It appears principally difficult to extract the relaxation times τ_q for $q > q_c$ from time-dependent scattering data. For experimental studies changes in the scattering intensity have to occur on the time scale of minutes. This can be accomplished for two different situations:

(a) Studies can be conducted, as Hashimoto et al.[1] and Snyder et al.[2] in their light-scattering experiments did, near to the critical temperature, where diffusion becomes slow. These experiments can yield relaxation times τ_q for q values up to the range around the growth rate maximum, provided that coarsening does not interfere. Relaxation times for higher q values are principally unattainable. For $qR_G > 1$ the structure usually has already relaxed before the measurements can start ($\tau_{x>1} \sim \tau_R \ll -\tau_{q_m}$); for $q > q_c$ the asymptotic equation (24) does not hold. The growth rates $R = \mathrm{d} \ln S(q,t)/\mathrm{d}t$ at times $t \gtrsim -\tau_{q_m}$, which are obtained by the experiment, will pass over a maximum at q_m and then continuously approach zero. Negative values of R, if they occur, are indicative of coarsening. They should not be associated with the exponential decay regime of the Cahn–Hilliard model.

(b) For suitable systems it is possible to perform a deep quench which transfers the blend to temperatures near to the glass transition. Here the fundamental diffusion time τ_R becomes sufficiently slow to enable time-dependent measurements. For deep quenches also the relaxation time at the growth rate maximum, $-\tau_{q_m}$, is on the order of τ_R (eq 17). In this case the structure evolution can be studied continuously from the initial stages up to the Cahn–Hilliard regime by using X-rays or neutrons. Analysis has to be based on the general equation of motion eq 9 rather than on the Cahn–Hilliard model. Relaxation times τ_q for $q > q_c$ can be determined only if the metastable structure factor $S_\chi(q)$ is reached before the onset of coarsening. We are performing studies on such deep quenches and shall give a report in a forthcoming paper.

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The Scanning Method with a Mean-Field Parameter: Computer Simulation Study of Critical Exponents of Self-Avoiding Walks on a Square Lattice

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ABSTRACT: The scanning method is a computer simulation technique for polymer chains applicable to a wide range of chain models (e.g., self-avoiding walks (SAWs), self-interacting SAWs, multiple-chain systems, chains which are subject to geometrical constraints such as boxes and tubes, etc.). In this paper we significantly improve the efficiency of the scanning method by incorporating a "mean-field" parameter. The method is applied to SAWs on a three-choice square lattice, where chains of up to 799 steps are studied. We obtain the critical exponents, $\gamma = 1.333$ (4) (which is smaller than Nienhuis's exact value), $\alpha = 0.5$ (1), and the connective constant $\mu = 2.6383$ (1). The data for the radius of gyration and for $\langle R^p \rangle$ (where R is the end-to-end distance and $p = 2$ and 4) are consistent with $\nu = 0.75$ and $\langle R^p \rangle \sim N^{p\nu}$. However, for $p < 0$, the behavior is different: $\langle R^p \rangle \sim N^{-f_p}$, where $f_p \neq \nu p$ and f_p is bounded from above by $f_\infty = 2\nu + (\gamma - 1) = 1.8437...$. For example, we obtain $\langle R^{-2} \rangle \sim N^{-1.4} \neq N^{-2\nu} = N^{-1.5}$. These results for $p < 0$ should be taken into account when calculating the diffusion coefficient with the help of Kirkwood's theory.

Introduction

The scanning method is a computer simulation technique for polymer chains that I recently suggested.[1,2] The method has been applied so far to self-avoiding walks (SAWs) on a square lattice and on a simple cubic lattice;[2] very recently it has also been employed for simulating a multiple-chain system.[3] The scanning method is a step-by-step construction procedure, based on scanning in each step for the possible future continuations of the chain, which consist of b steps. For SAWs this "looking-forward" procedure causes a considerable reduction in sample attrition, as compared to the direct Monte Carlo method;[4,5] the larger b is, the smaller the attrition. However, for a square lattice this procedure is limited in practice to $b \leq 10$, which means that only the immediate environment of a step can be scanned. Therefore, we introduce in this paper a "mean-field" parameter, which also takes into account the global shape of the chain. We describe two criteria, the minimum free energy principle and the criterion of minimum free energy fluctuation, which enable one to optimize this parameter. The method is applied again to SAWs on a square lattice. This model has attracted recently great interest in view of Nienhuis's analytical solution for the honeycomb lattice,[6] which is expected to be exact. He obtains $\nu = 0.75$ and $\gamma = 43/32$, where ν and γ are the critical exponents for the chain shape

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and the entropy, respectively. Several series expansion studies (based on corrections to scaling)[7-10] and a real space renormalization calculation[11] have been recently carried out in order to numerically check the validity of these results for SAWs on various two-dimensional lattices. In this paper we shall estimate ν, γ, and the exponent of ring closure α. We shall also calculate averages $\langle R^p \rangle$, where R is the end-to-end distance and p is *negative*. In this case the dependence of the critical exponents on p is different from that observed for $p > 0$, a fact which should be taken into account in calculation of the diffusion coefficient, for example.

