Computer simulation of the free energy of polymer chains with excluded volume and with finite interactions

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We have recently suggested an approximate computer simulation technique, based on the scanning method, which enables one to extract the entropy (and hence the free energy) of polymer chains from a relatively small sample. So far this technique has been discussed in terms of chains with excluded volume (EV); in the present work we extend its scope to chains, which also have finite interactions. In order to obtain better approximations for the entropy we utilize the concepts of the generalized Monte Carlo procedure suggested by Schmidt [Phys. Rev. Lett. **51**, 2175 (1983)] (and discussed in the preceding paper). We analyze our results from the preceding paper for self-attracting random walks (without EV) on square and simple-cubic lattices, and show that our techniques lead to accuracy which is better than 0.3% for both the free energy and the entropy. For chain models which include EV, we use, in addition to Schmidt's procedure, an alternative one based on "importance sampling." We test these two procedures as applied to self-avoiding walks (SAW's) on a square lattice, where the SAW's are unbounded in space or bounded in relatively small "boxes." Very accurate results for the entropy are also obtained here. It turns out, however, that importance sampling is slightly more efficient than the Schmidt procedure.

I. INTRODUCTION

Most simulation methods for polymer chains[1-4] do not provide the *value* of the sampling probability P and hence the entropy, which is related to $\ln P$, cannot be estimated in a statistical-mechanical manner. There is, however, an interest in calculating the entropy, stemming from three reasons. First, the entropy constitutes a measure of order. Second, it leads, together with the energy, to the free energy, from which all the thermodynamic properties can be derived. Third, the free energy constitutes a criterion of stability, which may be employed, for example, to determine the most stable state of a protein in a protein folding procedure. In this case simulation runs, starting from different conformations, lead the chain to different free-energy minima; the most stable state is defined as that with the lowest free-energy minimum. Gō and Scheraga[5,6] developed a method (based on normal coordinate analysis) for calculating the entropy of macromolecules undergoing small (i.e., harmonic) fluctuations around their stable state (e.g., the α-helical state of a polypeptide) and applied it to several short polypeptides.[7,8] They also calculated[5] the entropy of a polypeptide in its random coil state at the θ point,[9,10] i.e., neglected the excluded volume effect (see also Ref. 11). Karplus and Kushick[12] (see also Ref. 13) suggested calculating the covariances of the internal coordinates directly from the molecular-dynamics or Monte Carlo simulation rather than performing normal coordinate analysis and applied their method to the molecular-dynamics simulation of decaglycine and butane. These approximate treatments cover only the two extreme cases of very small and very large conformational fluctuations and are not applicable to states with intermediate chain flexibility.

Recently we have suggested a new technique,[14-16] based on the concepts of the scanning method,[16-18] which enables one to estimate approximately the *value* of the probability with which a conformation is sampled and hence to extract the entropy from a relatively small sample of chain conformations. This technique, in contrast to those described above,[5-13] can in principle be applied to *any* macromolecular state. So far[14-16] it has been discussed in terms of self-avoiding walks (SAW's) on a lattice; in the present work we extend its scope to general chain models, i.e., models with both excluded volume (EV) and *finite* attractive or repulsive interactions. We show that a better approximation for the entropy can be obtained by utilizing the concepts of Schmidt's procedure[19] that has been discussed in detail in the preceding article.[20] (In this work we shall refer frequently to Ref. 20, which for convenience will be denoted I.) In the first stage the theory is developed for chains with finite interactions but without EV and the accuracy of the technique is tested by analyzing results for the entropy and the free energy obtained in I for self-attracting random walks. In the next stage the more realistic case of a chain with both EV and finite interactions is discussed. We show that for such a model, one can also employ, in addition to Schmidt's procedure, an alternative one based on "importance sampling;"[21] however, the Schmidt procedure, in contrast to importance sampling, enables one to estimate the statistical error. We test the efficiency of these two procedures for SAW's on a square lattice. As in our previous work[14-16] we treat SAW's which are free to "grow" in space, and also SAW's which are bounded in small "boxes." This model, while relatively simple, has the advantage that its entropy is known from series expansion studies and other sources (see Sec. II). Finally, it should be pointed out that the theory of our technique, developed in Sec. II, is based, to a large extent, on the theory of the scanning method described in the preceding paper (I).

