an unrestricted random walk of N links of equal length l. When the walk is completed one checks for the set of values $\{\delta^{(\nu)}\}$, for which one wants to calculate $\langle R_N^2\rangle$ as well as the various $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle$, whether the excluded volume condition is satisfied for all distances $\mathbf{r}_n-\mathbf{r}_{n+m}$ in the chain, $|\mathbf{r}_n-\mathbf{r}_{n+m}|>\delta^{(\nu)}l$ [11]. For those $\delta^{(\nu)}$ for which this condition is satisfied this configuration of the chain is taken into account for the averaging, for the other $\delta^{(\nu)}$'s for which it is not satisfied this configuration is omitted. After having constructed 10^6 walks the average over the $W(\delta^{(\nu)},N,d)\cdot 10^6$ walks which have been kept is carried out. Obviously, this method has the following advantages:

(i) one can obtain results for a large number of values $\{\delta^{(\nu)}\}$ at the same time by one simulation run;

(ii) Since the different configurations are statistically independent of each other, the accuracy of the averages can be estimated by standard statistical analysis.

(iii) From recording the fraction $W(\delta^{(\nu)},N,d)$ of successful attempts to construct a configuration one immediately obtains the entropy S of the chain [S_0 being the entropy in the absence of excluded-volume interactions] [31, 32]

$$(S-S_0)/k_B=\ln W(\delta^{(\nu)},N,d). \tag{2}$$

On the other hand, it is easily seen from this equation that simple sampling becomes ineffective for very long chains: as the entropy is an extensive quantity, we have, to leading order [31], $(S-S_0)/k_B=-Ns$, with $s>0$, and hence the fraction W of successfull attempts to construct a configuration decreases exponentially fast with increasing number of links N (see also Fig. 6 below). Therefore this method could be used for $d=3$ only for $N\leqq 30$ in the regime of interest ($0.4\leqq\delta\leqq 0.6$), while for $d=2$ only chains up to $N=20$ could be generated. For other cases, we use "dynamic" methods for Monte Carlo simulation [30]. In the "kink-jump" method [21] a pair of neighboring links is rotated about the axis connecting the endpoints of the links by a randomly chosen angle φ for $d=3$ while for $d=2$ only the choice $\varphi=\pi$ is possible. The resulting state is accepted as a new configuration of the chain if it again satisfies the excluded volume restriction; otherwise it is rejected and the old configuration is counted once more in the averaging. The points $\mathbf{r}_i$ which are considered for one such move are selected at random. If an endpoint of the chain is chosen $\{\mathbf{r}_1,\mathbf{r}_{N+1}\}$ the link is rotated to a new position by specifying two randomly chosen angles (φ,ϑ) [for the case $d=3$], with $\cos\vartheta$

being equally distributed in the interval $-1<\cos\vartheta\leqq 1$. For the case $d=2$ it is only the angle φ which then can randomly be chosen (in the range $-\pi<\varphi<\pi$) [33, 34]. A second kind of dynamic simulation method is the so-called "reptation" method [35]: there one first selects one of the two ends of the chain at random and then removes the end link of the chain and adds it at the other end, specifying there the orientation of the link by angles as described above [34]. This mechanism, which corresponds to a movement of the chain along itself, produces an approach towards equilibrium which in some cases was found somewhat faster than the "kink-jump" method. In some cases, e.g., $N=16$ and $d=2$, as a check all three methods were used, and the results were found to be in excellent agreement. It must be noted that estimating the error of quantities obtained from dynamic simulations is nontrivial, as subsequent configurations are highly correlated (the "correlation time" is increasing with chain length as $\tau\propto N^{z\nu}$, with $z\nu\gtrapprox 2$, when the time is measured in units of Monte Carlo steps/link [19]). In addition, one has to perform new Monte Carlo runs for each value of δ, and does not obtain any direct information on the entropy of the chain.

2. *Numerical Results and Their Scaling Analysis*

"Raw Monte Carlo data" on end-to-end distances for various N and δ are shown in Tables 1-3. As far as the dynamic simulations are concerned, up to 10^5 Monte Carlo steps (MCS) per link have been used.

According to the scaling theory for polymers [3-5, 36] the end-to-end distance of long chains should not depend on the two parameters N, δ separately, but rather it should depend on them in the scaled form

$$\sqrt{\langle R_N^2\rangle}=lN^{1/2}f(N\delta^{d/\phi}),\qquad N\to\infty$$
$$x=N\delta^{d/\phi}\ \text{finite},\tag{3}$$

where ϕ is the appropriate crossover exponent and the function $f(x)$ has the following asymptotic behavior ($d<4$)

$$f(x)=Ax^{(\nu-1/2)},\qquad x\to\infty,\tag{4}$$

where A is an amplitude factor and ν a "critical exponent" describing the bahavior of very long chains. According to Flory [1] we have

$$\nu=3/(d+2),\tag{5}$$

while the most accurate estimate obtained from field-theoretic renormalization group methods [37] is

Table 1-3. Mean square end-to-end distances for various chain lengths N, hard sphere parameter δ and space dimensions ($d=2$: Table 1; $d=3$: Table 2; $d=4,5$: Table 3). The statistical error of the estimates is about $\pm 0.3\,\%$ and $\pm 0.1\,\%$ for $d=2,3$ and $d=4,5$ dimensions respectively

Table 1.