Theory

A. Thermodynamic and Geometrical Properties of SAWs. Assume a lattice of any dimensionality d with corrdination number q and let us denote by C_N the total number of SAWs of N steps with no immediate reversals. For large N, C_N is given by[12]

$$C_N = C_0 N^{\gamma-1} \mu^N \tag{1}$$

where C_0 and μ are lattice dependent but γ depends on the dimension d alone. The ensemble probability P_i of SAW i is constant

$$P_i = C_N^{-1} \tag{2}$$

and therefore the entropy $\langle S \rangle$ is

$$\langle S \rangle = -k_B \sum_{\text{SAWs}} P_i \log P_i = k_B \log C_N \tag{3}$$

where k_B is the Boltzmann constant. Since P_i is constant, the fluctuation $\langle \Delta^2 S \rangle$ vanishes

$$\langle \Delta^2 S \rangle = 0 \tag{4}$$

We are interested in the contribution to the entropy due to the excluded-volume (EV) effect, and therefore in the tables the results for $\langle S_{EV} \rangle$, rather than for $\langle S \rangle$, will be presented, where

$$\langle S_{EV} \rangle = S_I - \langle S \rangle \tag{5}$$

S_I, the entropy of ideal walks, is

$$S_I = k_B[\log q + (N-1) \log (q-1)] \tag{6}$$

Another quantity of interest is U_N, the number of rings, i.e., SAWs, which return to the first step,[12] where

$$U_N = U_0 N^{\alpha-2} \mu^N \tag{7}$$

The entropy functions $\langle S^U \rangle$ and $\langle S_{EV}{}^U \rangle$ for the rings are

$$\langle S^U \rangle = k_B \log U_N \tag{8}$$

$$\langle S_{EV}{}^U \rangle = S_I - \langle S^U \rangle \tag{9}$$

We shall also calculate the averages $\langle R^p \rangle$

$$\langle R^p \rangle = \sum_{\text{SAWs}} P_i R_i^p \qquad p = 2, 4, -\tfrac{4}{3}, -2, -4 \tag{10}$$

where R is the end-to-end distance and the values of p are positive or negative. $\langle R^p \rangle$ is expected to scale like

$$\langle R^p \rangle = A_p N^{p\nu_p} \tag{11}$$

(in most cases[12] ν_2 has been calculated, which is denoted by ν). Also of interest is the radius of gyration $\langle G^2 \rangle$, where

$$\langle G^2 \rangle = \sum_{\text{SAWs}} P_i G_i^2 \tag{12}$$

and G_i is

$$G_i^2 = (N+1)^{-1} \sum_{k=0}^{N} \sum_{m=1}^{d} (r_k{}^m - \bar{r}^m)^2 \tag{13}$$

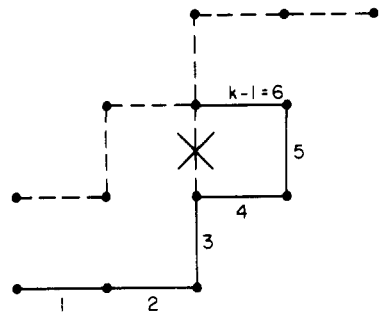

Figure 1. Schmatic illustration of the kth step of the scanning method construction procedure. At this stage steps 1 and $k-1$ have already been determined (full bonds). The dotted bonds define two future SAWs of $b = 3$. Notice that in one direction the future SAWs are forbidden.

In eq 13 $r_k{}^m$ and $\bar{r}^m$ are the coordinates of step k and of the center of mass, respectively.

$$\bar{r}^m = (N+1)^{-1} \sum_{k=0}^{N} r_k{}^m \tag{14}$$

$\langle G^2 \rangle$ is expected to scale like

$$\langle G^2 \rangle = A_G N^{2\nu_G} \tag{15}$$

B. Scanning Procedure. Let us construct a SAW which starts from the origin of the coordinate system. The first step is determined in one of the q directions with equal probability $1/q$. In the next steps of the process ($k > 1$) the probability to select a direction ν ($\nu = 1, ..., q$) out of $q-1$ allowed ones becomes a function of step k in the following way: Assume that we are at the kth step of the process; i.e., $k-1$ directions of the chain $\nu_1, ..., \nu_{k-1}$ have already been determined and we want to specify ν_k. For that let us first introduce the notion of a future SAW of b steps. This is a possible continuation of the chain in the future, consisting of b steps (i.e., $k, k+1, ..., k+b-1$), which does not violate the EV restriction (see Figure 1) [more strictly, the length of a future SAW is min $(b, N-k+1)$]. For each ν ($1 \le \nu \le q$) one can calculate $M_k(\nu,b)$, the total number of future SAWs starting in direction ν, and thereby define a transition probability, $p_k(\nu,b)$, for selecting ν

$$p_k(\nu,b) = M_k(\nu,b) / \sum_{\nu=1}^{q} M_k(\nu,b) \tag{16}$$

Obviously $M_k(\nu,b)$, as well as $p_k(\nu,b)$, depends on $\nu_1, ..., \nu_{k-1}$. ν_k is selected by a lottery according to the p_k's and the process continues. Once a SAW i of N steps has been constructed, one knows its construction probability $P_i(b)$

$$P_i(b) = q^{-1} \prod_{k=2}^{N} p_k(\nu_k,b) \tag{17}$$

which is the product of the N sequential transition probabilities with which the directions $\nu_1, ..., \nu_N$ have been chosen. It should be pointed out that for a practical value of b ($b \le 10$ for the square lattice) the future can be scanned only partially and therefore a construction of a SAW may fail. The efficiency of the process is conveniently expressed by the attrition constant[4] λ, which is defined by

$$W_N / W_0 = \exp(-\lambda N) \tag{18}$$

where W_N is the number of SAWs generated and W_0 is the number of SAWs attempted. Obviously, the larger b is, the smaller is λ. The occurrence of failures also means that $P_i(b)$ [in contrast to P_i (eq 2)] is not normalized over the ensemble of all SAWs, i.e.