II. THEORY

Consider a chain model of N steps (bonds) lying on a lattice with coordination number q. The chain has finite interactions but no EV. The Boltzmann probability P_i of chain conformation i is

$$P_i = \exp(-E_i/k_BT)/Z \ , \tag{1}$$

where E_i is the chain energy, k_B is the Boltzmann constant, T is the absolute temperature, and Z is the partition function. The entropy S, the energy E, and the free energy F are

$$S = -k_B \sum_i P_i \ln P_i \ , \tag{2}$$

$$E = \sum_i P_i E_i \ , \tag{3}$$

$$F = E - TS \ . \tag{4}$$

Assume now that a sample of n conformations has been generated with the help of an exact simulation method, such as the Metropolis method.[22,23] It should be pointed out that this method, while it does enable one to select conformation i correctly with its Boltzmann probability P_i [Eq. (1)], does not provide the *value* of P_i and therefore the entropy cannot be calculated with Eq. (2). We therefore suggest estimating the value of P_i by using the concepts of the scanning method[17,18,20] in the following manner.[14–16] Since a *large* sample in equilibrium can be obtained, in principle, by any exact simulation method, one can *assume* that the given sample has been constructed with the scanning method (rather than with the Metropolis method), employing certain values for the scanning parameter b and the mean-field parameter m (see I). Thus, taking into account the particular interactions of the model (any kind of finite repulsions or attractions) one can reconstruct for each step k, $1 \le k \le N$ of conformation i the transition probability $p_k(\nu_k,b,m)$ [see Eq. (I22); equations from the preceding paper being denoted by I], with which the direction ν_k has *hypothetically* been chosen and define $P_i(b,m)$ [Eq. (I23)], the probability of conformation i, where

$$P_i(b,m) = (1/q) \prod_{k=2}^{N} p_k(\nu_k,b,m) \ . \tag{5}$$

As has been already discussed in I, for $b \ll N$, $P_i(b,m)$ is approximate, i.e., it differs from the sampling probability P_i [Eq. (1)]. However, one can assign to each i a random variable $\ln P_i(b,m)$, and define approximations S^A and F^A for the entropy and the free energy, respectively, where

$$S^A = -k_B \sum_i P_i \ln P_i(b,m) \ , \tag{6}$$

$$F^A = E - TS^A \ . \tag{7}$$

One can show[24] rigorously (using Jensen's inequality[25]) that S^A overestimates the correct entropy S [Eq. (2)],

$$S^A \ge S \ . \tag{8}$$

This relation and the fact that F^A and F are both defined with the correct energy E [Eq. (3)] lead to

$$F^A \le F \ . \tag{9}$$

The above inequalities enable one to optimize $P_i(b,m)$, for a given b, with respect to m at the value $m = m^*$ at which S^A (F^A) obtains its minimal (maximal) value.

One can also define other approximations S^B and F^B where

$$S^B = -k_B \sum_i P_i(b,m) \ln P_i(b,m) \tag{10}$$

and

$$F^B = \sum_i P_i(b,m)[E_i + k_BT \ln P_i(b,m)] \ . \tag{11}$$

It should be noticed that Eq. (11) [in contrast to Eq. (7)] consists of one type of probability, $P_i(b,m)$, and therefore, according to the minimum free-energy principle, F^B is never smaller than the correct free energy F [Eq. (4)],

$$F^B \ge F \ . \tag{12}$$

Obviously, both F^B and F^A approach F (from above and below, respectively) as the approximation improves (i.e., as b is increased) and, therefore, one would expect their average,

$$F^M = (F^A + F^B)/2 \ , \tag{13}$$

to be a better approximation than each of them individually. Accordingly, the entropy S^M is expected to be a better approximation than either S^A or S^B, where

$$S^M = (E - F^M)/T \ . \tag{14}$$

It should be pointed out that S^A [Eq. (6)] is a statistical average defined with the exact probability P_i [Eq. (1)], which also constitutes the sampling probability; therefore S^A can be estimated from the given sample in the usual manner, by $\bar{S}^A$,