$N\rightarrow$	6	8	12	15	20	30
$\delta=0.50$	10.63	16.12	28.94	40.07		
0.55	11.29	17.22	31.19	43.43	68.7	120 ± 1
0.60	11.83	18.15	32.95	45.77	70.5	129
0.65	12.29	18.84	34.34	47.68	72.9	133
0.70	12.71	19.54	35.76	49.60	76.2	138
0.75	13.14	20.25	37.09	51.55	79.2	142
0.80	13.58	20.98	38.44	53.50	83.1	
0.85	14.03	21.72	39.82	55.50		

Table 2

N	8	12	16	24	40	60
$\delta=0.35$	8.91	13.84	18.84			
0.40	9.24	14.52	19.28	31.45	56.1	90.07
0.45	9.67	15.37	21.34	34.05	61.5	99.6
0.50	10.18	16.40	22.94	37.00	67.3	109.8
0.55	10.76	17.47	24.60	40.00	73.2	119.8
0.60	11.29	18.49	26.21	42.85	78.1	129.0
0.65	11.83	19.58	27.75	45.60		
0.70	12.39	20.48	29.16			

Table 3.

$N\rightarrow$	Dim = 4			Dim = 5	
	8	12	16	10	20
$\delta=0.0$	8.00	12.00	16.00	10.00	20.00
0.05	8.00	12.00	16.00	10.00	20.00
0.10	8.003	12.006	16.00	10.005	20.005
0.15	8.009	12.020	16.032	10.005	20.01
0.20	8.037	12.055	16.080	10.005	20.025
0.25	8.066	12.130	16.22	10.01	20.06
0.30	8.134	12.25	16.40	10.03	20.12
0.35	8.225	12.42	16.65	10.07	20.23
0.40	8.352	12.67	17.07	10.14	20.40
0.45	8.532	13.03	17.56	10.24	20.67

$$\nu=0.588\pm0.001\,(d=3),\qquad \nu\approx 0.77\,(d=2).\tag{6}$$

For $d>4$ we have instead of (4)

$$f(x)\xrightarrow[x\to\infty]{} A,\tag{7}$$

i.e., the chain asymptotically behaves ideal, while for $d=4$ logarithmic correction factors have been predicted [38]

$$f(x)\xrightarrow[x\to\infty]{} A(\ln x)^{1/4}.\tag{8}$$

The renormalization group analysis which is presented in Sect. III is based on the assumption that (3) does in fact become for very long chains, and studying the behavior in the vicinity of the nontrivial

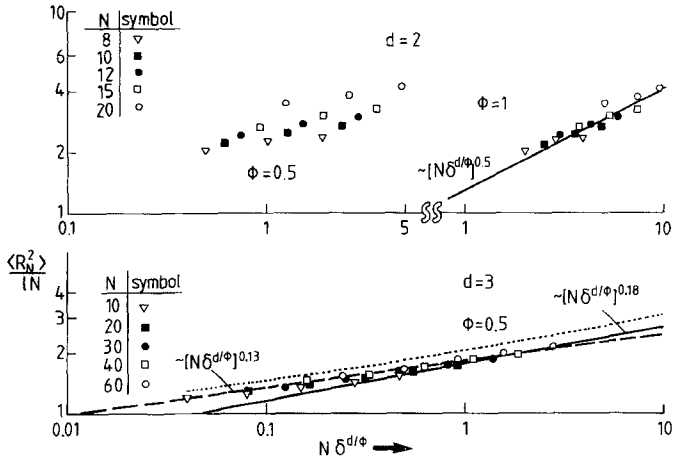

Fig. 1. Log-log plot of the "expansion factor" $\langle R_N^2\rangle/lN$ of the polymer chain versus scaled chain length for various values of N and excluded volume parameter δ. Data for dimensionalities $d=2$ and 3 are shown

fixed-point will then yield estimates for the quantities ν, ϕ, and A. However, our numerical analysis is based on data for fairly short chains, for which one has to expect correction terms to the leading asymptotic behavior of very long chains, (3). Thus it is interesting to check the extent to which (3) already holds for the short chains studied here, Fig. 1. Here we have assumed for ϕ the values appropriate for crossover from gaussian to nontrivial behavior: $\phi=1/2$ ($d=3$), $\phi=1$ ($d=2$) [39]. It is seen that the data for $d=3$, $d=2$ superimpose quite well and are close to a straight-line behavior already for $x=N\delta^{d/\phi}\lesssim 1$. For $d=3$, the slope of the straight line is found to be about 0.13 ± 0.02. which would imply an "effective exponent" (which need not be the correct asymptotic exponent ν due to the effect of correction terms) of $\nu_{\text{eff}}=0.56\pm0.01$. This estimate is in fact fairly close to (6). But one must note that the data do not even fall in the regime $x\gg 1$ where a simple power law, (4), should be valid: hence the accuracy of such direct Monte Carlo-estimates for critical exponents is rather doubtful [30].

For comparison, we have also included in the data for $d=3$ a closed-form approximation for the crossover function (implying $\nu=3/5$) discussed by Domb and Barrett [40]. It is seen that this approximation predicts systematically somewhat too large values. Note also, that for $d=2$ the data would not superimpose if one would take $\phi=1/2$ as for $d=3$. In fact, the best superposition of data points would be obtained if one would choose ϕ somewhat larger than $\phi=1$, e.g., $\phi\approx 1.3$; we interpret this finding as an effect of correction terms to the leading asymptotic behavior, as our chains for $d=2$ are so short. Anyway, within their error bars the data are consistent with the theoretical value $\phi=1$ [39]. After completion of our work we learned about similar results for the scaling function for $d=3$ [41].

While for $d=3$ the crossover between expanded chains and chains at the θ-point [5] should be analogous to the crossover described here, as the tricritical fixed point is still gaussian for $d=3$ [5, 6, 39], this is not true for $d=2$: there one expects a crossover exponent ϕ rather different from unity [42], which is not yet well known. It would hence be interesting to apply the present techniques to a $2-d$ chain with both repulsive and attractive parts of the interaction, such that a θ-point occurs [5].

