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LETTER TO THE EDITOR

A new method for simulation of real chains: scanning future steps

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Abstract. A new method for simulating real polymer chains is developed and applied to self-avoiding walks (SAWs) of length 49–599 on a three-choice square lattice. Very good results for the entropy are obtained which deviate from the series expansion estimates by 0.1–2%. We also discuss how to extend the method to models of polymer chains with both excluded volume and finite interactions (attractive or repulsive). Our method is expected to be more efficient than other simulation methods for treating self-interacting SAWs and chains which are subject to various lattice constraints.

In this letter we describe a new computer simulation method for real polymer chains and apply it preliminarily to self-avoiding walks (SAWs) (chains with excluded volume (EV)) on a three-choice square lattice. We also discuss how to extend the method to polymer chains with both EV and finite interactions (attractive or repulsive). The method is based on the concepts of a stochastic process described recently for the square Ising lattice (Meirovitch 1982a). These concepts have very recently been used to develop a technique for estimating the entropy of macromolecules with computer simulation (Meirovitch 1982b).

SAWs can be generated on a lattice by direct Monte Carlo (Wall *et al* 1954, 1963) which is an exact but extremely inefficient procedure, due to 'sample attrition' which can be characterised by the expression:

$$W_N/W_0 \cong \exp(-\lambda N) \qquad \text{for large } N. \tag{1}$$

W_N is the number of SAWs of N steps generated in the process out of W_0, the number of walks started, and λ is the attrition constant. In order to enrich samples of long SAWs, several methods have been suggested (Wall *et al* 1963, Rosenbluth and Rosenbluth 1955, Verdier and Stockmayer 1962), where the most efficient is the dimerisation method (Alexandrowicz 1969). In the present work we develop a method which reduces sample attrition considerably by taking into account, in each step of chain construction, the possible future steps. We expect the procedure to be much more efficient then the above mentioned methods for treating self-interacting SAWs (McCrackin *et al* 1973) or chains which are subject to boundary constraints or other lattice restrictions (Kremer 1981).

Let us first describe an *exact* procedure for generating SAWs with equal probability. Consider a lattice of any dimensionality with coordination number q, and let us construct a SAW which starts from the origin of the coordinate system. The first bond (step) is determined in one of q directions with equal probability $1/q$. In the next

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steps of the process ($k>1$), the probability to select a direction ν ($\nu=1,\ldots q$) out of $q-1$ allowed ones is not constant $1/(q-1)$, as with the direct Monte Carlo procedure (Wall *et al* 1954), but 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 $\nu_1,\ldots,\nu_{k-1}$ have already been determined and we want to specify ν_k. The *exact* transition probability $p_k(\nu|\nu_1,\ldots,\nu_{k-1})$, for selecting a direction ν should take into account all of the possible *partial* SAWs of $N-k+1$ bonds, which can be obtained in future steps of the process (steps $k,\ldots,N$). Those as yet undetermined partial SAWs should be distinguished from the $k-1$ bonds already fixed and therefore we call them the future SAWs. One can calculate $M_k^\nu(\nu_1,\ldots,\nu_{k-1})$, the number of future SAWs starting with a direction ν at step k (for a given set of $\nu_1,\ldots,\nu_{k-1}$), and define the transition probability for ν

$$p_k(\nu|\nu_1,\ldots,\nu_{k-1})=M_k^\nu(\nu_1,\ldots,\nu_{k-1})/\sum_\nu M_k^\nu(\nu_1,\ldots,\nu_{k-1}). \tag{2}$$

ν_k is selected by a lottery according to the p_k's and the process continues. Once a SAW i of N bonds has been constructed, one knows its construction probability P_i, which is the product of the N sequential transition probabilities with which the directions $\nu_1,\ldots,\nu_N$ have been chosen

$$P_i=q^{-1}\prod_{k=2}^{N}p_k(\nu_k|\nu_1,\ldots,\nu_{k-1}). \tag{3}$$

At each step of a particular construction *all* the possible future SAWs are taken into account with equal probability. Furthermore, a construction cannot fail (ν_k which might lead to a failure is associated with $M_k^\nu=0$ which means zero transition probability). Hence, for all i, $P_i=C_N^{-1}$ (where C_N is the total number of SAWs of length N) which means that the entropy S has zero fluctuations (Meirovitch and Alexandrowicz 1976),

$$S=k_B\log C_N \tag{4}$$

where k_B is the Boltzmann constant. We shall also be interested in S_{EV}, the entropy due to the EV effect