$$\bar{S}^A = n^{-1} \sum_{t=1}^{n} \ln P_{i(t)}(b,m) \ , \tag{15}$$

where $i(t)$ is conformation i obtained at time t and n is the sample size. On the other hand, S^B and F^B are defined with the probability $P_i(b,m)$ and, therefore, their estimation is not straightforward. To estimate them, we suggest utilizing the generalized Monte Carlo procedure of Schmidt[19] as outlined below. In I and Ref. 19 this procedure was employed to extract an unbiased sample from an initially biased one; here we propose to extract from the given unbiased sample (generated with P_i) an effectively smaller sample (which will be referred to as the biased sample) generated with $P_i(b,m)$. For that one should replace in Eq. (I34) T_{ij} by P_j and P_j by $P_i(b,m)$. The probability A_{ij} for accepting a trial conformation j, therefore, becomes

$$A_{ij} = \min[1, P_iP_j(b,m)/P_jP_i(b,m)] \tag{16}$$

and the acceptance rate $\mathscr{R}$ for the biased conformations is defined in the same way as in Eq. (I36), i.e.

$$\mathscr{R} = n_{\text{accepted}}/n \tag{17}$$

where n_{accepted} is the number of accepted chains. S^B can

now be estimated by $\bar{S}^B$ from the biased sample of accepted chains obtained with the above procedure [see Eq. (15)],

$$\bar{S}^B = n^{-1} \sum_{t=1}^{n}{}' \ln P_{i(t)}(b,m) , \tag{18}$$

where $\sum'$ denotes summation over the biased sample. It should be pointed out that the statistical error of S^B can be estimated from the number of accepted conformations in the biased sample (see I).

So far we have discussed chain models without EV. If EV is also taken into account the chains become self-interacting SAW's and some modifications should be made in the above theory. First, it should be pointed out that construction of a self-interacting SAW with the scanning method may fail because of trapping of the chain in a "dead end."[16–18] In this case the chain is discarded and a new one is started (sample attrition). This means that $P_i(b,m)$ is not normalized over the ensemble of all self-interacting SAW's and a normalized probability $P_i'(b,m)$ is

$$P_i'(b,m) = P_i(b,m) \Big/ \sum_{\text{SAW's}} P_i(b,m) = P_i(b,m)/A . \tag{19}$$

The value of A can easily be estimated from the numbers of SAW's attempted and generated.[16–18] However, in the present case, the sample is not obtained with the scanning method, hence the values of A and $P_i'(b,m)$ are unknown. We therefore redefine F^B [Eq. (11)], and denote it F^B_{EV}, where

$$F^B_{\text{EV}} = \sum_{\text{SAW's}} P_i'(b,m)[E_i + k_B T \ln P_i(b,m)] . \tag{20}$$

Obviously, F^B_{EV}, in contrast to F^B, is based on two different probability distributions and therefore does not necessarily satisfy $F^B_{\text{EV}} \geq F$. However, one can show from Eqs. (6)–(12), (19), and (20) that the following relation always holds,

$$F^B_{\text{EV}} \geq F^A , \tag{21}$$

and, therefore, one would still expect that the average F^M [Eq. (13)], defined with F^B_{EV}, constitutes a better approximation for F than either F^A or F^B_{EV}. F^B_{EV} can be estimated by employing the Schmidt procedure [Eq. (16)] using the known values of $P_i(b,m)$ [rather than $P_i'(b,m)$]; it can also be estimated with importance sampling[21] as follows. Let us define F_i by

$$F_i = E_i + k_B T \ln P_i(b,m) , \tag{22}$$

then, using Eqs. (1), (19), and (20), one obtains

$$F^B_{\text{EV}} = \sum_{\text{SAW's}} P_i'(b,m) F_i = \sum_{\text{SAW's}} P_i(b,m) F_i \Big/ \sum_{\text{SAW's}} P_i(b,m) = \sum_{\text{SAW's}} P_i[P_i^{-1} P_i(b,m) F_i] \Big/ \sum_{\text{SAW's}} P_i[P_i^{-1} P_i(b,m)] . \tag{23}$$