For $d=2$ the resulting crossover scaling function is again close to a straight line with slope of about 0.48 ±0.02, an effective exponent $\nu_{\text{eff}}=0.74\pm0.01$ is implied. Again this estimate is fairly close to (6) but the same reservations as above apply.

For $d=4$ the data yield more or less a horizontal line, and no clear effect of the logarithmic correction term, (8), is seen.

Figure 2 shows an example of internal distances $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle$ for $d=2$, for both two choices of N, m and δ, while Fig. 3 shows corresponding data for $d=3$ [43]. Since there is an obvious symmetry relation

$$\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle=\langle(\mathbf{r}_{N-m-n+1}-\mathbf{r}_{N-n+1})^2\rangle, \tag{9}$$

as both ends of the chain are equivalent, only points starting from one end of the chain up to its center are shown (which are obtained averaging both distances on the right and left hand side of (9) together for improving the statistics). It is seen that the distances between two points are distinctly smaller if one point is close to the end of a chain, as expected, since the excluded-volume repulsion is somewhat less important there. For small m and N large enough, the mean-square distance between two points m units apart is found to depend on m only, but not on n, provided both points are sufficiently far in the in-

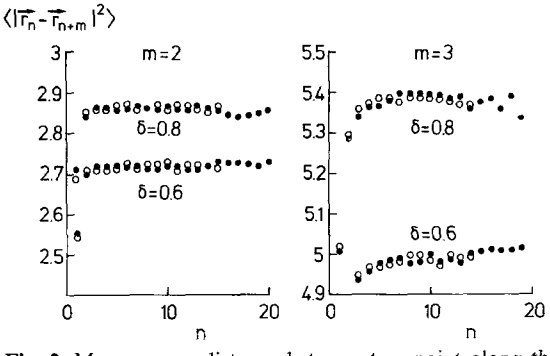

Fig. 2. Mean-square distance between two point along the chain which are m units apart plotted versus the label n of one point along the chain, for $m=2$ (left part) and $m=3$ (right part) in two dimensions. Full circles refer to $N=40$, open ones to $N=30$

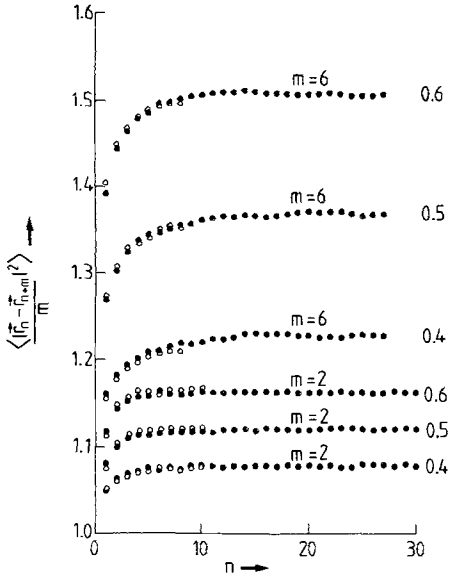

Fig. 3. Normalized mean-square distance between two points along the chain which are m units apart plotted versus the label n of one point along the chain, for $m=6$ (upper part) and $m=2$ (lower part), for $\delta=0.4$, 0.5 and 0.6, respectively, in three dimensions. Full circles refer to $N=60$, open ones to $N=20$

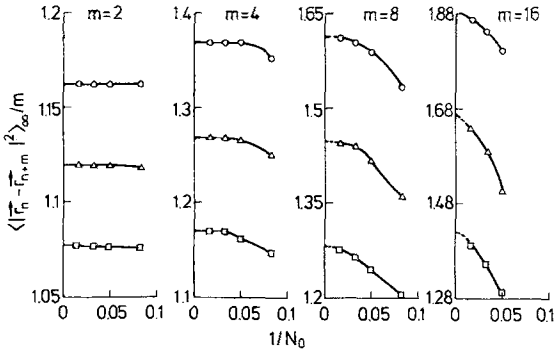

Fig. 4. Normalized mean-square distance between two points m units apart in the center of the chain plotted vs. inverse chain length for several m in three dimensions, for $\delta=0.4$ (squares), $\delta=0.5$ (triangles) and $\delta=0.6$ (circles), respectively

terior of the chain, as expected: keeping m fixed and considering the limit $N\to\infty$, it is clear that the end affects only a small fraction of these internal distances, the mean-square distance where both points are in the interior of the chain will be more characteristic for the bahavior of the chain. In the renormalization group of Sect. III, a mapping of chains containing N_0 links to those containing $N_1=N_0/s$ links will be constructed, where the new link length l_1 will be defined as $l_1^2=\langle(\mathbf{r}_n-\mathbf{r}_{n+2})^2\rangle$. In this procedure, the appropriate new link length clearly is an internal distance in the interior of a very long chain. In order to make finite-size effects as small as possible, we perform an extrapolation of the internal distances to the limit of infinite chain length, Fig. 4. It is seen that for the available values of N_0 the asymptotic behavior of the internal distances is in fact reached for $m\leqq 8$, while for larger m (e.g., $m=16$ as shown in Fig. 4) some ambiguity arises in the extrapolation $1/N_0\to 0$.