$$A = \sum_{\text{SAWs}} P_i(b) < 1 \tag{19}$$

and a normalized probability $P_i'(b)$ can be defined by

$$P_i'(b) = P_i(b)/A \tag{20}$$

Also, in contrast to P_i (eq 2), $P_i'(b)$ is not constant for all i but is larger for the compact SAWs than for the open ones. This can be deduced from the following argument: Consider, for example, the three-choice square lattice and the approximation $b = 1$. Obviously, for a very open SAW three future SAWs are allowed for most of the steps k, which means that the transition probability $p_k(\nu,b) = {}^1/_3$. On the other hand, for a compact SAW, at many steps k one or two future SAWs are forbidden; i.e., the transition probability equals ${}^1/_2$ or 1, respectively, and the probability $P_i'(b)$ is therefore larger in this case than for an open SAW. However, one would expect both $P_i(b)$ and $P_i'(b)$ to approach the exact P_i (eq 2) as b is increased. In fact, for $b = N - k + 1$, no failures can occur since the whole future is scanned at each step, which means that the process becomes *exact*

$$P_i(b = N - k + 1) = \frac{C_N/q}{C_N} \frac{M_2(\nu,b)}{C_N/q} \cdots \frac{1}{M_{N-1}(\nu_{N-1},b)} = C_N^{-1} \tag{21}$$

Obviously, the exact scanning procedure is impractical for large N, since the complete ensemble of SAWs should already be constructed for the first step.

To conclude, the scanning method described so far is approximate but can systematically be improved by increasing the parameter b. However, a large value of b is impractical, since computer time grows exponentially and therefore we shall now introduce a mean-field parameter which improves $P_i(b)$, almost without further expenditure of computer time.

C. Mean-Field Parameter. One can incorporate a mean-field parameter m in the transition probability (eq 16) in the following way:

$$p_k(\nu,b,m) = M_k(\nu,b)m^{-\vec{\nu}\cdot\vec{x}}/\sum_{\nu} M_k(\nu,b)m^{-\vec{\nu}\cdot\vec{x}} \tag{22}$$

In this equation $\vec{\nu}$ is a unit vector in direction ν and $\vec{x}$ ($=\vec{x}(k)$) is a unit vector, which points from the center of mass of the partial chain (of $k-1$ steps) toward step $k-1$. Clearly, for $m < 1$ a direction ν which points toward the outer (inner) part of the chain will generally lead to $\vec{\nu}\cdot\vec{x} > 0$ (<0), which means that $p_k(\nu,b,m)$ will be larger (smaller) than $p_k(\nu,b)$ (eq 16). Therefore, the preference given by $P_i(b)$ to the compact SAWs (see previous section) weakens in $P_i(b,m)$

$$P_i(b,m) = q^{-1} \prod_{k=2}^{N} p_k(\nu_k,b,m) \tag{23}$$

In other words, with the mean-field parameter the effect of the global shape of the chain is taken into account, in addition to the effect of the local environment of step k, which is taken into account by the scanning procedure. The effect of $m < 1$ is to open the chain, i.e., to increase the end-to-end distance and the radius of gyration. We shall now describe criteria for determining m^*, the optimal value of m. For that let us define the entropy functional $\langle S\rangle_{b,m}$

$$\langle S\rangle_{b,m} = -k_B \sum_{\text{SAWs}} P_i'(b,m) \log P_i'(b,m) \tag{24}$$

where for SAW i

$$P_i'(b,m) = P_i(b,m)/A \tag{25}$$

$$A = \sum_{\text{SAWs}} P_i(b,m) \tag{26}$$

Obviously, $\langle S\rangle_{b,m}$ is never larger than the true entropy $\langle S\rangle$ (eq 3) but can be maximized with respect to m, at $m = m^*$, to give the best approximation for $\langle S\rangle$. m^* can also be defined by the criterion of minimum fluctuation $\Delta S(b,m)$,[13] where

$$\Delta S(b,m) = \{\sum_{\text{SAWs}} P_i'(b,m)[\langle S\rangle_{b,m} + k_B \log P_i'(b,m)]^2\}^{1/2} \tag{27}$$

This fluctuation, which vanishes for the true entropy (eq 4), is expected to decrease with improving $P_i'(b,m)$. It should be pointed out that for chain models with finite interactions these criteria apply to the free energy F rather than the entropy. Hence, one should minimize both F and ΔF with respect to m.[13]

It should be emphasized that for a practical value of b any statistical average $\langle V\rangle_{b,m}$

$$\langle V\rangle_{b,m} = \sum_{\text{SAWs}} P_i'(b,m) V_i \tag{28}$$

of a random variable V_i will always be *biased*. $\langle V\rangle_{b,m}$ can be estimated by $\bar{V}(b,m)$ from a sample of n SAWs, generated with $P_i'(b,m)$

$$\bar{V}(b,m) = n^{-1} \sum_{t=1}^{n} V_{i(t)} \tag{29}$$

where $i(t)$ is SAW i obtained at time t of the process. A practical way to remove the bias in $\langle V\rangle_{b,m}$ is by employing "importance sampling".