Replacing P_i^{-1} by its explicit expression [Eq. (1)] leads to

$$F^B_{\text{EV}} = \sum_{\text{SAW's}} P_i[\exp(E_i/k_B T) P_i(b,m) F_i] \Big/ \sum_{\text{SAW's}} P_i[\exp(E_i/k_B T) P_i(b,m)] . \tag{24}$$

The expressions in the square brackets can be considered as random variables averaged with the sampling probability P_i [Eq. (1)].[26] Therefore, F^B_{EV} [Eq. (24)] can be estimated from the given sample by $\bar{F}^B_{\text{EV}}$ [see Eq. (15)], where

$$\bar{F}^B_{\text{EV}} = \sum_{t=1}^{n} \exp(E_{i(t)}/k_B T) P_{i(t)}(b,m) F_{i(t)} \Big/ \sum_{t=1}^{n} \exp(E_{i(t)}/k_B T) P_{i(t)}(b,m) . \tag{25}$$

It should be pointed out that Schmidt's procedure, as well as importance sampling, are efficient only if the probabilities $P_i(b,m)$ and P_i are sufficiently close. Otherwise the acceptance rate becomes very small, which means that the sample size n should be very large. It is of interest to compare the efficiency of these two procedures for estimating F^B_{EV}. We shall perform such a study for SAW's without finite interactions on a square lattice, which is a relatively simple model but has the advantage that its entropy can be calculated with other methods. For this model the Boltzmann probability [Eq. (1)] becomes

$$P_i = C_N^{-1} , \tag{26}$$

where C_N is the total number of SAW's. Obviously, here the entropy plays the role of the free energy, where

$$S = -k_B \sum_{\text{SAW's}} P_i \ln P_i = k_B \ln C_N . \tag{27}$$

A sample of SAW's will be generated with the direct Monte Carlo (DMC) procedure,[27] from which the entropy will be calculated by our techniques. With the DMC procedure a SAW is generated step by step, where at each step a direction is selected at random. Therefore, this procedure is exact, i.e., enables one to construct SAW i with P_i [Eq. (26)]; however, it is also extremely inefficient for generating long SAW's due to a strong sample attrition.[26] An advantage of the DMC procedure is the fact that it enables one to estimate the entropy from an asymptotically exact formula, based on the extent of attrition W_N/W_0, where W_0 is the number of SAW's attempted and W_N is the number of SAW's generated. The entropy due to the contribution of the EV effect, S_{EV}, is

$$S_{\text{EV}} = S_I - S = \sim k_B \ln(W_N/W_0) , \tag{28}$$

where S_I is the entropy of ideal walks (i.e., without EV),

$$S_I = k_B[\ln q + (N-1)\ln(q-1)] . \tag{29}$$

Correspondingly, we shall calculate

$$S_{\mathrm{EV}}^{A}=S_I-\sum_{\mathrm{SAW's}} P_i \ln P_i(b,m) , \tag{30}$$

$$S_{\mathrm{EV}}^{B}=S_I-\sum_{\mathrm{SAW's}} P_i'(b,m)\ln P_i(b,m) , \tag{31}$$

and

$$S_{\mathrm{EV}}^{M}=(S_{\mathrm{EV}}^{A}+S_{\mathrm{EV}}^{B})/2 . \tag{32}$$

S_{EV}^{B} (and hence S_{EV}^{M}) will be estimated in two ways, by importance sampling [see Eqs. (23)–(25), using $E_i=0$] and from the biased sample defined with Schmidt's procedure; these estimates will be denoted by IS and A, respectively.