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

where S_I is the entropy of an ideal chain (without EV) of length N. Obviously, this exact construction procedure is impractical for large N and we therefore suggest approximating it by defining, in the same manner as equation (2), transition probabilities $p_k(\nu|\nu_1,\ldots,\nu_{k-1},b)$ based on future SAWs consisting only of a few bonds b, rather than of $N-k+1$ (strictly speaking the length of a future SAW is $b'=\min(b,N-k+1)$). In this case, a probability $P_i(b)$ can be defined for SAW i:

$$P_i(b)=q^{-1}\prod_{k=2}^{N}p_k(\nu_k|\nu_1,\ldots,\nu_{k-1},b). \tag{6}$$

However, it should be pointed out that, in contrast to P_i (equation (3)), $P_i(b)$ depends on i since not all future SAWs are taken into account for their entire length. For that reason not every SAW attempted with the approximation procedure can successfully be completed, and hence $P_i(b)$ is not normalised in the ensemble of all SAWs, i.e.,

$$A=\sum_{\text{all SAWs}}P_i(b)<1. \tag{7}$$

The normalised probability $P_i'(b)$ is

$$P_i'(b) = P_i(b)/A. \tag{8}$$

It is convenient to express the statistical properties of our approximate procedure using the approximate entropy functions $S'(b)$, and $S'_{EV}(b)$

$$S'(b) = -k_B \sum_i P_i'(b) \log P_i'(b) \tag{9}$$

$$S'_{EV}(b) = S_I - S'(b). \tag{10}$$

Obviously, $S'(b)$ is never larger than the true entropy S (equation (4)) and therefore $S'_{EV}(b) \geq S_{EV}$. Also, both $S'(b)$ and $S'_{EV}(b)$ are expected to approach the true values monotonically with improving the approximation, i.e. increasing b. $S'_{EV}(b) - S_{EV}$ constitutes, therefore, a measure for the bias due to employment of approximate probabilities $P_i'(b)$ instead of the exact P_i. Another measure of this bias is the standard deviation of $S'(b)$, $\Delta S'(b)$ which is expected to decrease monotonically to zero with increasing b (Meirovitch and Alexandrowicz 1976). This bias can be removed by dividing each microscopic quantity obtained in the simulation by $P_i(b)$ (equation (6)); in this case the entropy S_{EV}, for example, is estimated by $\bar{S}_{EV}(b)$

$$\bar{S}_{EV}(b) = S_I - k_B \log\left(n^{-1} \sum_{t=1}^{n} 1/P_{i(t)}(b)\right) \tag{11}$$

where $i(t)$ is SAW i sampled at time t of the process and n is the sample size. This procedure was first suggested by Rosenbluth and Rosenbluth who applied it to SAWs using our lowest approximation $b = 1$ (Rosenbluth and Rosenbluth 1955); more recently this method (with $b = 1$) was extended to self-interacting SAWs (Mazur and McCrackin 1968, McCrackin *et al* 1973, Mazur *et al* 1973). It should be pointed out, however, that while the method is exact for an infinite sample (for any value of b), the results obtained from a finite sample can still be biased, due to the occurrence of an improbable fluctuation which dominates the summation (equation (11)) (see McCrackin 1972). Therefore, in order to increase accuracy, either the sample size should be increased or the fluctuation in entropy $\Delta S'(b)$ should be decreased by increasing b.