D. Importance Sampling. The *exact* statistical average $\langle V\rangle$ can be expressed in the ensemble of all ideal walks (IWs) as a ratio of two statistical averages with the probability $P_i(b,m)$ (eq 23)

$$\langle V\rangle = C_N^{-1} \sum_{\text{IWs}} V_i \exp(-E_i/k_BT)$$

$$= \sum_{\text{IWs}} P_i(b,m)[V_i \exp(-E_i/k_BT)/P_i(b,m)]/\sum_{\text{IWs}} P_i(b,m) \times [\exp(-E_i/k_BT)/P_i(b,m)] \tag{30}$$

where E_i, the interaction energy, equals 0 for a SAW and ∞ for a self-intersecting walk and T is the absolute temperature. The expressions in the brackets can be considered as random variables and therefore an estimation $\bar{V}$ for $\langle V\rangle$ is (see eq 29)

$$\bar{V} = W_0^{-1} \sum_{t=1}^{n} V_{i(t)}/P_{i(t)}(b,m)/W_0^{-1} \sum_{t=1}^{n} 1/P_{i(t)}(b,m)$$

$$= \sum_{t=1}^{n} V_{i(t)}/P_{i(t)}(b,m)/\sum_{t=1}^{n} 1/P_{i(t)}(b,m) \tag{31}$$

In eq 31 (as in eq 18) W_0 and n ($=W_N$) denote the numbers of SAWs attempted and obtained, respectively. In particular, the entropy $\langle S_{EV}\rangle$ (eq 5) and the entropy of rings $\langle S_{EV}{}^U\rangle$ (eq 9) are estimated by $\bar{S}_{EV}$ and $\bar{S}_{EV}{}^U$, respectively

$$\bar{S}_{EV} = S_I - k_B \log [W_0^{-1} \sum_{t=1}^{n} 1/P_{i(t)}(b,m)] \tag{32}$$

$$\bar{S}_{EV}{}^U = S_I - k_B \log [W_0^{-1} \sum_{t=1}^{n'} 1/P_{i(t)}(b,m)] \tag{33}$$

where n' is the number of SAWs in the sample which return to the origin. It should be pointed out that eq 32 also appears in ref 1 and 2, but with an error, which has been recently corrected.[14]

Let us now discuss the efficiency of the importance sampling procedure. It should first be stressed that, for an infinite sample, $\bar{V}$ (eq 31) will be equal to $\langle V\rangle$ for any value of b and m [in contrast to $\bar{V}(b,m)$ (eq 29), which is

Table I
Results for the Entropy of SAWs on a Three-Choice Square Lattice[a-c]

N	approx	$\langle S_{EV}\rangle$	$\langle S_{EV}\rangle_{b,m}$	$\Delta S(b,m)$	λ	$\langle S_{EV}{}^{U}\rangle$	n^d
49	m^* = 0.93	0.103 579 (4)	0.104 912 (7)	0.010	9.8×10^{-5}	0.2329 (3)	240 000
	m = 1		0.105 44 (3)	0.011	1.3×10^{-4}		
	series	0.103 650	0.103 650				
79	m^* = 0.88	0.111 020 (9)	0.113 916 (6)	0.012	3×10^{-4}	0.2025 (4)	280 000
	series	0.111 055	0.111 055				
99	m^* = 0.88	0.113 792 (5)	0.117 57 (2)	0.013	4.5×10^{-4}	0.1902 (5)	500 000
	m = 1		0.119 67 (3)	0.016	7.5×10^{-4}		
	series	0.113 806	0.113 806				
99 (b = 1)	m^* = 0.68		0.143 36 (7)	0.027	7.5×10^{-3}		40 000
	m = 1		0.162 7 (2)	0.038	1.5×10^{-2}		18 000
	series		0.113 806				
149	m^* = 0.88	0.117 803 (3)	0.123 23 (2)	0.014	7.9×10^{-4}	0.1736 (8)	340 000
	series	0.117 794	0.117 794				
199	m^* = 0.87	0.120 003 (7)	0.126 59 (2)	0.013	1.03×10^{-3}	0.1636 (9)	60 000
	m = 1		0.130 23 (5)	0.017	1.7×10^{-3}		
	series	0.119 974	0.119 974				
249	m^* = 0.86	0.121 41 (2)	0.128 77 (3)	0.013	1.2×10^{-3}	0.160 (2)	110 000
	series	0.121 37	0.121 37				
399	m^* = 0.84	0.123 66 (4)	0.132 67 (4)	0.011	1.5×10^{-3}		85 000
	m = 1		0.137 30 (5)	0.015	2.6×10^{-3}		
	series	0.123 62	0.123 62				
599	m^* = 0.83	0.125 14 (5)	0.135 29 (5)	0.010	1.7×10^{-3}		45 000
	m = 1		0.139 8 (3)	0.012	3.0×10^{-3}		
	series	0.124 9	0.124 99				
799	m^* = 0.86	0.125 9 (3)	0.136 7 (3)	0.009	2×10^{-3}		15 000
	series	0.125 7	0.125 7				