It turns out that the approach of the distance $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle$ to its limiting value describing internal distances of very long chains can also be interpreted in terms of scaling behavior. We start from the scaling expression for the probability distribution that a point n units away from the end of a long chain (which is taken as coordinate origin) is at a distance $\mathbf{x}$, and a point $n+m$ units away is at a distance $\mathbf{x}+\mathbf{R}$ [16, 17]

$$P(\mathbf{x},\mathbf{R},n,m)\xrightarrow[n\to\infty,m\to\infty]{} m^{-d\nu}\tilde{P}\left(\frac{x}{m^\nu},\frac{R}{m^\nu},\frac{n}{m}\right). \tag{10}$$

In our case it is convenient to rewrite this probability in terms of an equivalent scaling function $\tilde{P}'$ which is obtained by eliminating m in favor of n from the first scaling variable

$$P(\mathbf{x},\mathbf{R},n,m)=m^{-d\nu}\tilde{P}'\left(\frac{x}{n^\nu},\frac{R}{m^\nu},\frac{n}{m}\right). \tag{11}$$

We then obtain

$$\{\mathbf{r}_n-\mathbf{r}_{n+m}\equiv R,\ p(\mathbf{R},n,m)\equiv\int d\mathbf{x}\,P(\mathbf{x},\mathbf{R},n,m)\}$$

$$\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle=\int_0^\infty R^2\,d\mathbf{R}\,p(\mathbf{R},n,m)$$

$$=m^{2\nu}S_d\int_0^\infty y^{d+1}\tilde{p}'(y,n/m), \tag{12}$$

where S_d is the surface area of a d-dimensional sphere and $y=R/m^\nu$. From (12) we immediately see that $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle/m^{2\nu}$ should depend on the ratio n/m only. Since this quantity approaches a constant for $n\to\infty$, we subtract this limiting value to analyze in Fig. 5 the reduced quantity

$$\langle(\Delta\mathbf{R}_{nm})^2\rangle\equiv\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle-\lim_{N\to\infty,n\to\infty}\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle. \tag{13}$$

It is seen from Fig. 5 that for large n/m this deviation approaches zero exponentially. The scaling property derived in (12) seems roughly to be fulfilled to within our accuracy.

Finally $\ln W(\delta,N,d)$ is analyzed in Fig. 6 for both $d=2$ and $d=3$. It is seen that $\ln W$ varies linearly with N for N large enough. Thus the entropy difference s per link, which describes the behavior of the entropy of large chains [31],

$$(S-S_0)/k_B=Ns(\delta)+(\gamma-1)\ln N+c(\delta), \tag{14}$$

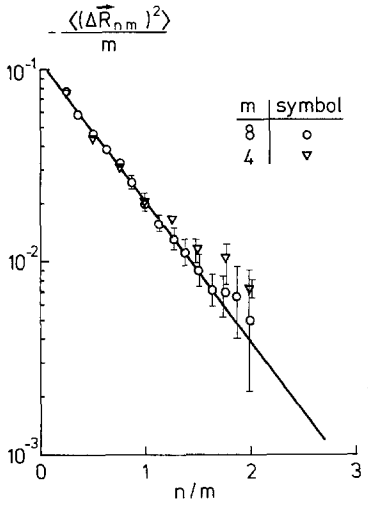

Fig. 5. Semi-log plot of the reduced deviation $\langle(\Delta\mathbf{R}_{nm})^2\rangle/m$ vs. n/m for $d=3$, $N=60$, and $\delta=0.5$

where γ is another critical exponent ($\gamma\approx 7/6$ for $d=3$ and $\gamma\approx 4/3$ for $d=2$ [5], independent of δ), and $c(\delta)$ is a number of order unity, can be estimated by extrapolating $(S-S_0)/Nk_B$ vs. $\ln N/N$ (Fig. 6b, c). Since for the available values of N the term $(\gamma-1)\ln N$ is smaller than unity, the term $c(\delta)/N$ is not negligible against the term $(\gamma-1)\ln N/N$ which is the asymptotically leading correction, and hence γ can not be estimated reliably from our data.

III. Renormalization of Polymers Along the Sequence of the Chain

In this section we develop a renormalization group analysis of the Monte Carlo data [29], based on de Gennes' suggestion of renormalization along the chemical sequence of the chain [4, 44]. As usual in