Since the essential contribution to sample attrition comes from the short loops, one would expect to obtain a significant decrease in λ (equation (1)) already by using small values of b. Our method is also expected to be useful for generating chains with EV as well as finite interactions. In this case, however, for each step k of the process, one has to calculate the energy $E_{l(\nu)}$ of every future SAW l starting in direction ν. $E_{l(\nu)}$ takes into account the interaction energy between future steps of l among themselves and the interaction energy between future steps of l and the $k-1$ past steps. $M_k^{\nu}(b)$ is then defined by Boltzmann factors

$$M_k^{\nu}(b) = \sum_{l(\nu)} \exp(-E_{l(\nu)}/k_B T) \tag{12}$$

where T is the absolute temperature. The transition probabilities are defined with the help of equation (2). It should be pointed out that with this procedure, the intra-chain interactions are taken into account in the process of construction and therefore, for self-interacting SAWs, one would expect this method to be more efficient than other simulation methods (Wall *et al* 1963, Alexandrowicz 1969) which consider only the chain self-avoidance. For similar reasons, we also expect our method to be

more suitable than the methods mentioned above for treating chains which are subject to various lattice restrictions (Kremer 1981, McCrackin 1966).

Confining ourselves at present to SAWs with EV alone, we have generated SAWs of length $N = 49, 99, 199, 399$ and 599 on a three-choice square lattice for five values of b; $b = 1, 2, 4, 6$ and 8. The chain is generated step by step where at each step all the future SAWs of length b are generated by the computer, the transition probabilities $P_k(\nu|\nu_1, \ldots, \nu_{k-1}, b)$ (equations (2) and (6)) are calculated and a direction ν is then selected by a Monte Carlo lottery. The quantities $S'_{\mathrm{EV}}(b)$ and $\Delta S'(b)$ are estimated by $\bar{S}'_{\mathrm{EV}}(b)$ and $\overline{\Delta S'}(b)$ respectively,

$$\bar{S}'_{\mathrm{EV}}(b) = S_{\mathrm{I}} + n^{-1} k_{\mathrm{B}} \sum_{t=1}^{n} \log P'_{i(t)}(b) \tag{13}$$

$$\overline{\Delta S'}(b) = \left(n^{-1} \sum_{t=1}^{n} [\bar{S}'_{\mathrm{EV}}(b) - S_{\mathrm{I}} - k_{\mathrm{B}} \log P'_{i(t)}(b)]^2 \right)^{1/2}. \tag{14}$$

The results for $\bar{S}'_{\mathrm{EV}}(b)$, $\overline{\Delta S'}(b)$ and $\bar{S}_{\mathrm{EV}}(b)$ (equation (11)) appear in table 1. In these calculations the normalisation factor A for $P'_i(b)$ (equation (8)) has been estimated by the ratio $A \simeq W_N / W_0$ ($W_N = n$). For comparison we also present in the table results for S_{EV} obtained with the asymptotic formula for C_N

$$C_N = C_0 N^{\gamma - 1} \mu^N \tag{15}$$

and equations (4) and (5). In this calculation the best series expansion estimates for C_0, γ and μ (equation (15)) are taken from McKenzie (1976).

The efficiency of our method in generating SAWs is expressed by the attrition constant λ calculated with equation (1) from the results for W_0 and W_N. Obviously, increasing b should lead to a decrease in λ but also to an exponential increase ($\sim (q-1)^b$) in the computer time required to generate the future SAWs. We therefore also provide in the table the average computer time required for generating 1000 SAWs, which takes into account these two opposing effects.

The sample size is relatively small and ranges from 500 ($b = 8$, $n = 399$) to 10^4. Only for $N = 49$, $b = 1$ and $b = 2$ is a relatively large sample ($n \sim 10^5$) used. For $N = 49$, $b = 1$ the result for $\bar{S}_{\mathrm{EV}}$ deviates by $\sim 10\%$ from the series expansion estimate; this deviation decreases dramatically with increasing b, down to $\sim 0.1\%$ for $b = 8$. The same behaviour is also observed for the other values of N but, as expected, the accuracy of the best results decreases with increasing N; however, even for the larger chains the results are very good. Their deviation from the series expansion estimates is less than 1% for $N = 399$, $b = 8$ and about 2% for $N = 599$, $b = 6$. In order to examine the effect of sample size on the bias we have employed for $N = 49$, $b = 1$ and $b = 2$ relatively large samples of $n \sim 10^5$. However, the results for $\bar{S}_{\mathrm{EV}}$ did not improve in the range $n = 10^4$ to 10^5 but rather fluctuated slightly around the values appearing in the table; this indicates that it is more efficient to decrease the bias by increasing b than by increasing sample size n. The results for $\bar{S}'_{\mathrm{EV}}(b)$ always overestimate the correct values (see discussion in previous section), and for all N they improve significantly with increasing b. However, the best values for $\bar{S}'_{\mathrm{EV}}(b)$ deviate by 1–12% from the series expansion estimates, which is a deviation about an order of magnitude larger than that obtained for $\bar{S}_{\mathrm{EV}}(b)$. As is also expected, for each N, $\overline{\Delta S'}(b)$ decreases with increasing b.