[a] N is the number of steps and m^* the optimal mean-field parameter. Results for m = 1 (no mean-field parameter) are taken from ref 1, 2, and 13. The scanning parameter is b = 6. For N = 99 results are presented also for b = 1. [b] $\langle S_{EV}\rangle$ (eq 32) and $\langle S_{EV}\rangle_{b,m}$ (eq 5 and 24) are approximations for the entropy. $\Delta S(b,m)$ (eq 27) is the fluctuation of the entropy and $\langle S_{EV}{}^{U}\rangle$ (eq 33) is the entropy of rings. These quantities are expressed in units of Nk_B where k_B is the Boltzmann constant. λ is the attrition factor (eq 18). n is the sample size. [c] The statistical error is denoted by parentheses, e.g., 0.2329 (3) = 0.2329 ∓ 0.0003. The results for $\Delta S(b,m)$ and λ are rounded off to two significant figures. The series expansion values are calculated from a formula derived by Watts.[22,23] [d] n is the sample size, $n = W_N$.

always biased]. However, for a finite sample size n the extent of convergence of $\bar{V}$ to $\langle V\rangle$ is determined by the standard deviations of the two averages defining $\langle V\rangle$, which are functions of N, b, and m via $P_i(b,m)$. In other words, in order to obtain a good estimation of $\langle V\rangle$, the sample generated with $P_i'(b,m^*)$ should contain a sufficiently large number of the (relatively improbable) typical equilibrium SAWs, which will dominate the summation defining $\bar{V}$ by their large factors $1/P_i(b,m^*)$ (see ref 2 and a discussion in ref 15).

It should be pointed out that the present procedure, with b = 1 only and without employing a mean-field parameter, was suggested long ago by Rosenbluth and Rosenbluth.[16] Their method (with b = 1) has been extended to self-interacting SAWs[17-19] and to adsorption problems[20] by Mazur, McCrackin, and Guttman. These authors have also employed parameters (different from our mean-field parameter); however, they have not provided a criterion for optimizing their parameters.

Finally, it should be emphasized that a mean-field parameter can also be used in the same way for self-interacting SAWs (see ref 2, section E). For more complicated chain models, however, it may be necessary to define parameters in a different way which will optimally take into account the particular properties of the model. For example, in the lattice model for proteins introduced by Go,[21] several contacts between amino acid residues are formed, which give rise to loops. Therefore, in order to construct protein conformations efficiently with the scanning method, one should assign to each such loop a parameter which will increase the probability for loop closure. In this case, however, the free energy (rather than the entropy) should be minimized with respect to the various parameters.

Results and Discussion

In the present work we are studying SAWs of variable length $49 \le N \le 799$ on a three-choice square lattice. The SAWs are constructed step-by-step, where at each step k all the future SAWs of length b = 6 are generated and the values for $M_k(\nu,b)$ are calculated. Also are calculated the center of mass of the $k-1$ steps, and the unit vector $\vec{x}$ which points from the center of mass to step $k-1$; all these quantities lead to $p_k(\nu,b,m)$ (eq 22). A direction ν is then selected by a Monte Carlo lottery according to the p_k's. In order to determine the optimal parameter m^* we first generate relatively small samples (each consisting of several thousand SAWs) for different values of m and minimize $\langle S_{EV}\rangle_{b,m}$. It should be pointed out that in order to save computer time, we calculate the center of mass and the vector $\vec{x}$, for the longer chains, only every five steps. This has been found to change the value of m^* very slightly. Therefore, the additional computer time required for calculating the effect of m is insignificant as compared to the time spent in calculating the future SAWs. The factor A (eq 26) required for calculating $P_i'(b,m)$ (eq 25) is estimated by the ratio $A = W_N/W_0$ ($W_N = n$), obtained from the simulation. This ratio also enables one to calculate the attrition constant λ (eq 18).

In Table I results are presented for $\langle S_{EV}\rangle$ (eq 32), $\langle S_{EV}\rangle_{b,m}$ (eq 24), $\Delta S(b,m)$ (eq 27), and λ (eq 18) and for the entropy of rings $\langle S_{EV}{}^{U}\rangle$ (eq 33) obtained with $m = m^*$