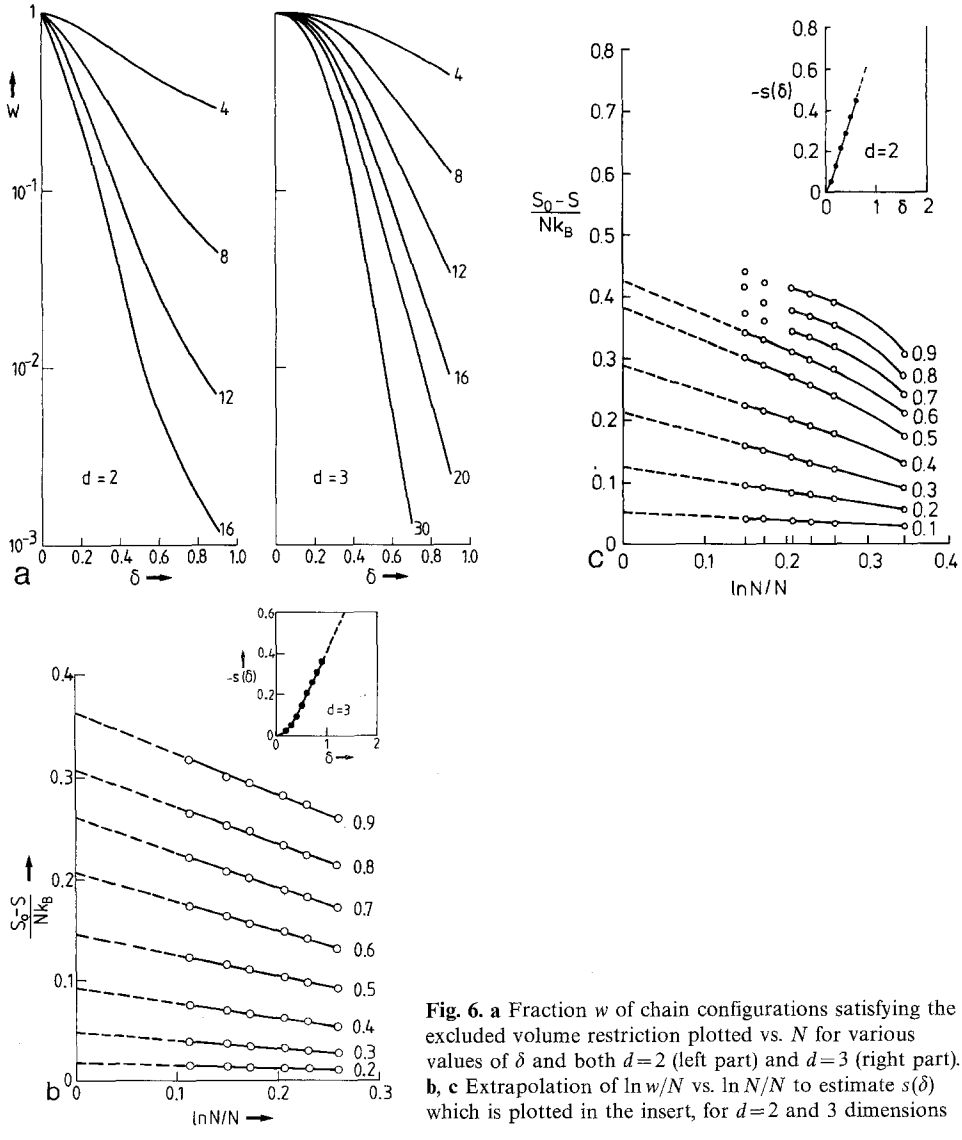

Fig. 6. a Fraction w of chain configurations satisfying the excluded volume restriction plotted vs. N for various values of δ and both $d=2$ (left part) and $d=3$ (right part). **b, c** Extrapolation of $\ln w/N$ vs. $\ln N/N$ to estimate $s(\delta)$ which is plotted in the insert, for $d=2$ and 3 dimensions

the renormalization group analysis of critical phenomena [6] one considers an iterative elimination of the degrees of freedom. Starting with N_0 links of length l_0 and sphere diameter h_0, the chain is mapped onto another chain consisting of $N_1 = N_0/s$ so-called "block-links" of length l_1 with a hard-sphere diameter h_1. This is analogous to the real-space renormalization group transformation of spin systems, where groups of s spins are taken together as a "block-spin" of the renormalized hamiltonian [45]. The length l_1 of the block-link is identified as the root mean square internal distance between points s units apart, as estimated in the previous section (Fig. 4),

$$l_1 = \langle (\mathbf{r}_n - \mathbf{r}_{n+2})^2 \rangle_{N_0}^{1/2}. \tag{15}$$

The renormalized hard-sphere diameter h_1 is estimated using the condition that the renormalization transformation leaves the end-to-end distance $R(l_0, h_0, N_0) \equiv \langle R_{N_0}^2 \rangle$ invariant

$$R(l_0, h_0, N_0) = R(l_1, h_1, N_0/s). \tag{16}$$

In analogy to the usual renormalization group approach [45] it would seem more natural to request that the free energy (or entropy in our case) of the chain is left invariant under the transformation; since the entropy is accessible by the simple sampling-technique only while R can be obtained from the dynamical simulations as well, it is more convenient to use the end-to-end distance in our case. Any quantity could by used, of course, in the case of a renormalization group transformation which constitutes an exact elimination of degrees of freedom. For spin systems it is well known that block transformations are approximate only [45], and hence it is important to establish the accuracy of such an approximate renormalization group transformation. In our case, there are several sources of inaccuracy:

(i) Statistical inaccuracy of the Monte Carlo data used for l_1 and R in the transformation. This inaccuracy prevented us from using N_0 larger than $N_0 = 60$.

(ii) Finite size effects: while effects of the finite chain length on estimating l_1 are eliminated with good accuracy by the extrapolation described in Fig. 4, there is some effect of finite chain length by the use of the end-to-end distances in (16), although the direct scaling analysis of end-to-end distances (Fig. 1) suggests these effects to be small. Nevertheless we consider it important to study how the fixed point of the renormalization group transformation (and the associated exponents) depend on N_0, see Fig. 11 below.

(iii) In an exact block transformation one would obtain effective links l_1 not of fixed length as used here but rather given in terms of a distribution. Also the renormalized potential should no longer be a hard-sphere potential but somewhat smoothed out. Therefore one must expect that both the fixed point and the associated exponents depend on the scale factor s, and this dependence will be studied below.

For Ising spin systems, it turns out that an exact real-space transformation which keeps the structure of the interaction potential unchanged is obtained in the limits $s \to 1$ ("differential real space renormalization" [46]). Hence we propose here the use of a "differential Monte Carlo renormalization group", which is based on using rational $s > 1$ and extrapolating to $s = 1$ numerically. In this method, the invariance condition, (16), is kept, but (15) is replaced by (cf. Fig. 7)

$$\frac{l_1}{l_0} = \frac{\langle (\mathbf{r}_n - \mathbf{r}_{n+m_0})^2 \rangle_{N_0}^{1/2}/l_0}{\langle (\mathbf{r}_n - \mathbf{r}_{n+m_1})^2 \rangle_{N_1}^{1/2}/l_1}, \quad \frac{m_0}{m_1} = s, \; N_1 = \frac{N_0}{s}. \tag{17}$$

Of course, (17) reduces to (15) for $m_1 = 1$. We speculate that also the present method might become exact in the limit $s \to 1$.