Table 1. Results for the entropy $\bar{S}_{EV}(b)$ (equation (11)) and $\bar{S}'_{EV}(b)$ (equations (9) and (13)) obtained for chains of length N and future SAWs of length b. $\overline{\Delta S'}(b)$ is the calculated fluctuation of $S'_{EV}(b)$ obtained with equation (14) and λ is the attrition constant calculated with equation (1). Series expansion estimates for the entropy have been obtained with equations (4), (5) and (15) using the best parameters from McKenzie (1976). The estimated statistical error is denoted by parentheses, e.g., $0.1026(2) = 0.1026 \pm 0.0002$. For $\overline{\Delta S'}(b)$ and λ the results are rounded off to two significant figures. t is the average time (in seconds) required to generate 1000 SAWs on the Golem B computer.

N	b	$\bar{S}_{EV}(b)/Nk_B$	$\bar{S}'_{EV}(b)/Nk_B$	$\overline{\Delta S'}(b)/Nk_B$	λ	t seconds
49	1	0.0927 (3)	0.1444 (3)	0.048	0.011	13
	2	0.09953 (5)	0.12037 (5)	0.032	0.0040	18
	4	0.1026 (2)	0.1088 (2)	0.019	0.00077	84
	6	0.1033 (1)	0.1053 (1)	0.011	0.00012	550
	8	0.1035 (1)	0.1044 (1)	0.0070	0.000020	750
	series	0.1035	0.1035			
99	1	0.100 (1)	0.163 (1)	0.038	0.015	48
	2	0.1067 (3)	0.1373 (3)	0.027	0.0070	50
	4	0.1115 (1)	0.1240 (1)	0.021	0.0020	190
	6	0.1129 (1)	0.1197 (1)	0.016	0.00075	1220
	8	0.1134 (1)	0.1174 (1)	0.014	0.00030	8240
	series	0.1137	0.1137			
199	1	0.096 (4)	0.174 (1)	0.029	0.018	460
	2	0.110 (1)	0.1483 (2)	0.023	0.0093	220
	4	0.1164(2)	0.1356 (1)	0.019	0.0035	520
	6	0.1183 (2)	0.1302 (2)	0.017	0.0017	2930
	8	0.1195 (3)	0.1272 (3)	0.014	0.00086	18300
	series	0.1199	0.1199			
399	2	0.111 (3)	0.155 (1)	0.018	0.011	3260
	4	0.1192 (2)	0.1422 (2)	0.016	0.0047	2370
	6	0.1210 (2)	0.1370 (5)	0.015	0.0025	8800
	8	0.1225 (3)	0.1344 (3)	0.013	0.0015	50000
	series	0.1236	0.1236			
599	4	0.120 (1)	0.1450 (2)	0.014	0.0053	10000
	6	0.1225 (3)	0.1398 (3)	0.012	0.0030	21000
	series	0.1250	0.1250			

For each value of N we observe in the table a significant decrease in λ with increasing b: the ratio $\lambda(b=1)/\lambda(b=8)$ is ~ 550 for $N=49$ and decreases to ~ 21 for $N=199$. For each b, λ increases monotonically in going from $N=49$ to $N=599$, which is due to the larger loops which can be formed in the longer chains but not in the shorter ones. It should be noted that the value of λ for $N=599$, $b=6$ is about 40 times smaller than the value $\lambda=0.128$ obtained for the direct Monte Carlo procedure for the infinite chain (Wall *et al* 1963). This decrease in λ should be compared to the significantly smaller decrease in λ (about 3 times) obtained with the method of strides (Wall *et al* 1957). The calculations have been carried out on the Golem B computer of the Weizmann Institute, which is ~ 3 times slower than the IBM 370/165 (using the Q compiler). In the last column of the table we present for each pair of N and b the average computer time t required for generating 1000 SAWs.