and $b = 6$. However, for several chain lengths we also present for comparison the results for $\langle S_{EV}\rangle_{b,m}$, $\Delta S(b,m)$, and λ, obtained in ref 2 and 13 for $b = 6$ and $m = 1$ ($m = 1$ means that the mean-field parameter is not effective). For $N = 99$ these quantities have also been calculated with the approximations $b = 1$, $m = 1$, and m^*, which enable one to examine the dependence of the results on both b and m^*. In order to obtain statistically reliable results for the entropy of rings, relatively large samples have been employed (see values for n in the table). The results in the tables are averages of results obtained from at least three such samples, generated with different random number sequences. It should first be pointed out that the results for $\langle S_{EV}\rangle$ are very close to those obtained with a formula based on series expansion.[22,23] As expected the accuracy of $\langle S_{EV}\rangle$ decreases with increasing N because of a decrease in both the sample size n and the ratio b/N (which means that the approximation worsens). For $m = 1$ the results for $\langle S_{EV}\rangle$ are not presented since they have been obtained for significantly smaller sample size. The table reveals that the values of m^* decrease with increasing N, from 0.93 for $N = 49$ to 0.84 for $N = 599$, which means that the parameter becomes more effective as the approximation worsens. As expected, always $\langle S_{EV}\rangle_{b,m^*} < \langle S_{EV}\rangle_{b,1}$ and correspondingly $\Delta S(b,m^*) < \Delta S(b,1)$, which means that $P_i'(b,m^*)$ is a better probability distribution than $P_i'(b,1)$. The normalized difference, $[\langle S_{EV}\rangle_{6,1} - \langle S_{EV}\rangle_{6,m^*}]/\langle S_{EV}\rangle_{6,1}$, increases from 0.005 to 0.035 as N increases from 49 to 599, respectively; $[\Delta S(6,1) - \Delta S(6,m^*)]/\Delta S(6,1)$ increases in this range from 0.10 to 0.26. This again reflects the increasing effect of m^* with decreasing b/N. The effect of the mean-field parameter is even much more pronounced in the results for $n = 99$ and $b = 1$, where m^* decreases to 0.68, $(\langle S_{EV}\rangle_{1,1} - \langle S_{EV}\rangle_{1,m^*})/\langle S_{EV}\rangle_{1,1} = 0.118$ and $[\Delta S(1,1) - \Delta S(1,m^*)]/\Delta S(1,1) = 1.4$. It should be pointed out that we have also attempted to determine m^* by minimizing $\Delta S(b,m)$ and have always obtained lower values for m^* in this way than by minimizing $\langle S_{EV}\rangle_{b,m}$; for $N = 99$ and $b = 6$, for example, $m^* = 0.80$ and 0.88 have been obtained, respectively. As one would expect, decreasing of m leads to more open chains and therefore to lower values of the attrition factor λ (eq 18). Therefore, as far as λ is concerned, the optimization criterion based on $\Delta S(b,m)$ is more efficient than that based on $\langle S_{EV}\rangle_{b,m}$; however, there is no way to determine which of these criteria leads to a better probability distribution $P_i'(b,m^*)$. The results for λ obtained for m^* are indeed always smaller than those obtained for $m = 1$; the ratio $W_N(m^*)/W_N(m = 1)$ (for the same value of W_0, see eq 18) increases with increasing N from 1.001 for $N = 49$ to 2.2 for $N = 599$, which is a consequence of the corresponding decrease of m^* discussed above. It should be pointed out that this gain in efficiency has been achieved without a significant increase in computer time. Obviously, such a decrease in λ could also be obtained by increasing b but this would be very time-consuming. For example, for $N = 599$ and $b = 6$, $W_N(m^*)/W_N(m = 1) = 1.55$, whereas from ref 2, for $m = 1$, $W_N(b = 8)/W_N(b = 6) = 1.48$; however, the calculation with $b = 8$ requires approximately 6 times more computer time than that with $b = 6$. For $N = 99$ and $b = 1$ $W_N(m^*)/W_N(m = 1) = 2.1$. This value is significantly larger than 1.03 obtained for $b = 6$, which again reflects the larger effect of m^* as the approximation worsens.

The relatively high accuracy of the resuls for $\langle S_{EV}\rangle$ for $N \leq 199$ (the statistical error does not exceed 0.006%) enables one to extract the exponent γ and the constants μ and C_0 (eq 1) by a least-squares procedure. Our results

$$\gamma = 1.333\ (4), \qquad \mu = 2.6383\ (1); \qquad C_0 = 1.24\ (2) \tag{34}$$

are in very good agreement with the series expansion results of Watts;[23] $\gamma = 1.333$ (5), $\mu = 2.6385$ (3), and Derrida's[24] result $\mu = 2.63817$ (2), which is based on a phenomenological renormalization scheme (the statistical error is defined in the footnotes of Table I). For many years it was believed that $\gamma = {}^4/_3$; however, Nienhuis's[6] exact result for the honeycomb lattice, $\gamma = 43/32 = 1.3437...$ is larger. The Nienhuis solution has motivated several researchers to reanalyze the series expansion data more carefully. Indeed, Guttman[9] (who has studied the square and triangular lattices) and Majid et al.[7] (who studied the triangular lattice) have found strong evidence to support the Nienhuis value rather than ${}^4/_3$. Guttman has also obtained $\gamma = 2.6381$ (2), which is equal, within the statistical error, to our result. Very recently Kremer and Barber[11] have estimated γ using a real space renormalization calculation on a square lattice and obtained $\gamma = 1.35$ (3), which is also closer to the Nienhuis result than to ${}^4/_3$. Also it should be mentioned the Monte Carlo estimates $\gamma = 1.36$ and 1.345 for the square and triangular lattices, respectively, obtained by Alexandrowicz[25] under the assumption of what is called "strong universality"; very recently he has also obtained[26] $\gamma = 1.318$ (15) by his dimerization method.[27] Our value for γ is therefore smaller, not only from the Nienhuis value, but also from most of the recent numerical estimates. This, however, might be a consequence of using insufficiently long chains in our calculations.