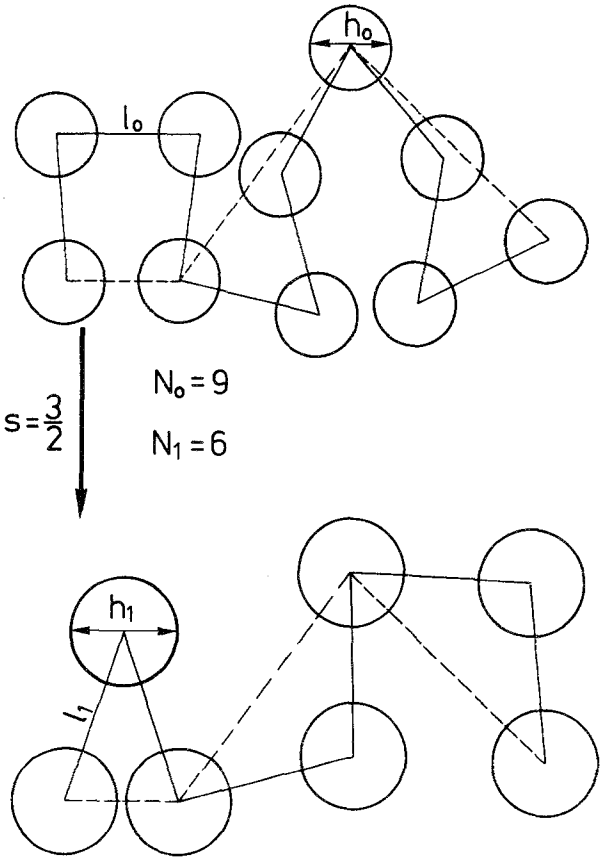

Fig. 7. Monte-Carlo renormalization for non-integer scale factor s

The practical realization of this Monte-Carlo renormalization group is done as follows. For a given choice of N_0 and s, we use the data of Tables 1-3 as well as the internal distances (Fig. 4) to construct δ_1, l_1 for a given choice of δ_0. It is then convenient to plot δ_1 as well as $\ln(l_1/l_0)$ as functions of $\ln(\delta_0/\delta_1)$, Figs. 8, 9, because from these plots both the fixed point and the exponents can be read off immediately from the behavior near $\ln(\delta_0/\delta_1)=0$. This fact is easily seen from the following consideration: suppose we iterate the renormalization transformation k times, with $k\to\infty$. If $\delta_k\to\delta_{k+1}\to\ldots\to 0$, the chain becomes asymptotically noninteracting, and we approach the gaussian fixed point. This is the behavior which occurs for $d=4$ and $d=5$, where the difference $\delta_0-\delta_1$ is positive for all δ_0 (Fig. 10). Hence our renormalization group transformation is consistent with gaussian behavior ($\nu=1/2$) for $d\geqq 4$. While for $d=5$ the difference $\delta_0-\delta_1$ approaches zero for $\delta_0\to 0$ with finite slope, the slope is zero for $d=4$, indicating that 4 is in fact the "marginal dimensionality", below which a nontrivial fixed point exists: for $d<4$ the quantity $\delta_0-\delta_1$ starts out negative for small δ_0, i.e., the interaction parameter gets enhanced upon iteration: the gaussian fixed point is unstable, one approaches a nontrivial fixed point $\delta_k\to\delta_{k+1}\to\ldots\to\delta^*>0$. This fixed point is attractive, the difference $\delta_1-\delta_0$ changes sign for $\delta_0=\delta^*$ (the other trivial fixed point, $\delta=2$, which corresponds to stretched chains with $\langle R^2_{N_0}\rangle^{1/2}=l_0 N$, is always unstable). This behavior, which can be expected on the basis of the general renormalization group ideas [6, 45], is fully born out by the data for $d=3, 2$ included in Fig. 10.

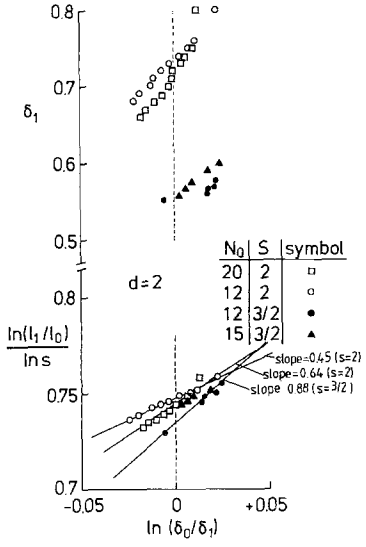

Fig. 8. Renormalized interaction parameter δ_1 (upper part) and change of the length scale $\ln(l_1/l_0)$ (lower part) plotted vs. $\ln(\delta_0/\delta_1)$ for various scale factors s and chain lengths N_0 at two dimensions

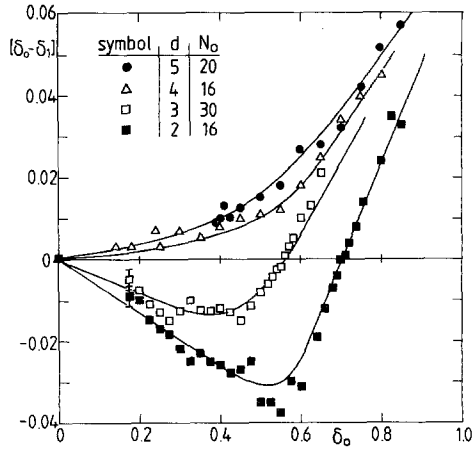

Fig. 10. Difference between renormalized interaction parameter δ_1 and original interaction parameter δ_0 plotted vs. δ_0 for $2\leqq d\leqq 5$ and various chain lengths N_0; $s=2$