III. RESULTS AND DISCUSSION

A. Self-interacting chains without EV

We first test our theory for a model without EV, the model of self-attracting random walks, studied in I. To do so one should generate a sample of unbiased walks [i.e., with P_i Eq. (1)] using any *exact* technique (e.g., the Metropolis method[22,23]) and estimate F^A [Eq. (7)] from this sample. F^B [Eq. (11)] can be estimated from a biased sample (defined with $P_i(b,m)$ [Eq. (5)]) extracted from the unbiased one by the Schmidt procedure. However, we shall not carry out this lengthy procedure but will rather demonstrate the efficiency of our techniques in a simple way, by analyzing results for the free energy obtained in I. In I $\langle F\rangle_{b,m^*}$ [Eq. (I24)] has been obtained from the originally biased sample [generated with $P_i(b,m)$] and therefore one would expect that for a sufficiently large sample size n [Eq. (18)] $F^B\to\langle F\rangle_{b,m^*}$. On the other hand, $\langle F\rangle_{\mathrm{A}}$ [Eq. (I39)] has been estimated from an unbiased sample (defined with P_i [Eq. (1)]) extracted from the original one by Schmidt's procedure. Hence one would expect $\langle F\rangle_{\mathrm{A}}\to F^A$. This suggests that F^M [Eq. (13)] and S^M [Eq. (14)] can be estimated from the results for $\langle F\rangle_{\mathrm{A}}$ and $\langle F\rangle_{b,m^*}$, obtained in I, instead of performing additional simulations. Our results for F^M and S^M can be compared to those of $\langle F\rangle_{\mathrm{IS}}$ [Eq. (I32)] and $\langle S\rangle_{\mathrm{IS}}$ [Eq. (I33)], respectively (see I), which are considered by us to be exact. In Table I we present results, obtained with the scanning method (see I), for the free energy $\langle F\rangle_{b,m^*}$, $\langle F\rangle_{\mathrm{A}}$, and $\langle F\rangle_{\mathrm{IS}}$ and the entropy $\langle S\rangle_{\mathrm{A}}$ and $\langle S\rangle_{\mathrm{IS}}$, for self-attracting random walks at the percolation threshold. These results are not presented in Table I of I. The results for $\langle M\rangle_{\mathrm{IS}}$, the average number of distinct sites visited, which plays the role of the energy in this model, are taken from Table II of I. Table I reveals that, as expected [see Eqs. (9) and (12)], the results for $\langle F\rangle_{b,m^*}$ and $\langle F\rangle_{\mathrm{A}}$ always overestimate and underestimate, respectively, the values of $\langle F\rangle_{\mathrm{IS}}$, where the deviations are particularly large ($\sim 4\%$) for the simple cubic lattice ($d=3$) for $b=1$. However, the results for F^M are significantly closer to the correct values with a maximal deviation of $\sim 0.3\%$ ($d=3$ and $b=1$). Again the results for $\langle S\rangle_{\mathrm{A}}$ overestimate the correct values by up to $\sim 2.5\%$ ($d=3$ and $b=1$), whereas those for S^M are 1 order of magnitude better with a maximal deviation of $\sim 0.25\%$. Obviously, this relatively high accuracy of the results for F^M and S^M stems from the fact that the corresponding values of $\langle F\rangle_{b,m^*}$ and $\langle F\rangle_{\mathrm{A}}$ are approximately equally deviated (in opposite directions) from the correct values. It is important to point out that similar accuracy for F^M and S^M is also obtained for the longer walks studied in I.

B. Results for SAW's

Results for $S_{\mathrm{EV}}^{A}(b,m^*)$ [Eq. (30)] and $S_{\mathrm{EV}}^{M}(b,m^*)$ [Eq. (32)] for SAW's on a three-choice square lattice are presented in Tables II and III. $S_{\mathrm{EV}}^{M}(b,m^*)$ is estimated by importance sampling [denoted $S_{\mathrm{EV}}^{M}(\mathrm{IS})$] and from the biased sample defined with Schmidt's procedure [Eq. (16)] [denoted $S_{\mathrm{EV}}^{M}(\mathrm{A})$]. We also present in the tables the acceptance rate $\mathscr{R}$ [Eq. (17)] and the number of accepted