We have also calculated the entropy of SAWs, which return to the origin, i.e., those with the end-to-end distance equals 1. These results enanble one to extract the exponent α using eq 7. However, because of insufficient statistics the accuracy of the results for $\langle S_{EV}{}^U\rangle$ is considerably lower than that obtained for $\langle S_{EV}\rangle$; therefore, our least-squares analysis is based only on the four points, $N = \leq 149$, and the value for μ obtained from the results for $\langle S_{EV}\rangle$. The result for α is rather crude

$$\alpha = 0.5\ (1) \tag{35}$$

which agrees with the accepted value ${}^1/_2$.[28]

In Table II results are presented for the statistical averages of various powers of the end-to-end distance R (eq 10) and the radius of gyration, G (eq 12–14). In order to obtain highly accurate estimates for the critical exponents ν_p and ν_G from the scaling equations 11 and 18, respectively, relatively long SAWs should be simulated. Our chains, however, are insufficiently long and therefore one has to analyze the data by taking into account corrections to scaling.[7-10,29] However, we have found it impossible to determine the ν's with such an analysis because of insufficient accuracy of our results. As an alternative analysis, we present in Table III, as a function of N, a sequence of estimates for A_p and ν_p (for $p = 2$ and 4, see eq 11) and A_G and ν_G (eq 15), based on only three results for $\langle R^p\rangle$ and $\langle G^2\rangle$, respectively. Our aim is to examine the convergence of these parameters for large N. The table reveals that for the shorter chains the values of ν_2 and ν_G are significantly below the Nienhuis result 0.75 and they increase monotonically with increasing N; for the longest chains (5 and 6) they become 0.75, within a relatively large statistical error. This means that in order to check the validity of the Nienhuis value with sufficient accuracy still longer SAWs and larger samples are required. It should be pointed out that, before the appearance of the Nienhuis solution, calculations of ν with various methods have led, in most cases, to values which are very close to but different from 0.75.[24,30-33] $\nu = 0.75$ has been obtained by

Table II
Results for the End-to-End Distance and the Radius of Gyration Obtained for $b = 6$ and m^* [a,b]

N	$\langle R^2\rangle/N$	$\langle G^2\rangle/N$	$\langle R^4\rangle/N^2$	$(N\langle R^{-1.333}\rangle)^{-1}$	$(N\langle R^{-2}\rangle)^{-1}$	$(N^2\langle R^{-4}\rangle)^{-1}$
49	5.514 (4)	0.7749 (3)	43.31 (5)	0.5365 (6)	1.930 (5)	0.190 (2)
series	5.525					
79	6.958 (1)	0.9752 (2)	69.42 (2)	0.5284 (4)	2.332 (4)	0.176 (4)
series	6.951					
99	7.764 (4)	1.0883 (2)	86.51 (7)	0.5251 (8)	2.54 (1)	0.157 (4)
series	7.752					
149	9.479 (6)	1.3294 (4)	129.3 (2)	0.522 (2)	3.03 (2)	0.15 (1)
series	9.456					
199	10.94 (2)	1.533 (1)	172.4 (4)	0.517 (3)	3.41 (7)	0.17 (3)
series	10.89					
249	12.22 (2)	1.715 (2)	215.2 (2)	0.511 (5)	3.6 (2)	0.16 (4)
series	12.15					
399	15.49 (9)	2.17 (1)	345 (4)		4.9 (6)	
series	15.3					
599	19.2 (2)	2.71 (2)	522 (6)		8.8 (7)	
series	18.7					

[a] R is the end-to-end distance, and G the radius of gyration. $\langle R^p\rangle$ is defined in eq 10, and $\langle G^2\rangle$ in eq 12–14. N and the statistical error are defined in the footnotes of Table I. [b] The results denoted "series" have been calculated with a formula derived by Domb.[34]

Table III
Results for the Critical Exponents ν_p for Positive Values of p [a,b]

	N			ν_2	A_2	ν_G	A_G	ν_4	A_4
1	49	79	99	0.743	0.83	0.741	0.118	0.746	0.94
2	79	99	149	0.744	0.83	0.744	0.115	0.745	0.96
3	99	149	199	0.746	0.81	0.745	0.114	0.747	0.93
4	149	199	249	0.747	0.80	0.748	0.111	0.748	0.90
5	199	249	399	0.750 (5)	0.77 (5)	0.750 (4)	0.109 (5)	0.749 (5)	0.87 (9)
6	249	399	599	0.757 (8)	0.71 (6)	0.760 (5)	0.097 (6)	0.752 (6)	0.82 (8)

[a] The results for ν_p and A_p for $p = 2$ and 4 (eq 11) and for ν_G and A_G (eq 15) have been obtained by a least-squares procedure. Each pair (A,ν) is based on three results for $\langle R^p\rangle$ or $\langle G^2\rangle$ obtained for successive values of N. [b] The statistical error is defined in the footnotes of Table I. The statistical errors for 1–4 (not inidcated) are significantly smaller than those for 5 and 6.

Havlin and Ben Avraham[29] from Monte Carlo results and was also employed by Domb[34] long ago, to fit series expansion data. These two studies are based on corrections to scaling. Similar analyses with longer series have been carried out recently for the triangular and square lattices.[7,8,10] which also strongly support $\nu = 0.75$. It should be pointed out that the results for ν_4 (obtained from the values of $\langle R^4\rangle$) behave like those for ν_2 and ν_G and they are even slightly closer to 0.75; this suggests that $\nu_2 = \nu_p$ also for larger values of p, which means that ν can be extracted from results for $\langle R^p\rangle$, for any value of $p > 0$.