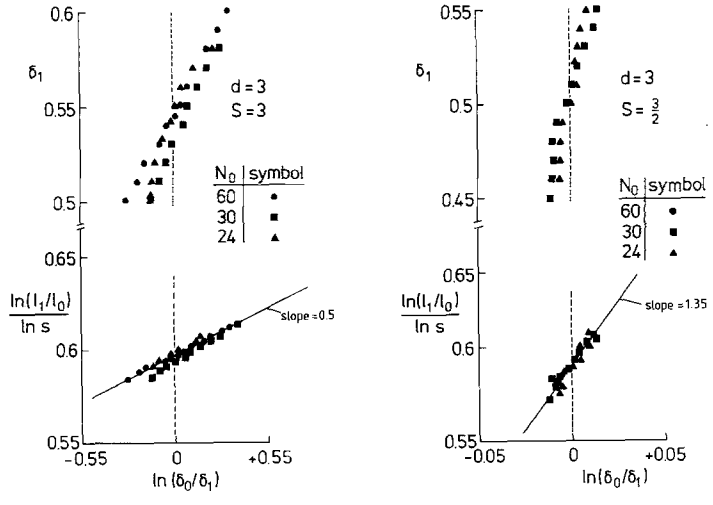

Fig. 9. Renormalized interaction parameter δ_1 (upper part) and change of the length scale $\ln(l_1/l_0)$ (lower part) plotted vs. $\ln(\delta_0/\delta_1)$ for various chain lengths N_0, $s=3$ (left figure) and $s=3/2$ (right figure)

We now proceed by analyzing the approach towards the nontrivial fixed point in order to relate it to critical exponents and amplitude factors. Suppose we start the iteration with $\delta_0=\delta^*$ at the fixed point. Iterating k times the block-link l_k is the end-to-end distance between points s^k units apart. Since for k large enough s^k is a large number already, the formulas (3), (4) apply to the distance l_k also,

$$l_k=l_0(s^k)^{1/2}f(s^k\,\delta_0^{d/\phi})$$
$$=Al_0\,s^{\nu k}\,\delta_0^{d(\nu-1/2)/\phi}, \quad \text{for } \delta_0=\delta^*. \tag{18}$$

Hence we find for the change of length scale

$$l_{k+1}/l_k=s^\nu, \quad \nu=\ln(l_{k+1}/l_k)/\ln s. \tag{19}$$

Since with our choice of renormalization transformation the nature of the steps $l_0\to l_1$ and $l_k\to l_{k+1}$ is precisely the same (the nature of this hard-sphere model is not changed during the iteration), (19) holds even for $k=0$ if $\delta_0=\delta^*$. Thus we have plotted the ratio $\ln(l_1/l_0)/\ln s$ in Figs. 8, 9, since from the value of this quantity at the fixed point (which occurs for $\ln(\delta_0/\delta_1)=0$) one can read off the exponent ν directly. From Fig. 8 we conclude for $d=2$ that $\nu\approx 0.74\pm 0.01$, $\delta^*=0.64\pm 0.09$, while Fig. 9 implies $\nu=0.58\pm 0.01$, $\delta^*=0.52\pm 0.02$. It is seen that the exponent ν found by our method slightly depends on both the choice of the scale factors s and the chain length N_0, and the fixed point value itself depends on both quantities even more strongly. This fact is somewhat unfortunate, as the fixed-point interaction parameter δ^* is related to the critical amplitude A, which hence cannot be obtained with very good precision as yet. From (19) we conclude, by iteration, that $l_k=l_0\,s^{\nu k}$ at the fixed point. Comparing this result to (18) we immediately find

$$A=\delta^{*-d(\nu-1/2)/\phi}, \tag{20}$$

and hence the asymptotic behavior of very long chains is, for arbitrary $\delta>0$, given by [(3), (4) and (20)]

$$\sqrt{\langle R_N^2\rangle}=l(\delta/\delta^*)^{d(\nu-1/2)/\phi}N^\nu. \tag{21}$$

It remains to estimate the crossover exponent ϕ from the renormalization. To this end we consider the renormalization transformation for δ very close but not precisely at the fixed point δ^*. Applying once more the argument used to write down (18) we now conclude

$$l_k=l_0(\delta_k/\delta^*)^{d(\nu-1/2)/\phi}s^{\nu k},$$
$$l_{k+1}/l_k=s^\nu(\delta_k/\delta_{k+1})^{d(\nu-1/2)/\phi}, \tag{22}$$

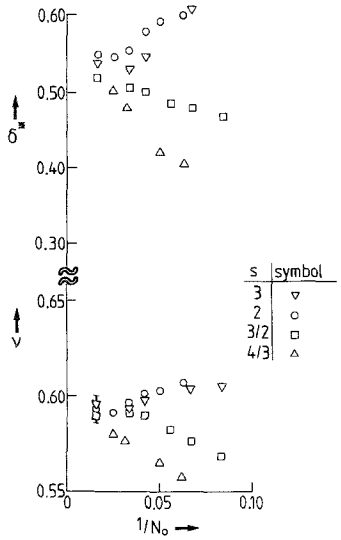

Fig. 11. Fixed-point interaction parameter δ^* and exponent ν plotted vs. inverse chain length for various choices of the scale factor in three dimensions