TABLE I. Results for the free energy and the entropy of self-attracting random walks at the percolation threshold. The results for the free-energy functionals $\langle F\rangle_{b,m^*}$ [Eq. (I24)], $\langle F\rangle_{\mathrm{A}}$ [Eq. (I39)], $\langle F\rangle_{\mathrm{IS}}$ [Eq. (I32)], and F^M [Eq. (13)] are in units of Nk_BT, where k_B is the Boltzmann constant, N the number of steps, and T the absolute temperature. The results for the entropy $\langle S\rangle_{\mathrm{A}}$ [Eq. (I40)], $\langle S\rangle_{\mathrm{IS}}$ [Eq. (I33)], and S^M [Eq. (14)] are in units of Nk_B. Equation numbers which appear with I are of the preceding article (Ref. 20), but the corresponding results do not appear in Table I or Ref. 20. The result for $\langle M\rangle_{\mathrm{IS}}$, the average number of distinct sites visited, is taken from Table II of I. K_c, the interaction parameter ($K_c=-\ln p_c$), is 0.522 95 for the square lattice ($d=2$) and 1.1657 for the simple cubic lattice ($d=3$).

b	$-\langle F\rangle_{b,m^*}$	$-\langle F\rangle_{\mathrm{A}}$	$-F^M$	$-\langle F\rangle_{\mathrm{IS}}$	$\langle S\rangle_{\mathrm{A}}$	$S^M=-F^M+\langle M\rangle_{\mathrm{IS}}/N$	$\langle S\rangle_{\mathrm{IS}}$
				$d=2,\ N=150$			
1	1.212 58(1)	1.2390(2)	1.2258	1.2270(1)	1.356(4)	1.3373	1.3385(1)
2	1.213 98(2)	1.2382(2)	1.2261	1.226 93(2)	1.3496(3)	1.3376	1.338 40(7)
4	1.216 77(2)	1.2358(2)	1.2263	1.226 94(1)	1.3476(4)	1.3378	1.338 55(5)
				$d=3,\ N=70$			
1	1.179 48(4)	1.2647(1)	1.2221	1.226 07(8)	1.621(2)	1.5781	1.5823(2)
2	1.191 23(5)	1.2558(4)	1.2235	1.226 12(6)	1.611(2)	1.5795	1.5824(8)
3	1.201 16(3)	1.2480(3)	1.2246	1.226 10(3)	1.604(1)	1.5806	1.5819(5)

TABLE II. Results for unbounded self-avoiding walks on a square lattice. N is the number of steps of a SAW, b is the scanning parameter, and m^* is the optimal mean-field parameter. S_{EV}^{A} [Eq. (30)], S_{EV}^{M}(IS), and S_{EV}^{M}(A) [Eq. (32)] are estimates for the entropy. IS and A mean that S_{EV}^{M} has been obtained by importance sampling and by the Schmidt procedure, respectively. These results are expressed in units of Nk_B where k_B is the Boltzmann constant. DMC denotes results for the entropy obtained with Eq. (28); "Series" denotes results obtained with a formula based on series expansion (Refs. 28 and 29). Acceptance rate is defined in Eq. (17). Statistical error is denoted by parentheses; for example, 0.0733(3)=0.0733±0.0003.

b	m^*	S_{EV}^{A}	S_{EV}^{M}(IS)	S_{EV}^{M}(A)	Acceptance rate	Number of accepted walks
			$N=49$			
1	0.71	0.076 49(7)	0.0991(6)	0.101(2)	0.29(1)	3600
4	0.88	0.100 90(5)	0.103 8(5)	0.1036(5)	0.75(2)	9400
7	0.94	0.102 96(3)	0.103 57(4)	0.103 57(3)	0.88(1)	10 990
DMC		0.103 55(6)	0.103 55(6)	0.103 55(6)		
Series		0.103 65	0.103 65	0.103 65		
			$N=59$			
1	0.71	0.0793(3)	0.1014(7)	0.1016(6)	0.25(1)	2950
4	0.87	0.103 46(3)	0.106 10(9)	0.106 06(6)	0.72(1)	8440
7	0.93	0.105 86(2)	0.106 72(5)	0.106 67(6)	0.85(1)	9970
DMC		0.106 76(4)	0.106 76(4)	0.106 76(4)		
Series		0.106 81	0.106 81	0.106 81		
			$N=79$			
1	0.71	0.081 71(8)	0.104 5(3)	0.103 3(3)	0.18(1)	2340
4	0.87	0.106 76(2)	0.110 81(3)	0.110 7(2)	0.62(1)	7740
7	0.92	0.109 626(7)	0.110 89(2)	0.110 97(3)	0.77(1)	9650
DMC		0.110 89(2)	0.110 89(2)	0.110 89(2)		
Series		0.111 06	0.111 06	0.111 06		