The last conclusion, however, does not hold for negative values of p: As $|p|$ ($p < 0$) increases, there is also an increase in the relative contribution to $\langle R^p\rangle$, which comes from the integration over the region of small R. The probability distribution in this region, $P(\bar{R})$, is[12,35]

$$P(\bar{R}) = (\text{constant})\langle R\rangle^{-d}(R/\langle R\rangle)^{(\gamma-1)/\nu}$$

$$\langle R\rangle = \langle R^2\rangle^{1/2}; \qquad R \ll \langle R\rangle \tag{36}$$

Therefore, in two dimensions, for sufficiently large values of $|p|$ ($p < 0$) one obtains

$$\langle R^p\rangle = 2\pi \int_0^{R\ll\langle R\rangle} r^{p+1}P(r)\,dr \sim N^{-2\nu-(\gamma-1)} = N^{-1.8437...} \tag{37}$$

where the exponent $f_p = 1.8437...$ (based on Nienhuis's exact results) constitutes an upper bound. For smaller values of $|p|$ ($p < 0$) this integral (eq 37) together with the integral over the larger values of R (which cannot be neglected in these cases) is expected to lead to smaller values of the exponent $f_p = -p\nu_p$. In Table IV results are presented for ν_p and A_p for $p = -1.333$, -2, and -4, obtained from the values of $\langle R^p\rangle$ (for $N \le 199$) by a least-squares procedure. The table reveals that the trend of f_p discussed above is indeed realized, where these values increase monotonically toward the upper bound value of 1.8437... as $|p|$ is increassed. It should be pointed out that the averages $\langle R_{k,m}{}^{-1}\rangle$, where k and m are inner steps of the chain, appear in the expression for the diffusion coefficient in Kirkwood's theory.[36] Calculation of $\langle R_{k,m}{}^{-1}\rangle$ for self-interacting SAWs in the Θ region has been carried out recently by Guttman et al.[37] with the help of a Monte Carlo procedure. However, in view of our results, one should be careful in computing these quantities for SAWs since for $p < 0$ (in contrast to the case of $p > 0$) ν_p is a function of p.

Table IV
Results for the Critical Exponents ν_p for Negative Values of p [a]

p	ν_p	f_p [b]
−1.333	0.731 (6)	0.975 (6)
−2	0.70 (1)	1.40 (2)
−4	0.53 (2)	1.78 (7)
$-\infty$		1.8437...

[a] The results for $p = -1.333$ and -2 are based on data for $N \le 199$ (Table II); those for $p = -4$ on $N \le 149$. The result for $p = -\infty$ is discussed in the text. The statistical error is defined in the footnotes of Table I. [b] $f_p = -p\nu_p$.

Summary

In this paper the efficiency of the scanning method has been significantly improved by incorporating a mean-field parameter. This enabled us to treat chains of up to 799 steps. Relatively accurate results have been obtained for the entropy, the entropy of rings, and for averages $\langle R^p\rangle$, where p has positive as well as negative values, which have led to good estimates for the corresponding critical exponents ν, α, and ν_p. For $p > 0$ our results suggest that for any p, $\nu_p = 0.75$; however, for $p < 0$ we show (as far as we know in the first time) that $\langle R^p\rangle \sim N^{-f_p} \neq N^{-p\nu}$ (f_p is

bounded from above by 1.8437...). It should be pointed out that for a single SAW the scanning method is comparable in efficiency to the enrichment method[4] and still significantly less efficient than the dimerization method[25,27] where chains of up to 10^4 steps have been studied. However, the advantage of the scanning method over these two methods is in its much better suitability to handle a large variety of other chain models, multiple-chain systems (see ref 3 and references cited therein), chains which are subject to boundary constraints such as boxes, surfaces, etc. (see ref 38–40 and references cited therein) and self-interacting SAWs.[17-19,41] The scanning method is also expected to be the most efficient simulation method for estimating the entropy.[42,43]

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Computer Simulation Technique for Calculating the Entropy of Polymer Chains, Based on the Scanning Method with a Mean-Field Parameter

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ABSTRACT: Recently I have suggested a technique, based on the scanning method, which enables one to extract the entropy of a polymer chain from a sample of chain conformations. This technique is further improved here, by incorporating a mean-field parameter, m, and applied as a test to self-avoiding walks (SAWs) on a square lattice. We study SAWs (longer than in previous work) which are unbounded in space and also SAWs which are bounded by relatively small "boxes". The results for the entropy of the unbounded SAWs improve significantly, as compared to those of previous work, without a significant increase in computer time. The results for the bounded SAWs, however, are only slightly improved. We show that the parameter should optimally be defined to fit the particular properties of a model.

Introduction

The concepts of the scanning method,[1-3] described in the preceding article[4] (ref 4 will be denoted as paper I), constitute the basis for a technique[5,6] which enables one to extract the entropy of chains from a relatively small sample of chain conformations. This technique has been applied preliminarily to self-avoiding walks (SAWs) on square and simple cubic lattices and to SAWs which are bounded by relatively small "boxes" of size $(2L + 1)^d$, where d is the dimensionality.[5] Recently the technique has been significantly improved for the special case of chain models with hard core potential.[6] In the present paper it will be extended to chains which also have finite attractive or repulsive interactions and it will be further improved by introducing a "mean-field" parameter in the same way as has been defined in paper I for the scanning method. The technique will again be applied to bounded and unbounded SAWs on a three-choice square lattice, which constitute a convenient test case, since the entropy is known, with high accuracy, from series expansion[1,8] and other studies (see below). The SAWs will be generated with the direct Monte Carlo (MC) method,[9] which has the following advantages: (1) It is *exact*, i.e., generates SAW i of N steps, with its ensemble probability P_i

$$P_i = C_N^{-1} \tag{1}$$

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