For the shorter chains (where only short loops can occur) one would expect the calculations with $b = 1$ to be the most efficient since future SAWs of size 1 are already sufficient to avoid most of the chain self-intersections. However, for longer chains, sample attrition with $b = 1$ is significant and therefore, in order to increase efficiency, larger values of b should be employed. Indeed, for $N = 49$, chain generation with $b = 1$ is the most efficient (13 seconds); for $N = 99$, $b = 1$ and $b = 2$ have a comparable efficiency whereas for $N = 199$ and $N = 399$, larger values of b, $b = 2$ and $b = 4$ respectively, lead to the most efficient chain generation. It should also be pointed out that for $N = 399$, $b = 1$ and $N = 599$, $b = 1$ and 2 chain generation has been found to be highly inefficient and the results for $\bar{S}_{EV}(b)$ did not converge. We therefore do not present them in the table.

In summary, we have developed a method for generating real chains, based on scanning future steps, and have applied it preliminarily to SAWs on a three-choice square lattice. The new procedure enables one to reduce systematically the bias in the results for the entropy by increasing b, the length of the future SAWs. Our lowest approximation ($b = 1$), which is identical to the method suggested by Rosenbluth and Rosenbluth, provides relatively poor results for the entropy which deviate from the series expansion estimates by 10–16%. We point out this fact in view of the extensive employment of this procedure (with $b = 1$) for SAWs, self-interacting SAWs (Mazur and McCrackin 1968, McCrackin 1972, McCrackin *et al* 1973, Mazur *et al* 1973) and other systems (McCrackin 1966).

Our best approximations ($b = 8$ and $b = 6$ for $N = 599$) lead to very good estimates for the entropy (with accuracy of 0.1–2%) and to a significant decrease in sample attrition. It should be pointed out that at this stage our procedure is still significantly less efficient than the dimerisation method, where SAWs of $N \sim 8000$ have been generated (Alexandowicz 1969). However, we expect our method to be more efficient than other methods (Wall *et al* 1963, Alexandrowicz 1969) for treating self-interacting SAWs and chains which are subject to boundary restrictions or other lattice constraints (Kremer 1981, McCrackin 1966). At present we are also studying (for significantly larger samples) geometrical properties such as the end-to-end distance, the radius of gyration, etc, for chains on both square and simple cubic lattices.

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References

Alexandrowicz Z 1969 *J. Chem. Phys.* **51** 561–5
—— 1971 *J. Chem. Phys.* **55** 2765–79
Kremer K 1981 *Z. Phys.* B **45** 149–52
Mazur J and McCrackin F L 1968 *J. Chem. Phys.* **49** 648–65
Mazur J, Guttman C M and McCrackin F L 1973 *Macromolecules* **6** 872–4
McCrackin F L 1966 *J. Chem. Phys.* **47** 1980–6
—— 1972 *J. Res. NBS* (Math. Sci.) Nos 3 and 4 193–200
McCrackin F L, Mazur J and Guttman C M 1973 *Macromolecules* **6** 859–71
McKenzie D S 1976 *Phys. Rep.* **27C** 37–88
Meirovitch H 1982a *J. Phys. A: Math. Gen.* **15** 2063–75
—— 1982b *Macromolecules*
Meirovitch H and Alexandrowicz Z 1976 *J. Stat. Phys.* **15** 123–7
—— 1977 *J. Stat. Phys.* **16** 121–38

Rosenbluth M N and Rosenbluth A W 1955 *J. Chem. Phys.* **23** 356–9
Verdier P H and Stockmayer W N 1962 *J. Chem. Phys.* **36** 227–35
Wall F T, Hiller L A Jr and Wheeler D J 1954 *J. Chem. Phys.* **22** 1036–41
Wall F T, Rubin R J and Isaacson L M 1957 *J. Chem. Phys.* **27** 186–8
Wall F T, Windwer S and Gans P J 1963 in *Methods of Computational Physics* vol I (New York: Academic) pp 217–43