SAW's, which define the biased sample. The results in Table II are for chains, which are not restricted in space (unbounded); in Table III, however, we also study SAW's, which are bounded in relatively small boxes of size $(2L+1)^2$ (the chains start at the center of the box, the walls of which are also excluded). Results are presented for three values of the scanning parameter, $b=1$, 4, and 7, for the optimal value m^*. Self-avoiding walks of length $N=49$, 59, and 79 have been generated with the DMC procedure[27] and the results are averages of results obtained for three samples, each of size $W_N \sim 12\,000$ ($W_N=n$), based on different random number sequences. This relatively large sample size is required in order to obtain statistically reliable results for S_{EV}^{M}(A) for $b=1$. It should be pointed out that because of the strong sample attrition occurring with the DMC method, we are limited to a chain length of $N \leq 79$. In fact, the number of walks attempted [see Eq. (28)] is $W_0=2\times10^6$, 6.4×10^6, and 80×10^6 for $N=49$, 59, and 79, respectively; for the bounded SAW's $W_0=29.6\times10^6$ and 36×10^6 for $N=49$ and 59, respectively. These values and the values for W_N, the number of SAW's generated, enabled us to estimate

TABLE III. Results for self-avoiding walks on a square lattice, bounded in a box of size $(2L+1)\times(2L+1)$. For details see the caption of Table II.

b	m^*	S_{EV}^{A}	S_{EV}^{M}(IS)	$S_{EV}^{M}(A)$	Acceptance rate	Number of accepted walks
			$N=49,\ L=10$			
1	0.86	0.0967(1)	0.1478(8)	0.149(3)	0.11(1)	1380
4	1.03	0.140 47(2)	0.1584(7)	0.159(2)	0.36(2)	4600
7	1.04	0.149 39(2)	0.159 42(8)	0.1600(2)	0.50(1)	6390
DMC		0.1580(1)	0.1580(1)	0.1580(1)		
			$N=59,\ L=14$			
1	0.84	0.0848(1)	0.130(3)	0.131(4)	0.11(2)	1400
4	1.01	0.121 55(2)	0.1353(1)	0.1369(5)	0.38(1)	4860
7	1.07	0.127 80(2)	0.1358(2)	0.1376(5)	0.49(1)	6330
DMC		0.1346(1)	0.1346(1)	0.1346(1)		

the entropy also from the asymptotically exact expression [Eq. (28)] (these results are denoted DMC in the tables). For the unbounded chains we also provide the series expansion estimates for the entropy obtained from the very accurate formula derived by Martin *et al.*[28] and Watts.[29] In order to determine the optimal parameter m^* the program calculates at each step k of SAW i, for each value of b, the values of the transition probability $p_k(v_k,b,m)$ [Eq. (I22)] for ten different values of m (see details in I). This leads to ten different results for $S_{\rm EV}^A$ and $S_{\rm EV}^M$, where m^* is the value which minimizes $S_{\rm EV}^A$. The application of the generalized Monte Carlo procedure of Schmidt[19] is described in detail in Sec. II E of I. Approximately six hours are required on the IBM 3081D computer to perform the entire calculation for $N=79$ and $W_N \sim 12\,000$. It should be pointed out that the introduction of the mean-field parameter does not increase computer time significantly (see discussion in I).