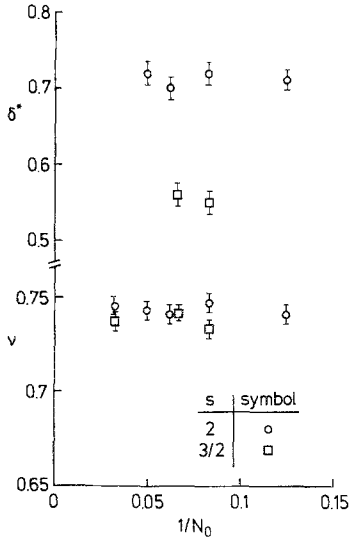

Fig. 12. Fixed-point interaction parameter δ^* and exponent ν plotted vs. inverse chain length for various choices of the scale factor in two dimensions

hence the slope of the $\ln(l_1/l_0)/\ln s$ vs. $\ln(\delta_0/\delta_1)$-curve at the fixed point yields $d(\nu-1/2)/(\phi\ln s)$. In Fig. 9 this slope (using $\nu=0.59$, $\phi=1/2$) has been included, and it is seen to describe our presults precisely. For $d=2$, where $\phi=1$ [39], the slope of our data seems to depend on N_0 very distinctly. Thus we can obtain only a very rough estimate

$$\phi_t=1.3\pm 0.3 \tag{23}$$

which is also included as a straight line in Fig. 8.

For three-dimensional chains we have carried out this renormalization group analysis (as illustrated in

Figs. 8, 9) for scale factors $s=3$, 2, 3/2 and 4/3, and extrapolate the results to infinite chain length in Fig. 11. Since the renormalization using small s requires the use of internal distances $\langle(\mathbf{r}_n-\mathbf{r}_{n+m})^2\rangle$ with relatively large m, it is more strongly affected by finite size effects. Thus the estimates for small N_0 clearly are not yet reliable, while for larger N_0 the estimates of both ν and δ^* become nearly independent of s and yield as final estimate

$$\nu=0.59\pm0.01 \quad (d=3). \tag{24}$$

A similar analysis in two dimensions (Fig. 12) yields a qualitatively similar picture resulting in

$$\nu=0.74\pm0.01 \quad (d=2). \tag{25}$$

Hence while this Monte-Carlo renormalization yields estimates for ν, which have an accuracy similar to field-theoretic renormalization group [7] if only the statistical error is taken into account [29], the systematic inaccuracy (dependence on s and N_0) allows to estimate exponents with an accuracy of about 1%; this accuracy is somewhat better than that of the direct analysis of Monte Carlo data [21], particularly if one considers values of δ far away from the fixed point value, where the "naive" Monte Carlo estimates of the exponents are much worse than those described in Sect. II. The renormalization group analysis presented here incorporates the universality of the exponent ν, i.e., its independence of δ, in a very natural way, while "naive" Monte Carlo analysis is hampered by the fact that correction terms to the leading asymptotic behavior are much more important if δ is far away from its fixed-point value (see [21] for a discussion of earlier Monte-Carlo work, which has been mis-interpreted in terms of an exponent ν depending on δ). On the other hand, the accuracy of the present methods ((24), (25)) is clearly not good enough to rule out the Flory prediction, (5). The accuracy reached here is similar to the accuracy reached in Monte Carlo renormalization of percolation [27, 28] or of Ising and Potts models [22–26].

IV. Conclusions

In this paper a Monte-Carlo renormalization group for polymers with hard-sphere interaction has been investigated, and applied for dimensionalities $d=2$, 3, 4 and 5. It is shown that for $d\geqq4$ there is only the gaussian fixed point (interaction parameter $\delta^*=0$) stable, and hence the polymer chains behave asymptotically as non-interacting random walks ($\nu=1/2$). For $d=2$, 3 the gaussian fixed point is found to be unstable, and the renormalization group transformation leads to a non-trivial fixed point $\delta^*>0$, which is estimated with an accuracy of a few percent. While the value of theis fixed point is related to a critical amplitude in the power law for the end-to-end distance of the chain, the behavior of the renormalization group transformation in the vicinity of this fixed point yields information on both the exponent ν and the cross-over exponent ϕ. By carefully analyzing the dependence of these results on the scale factor s and the finite chain length N_0 we show that the exponent ν can be estimated with an accuracy of about one percent ($\nu=0.59\pm0.01$ por $d=3$ and $\nu=0.74\pm0.01$ for $d=2$), while the crossover exponent is estimated with considerably less precision ($\phi\approx\frac{1}{2}$ for $d=3$, as expected, while $\phi=1.3\pm0.3$ for $d=2$). Unfortunately the present accuracy cannot rule out the Flory predictions, (5), although our estimates are somewhat better consistent with the predictions of field-theoretic renormalization, (6). The accuracy of our method is somewhat better than the "naive" analysis of Monte-Carlo data, where one straightforwardly fits data on the end-to-end distance to a power law. Moreover our renormalization group analysis incorporates the universality of exponents (ν being independent of the interaction parameter δ as long as $\delta>0$, etc.). On the other hand, it is not yet clear how to obtain other quantities like the gyration radius, structure factor of the chain, etc., from this renormalization group method. Also an extension to other forms of the interaction potential seems desirable.

In the present study we have also extended the idea of performing a "differential real space renormalization group" (scale factor $s\to1$) to Monte-Carlo renormalization, using rational values of s with $1<s<2$, which can be extrapolated to $s\to1$ numerically. Although we speculate that our approximate renormalization group would become exact in this limit, in practice the accuracy of our estimates could be improved only slightly due to finite-size effects. Due to this experience we suggest that other work on Monte-Carlo renormalization for different systems should pay proper attention to such finite size effects, too.

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