Let us first discuss the results for the unbounded chains (Table II). As expected, the results for $S_{\rm EV}^A(b,m^*)$ for a given N significantly improve as b increases and they always underestimate the DMC and the series expansion values, which are considered here to be exact. [A discussion about the effect of m on the results for $S_{\rm EV}^A$ and $S_{\rm EV}^M$ appears in Ref. 16.] For the relatively short SAW's studied, the deviation of the results for our best approximation $S_{\rm EV}^A(7,m^*)$ from the DMC values is relatively small, increasing from 0.6% for $N=49$ to 1.14% for $N=79$. However, one would expect the deviation to increase to several percent when chain length N increases to several hundred steps, which is unsatisfactory. On the other hand, the results for $S_{\rm EV}^M$(IS) for $b=7$ are significantly more accurate; they are equal, within a statistical error of less than 0.1%, to the corresponding DMC values. The results for $S_{\rm EV}^M$(A) show similar accuracy except for some cases ($b=1$ and 4), where a significantly large statistical error is observed. (This stems probably from the fact that the accepted SAW's are obtained in a statistical procedure.) It should be pointed out that for $S_{\rm EV}^M$(IS) and $S_{\rm EV}^M$(A), the difference between the results for $b=1$ and 7 is not larger than 6%, whereas for $S_{\rm EV}^A$ it is $\sim 26\%$. This demonstrates that $S_{\rm EV}^M$ is relatively accurate even for small values of b, which might be important in systems with many degrees of freedom, where only small values of b are feasible. The results for the acceptance rate behave as expected. They increase monotonically with improving the approximation, i.e., increasing b/N. Therefore, this is another example (see also Refs. 19 and 30 and the results for self-attracting random walks in I) which demonstrates that the acceptance rate constitutes a measure of the extent of bias in a sample, when b/N increases $P_i(b,m^*) \rightarrow P_i$ and the acceptance rate correspondingly increases.

Confining the chain within the walls of a $(2L+1)\times(2L+1)$ box imposes additional long-range restrictions, which significantly increase the value of the entropy $S_{\rm EV}$. The results for the entropy in Table III, always improve as b is increased. However, the results for $S_{\rm EV}^A$ are less accurate in Table III than in Table II. For $b=7$ and $N=49$ and 59 these results underestimate the values obtained with the DMC procedure by $\sim 5\%$.

The results for $S_{\rm EV}^M$(A) are always slightly larger than those for $S_{\rm EV}^M$(IS). For $b=7$ the results for $S_{\rm EV}^M$(IS) deviate from the DMC values by less than 0.9% whereas those for $S_{\rm EV}^M$(A) deviate by $\sim 1.2\%$ and 2.2% for $N=49$ and 59, respectively. Also, in most cases the statistical error of $S_{\rm EV}^M$(A) is larger than that of $S_{\rm EV}^M$(IS). The values of the acceptance rate (and hence the number of accepted SAW's) are significantly lower than the corresponding values in Table II, which reflects the fact that $P_i'(b,m^*)$ of the restricted walks is more biased. As in Table II the acceptance rate increases monotonically with improving the approximation, i.e., increasing b.

We summarize as follows. Our method for estimating the free energy uses the concepts of the scanning method to define two free-energy functionals F^A and F^B. It is proved that $F^A \leq F$ and $F^B \leq F^A$ where F is the true free energy. The arithmetic average of F^A and F^B, F^M, is therefore expected to constitute a better approximation for F than either F^A or F^B. In this work the theory is first described for self-interacting chains without EV, where estimation of F^B requires the application of Schmidt's procedure. We analyze results for self-attracting random walks obtained in I and conclude that F^M is 1 order of magnitude more accurate (the accuracy is better than 0.3%) than both F^A and F^B. When the excluded volume interaction is also included F^B can be estimated by both Schmidt's procedure [F^B(A)] and by importance sampling [F^B(IS)]; however, the Schmidt procedure, in contrast to importance sampling, enables one to estimate the statistical error of both F^B and S^B. We test the accuracy of these two procedures for SAW's on a square lattice and find that the entropy S^B(IS) is slightly more accurate than S^B(A). These calculations show that for SAW's (as for other systems studied before) the acceptance rate constitutes a measure of the extent of bias; it increases monotonically as the bias decreases. Finally, we would like to state that in our opinion the method has now reached the stage where it can be applied to more-complex lattice models[31] as well as to continuum models of macromolecules, such as polypeptides.

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