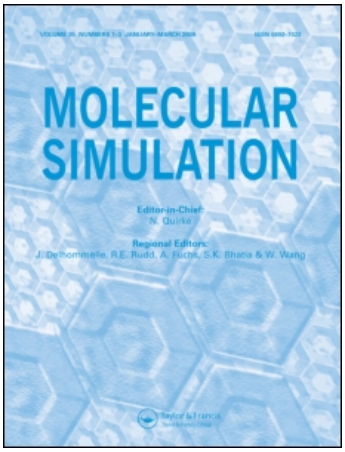

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Monte Carlo Simulation of Tetrahedral Chains II: Properties of "First Self-avoiding Walks" and their Usability as Starting Configurations for Dynamic Relaxation Mechanisms

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MONTE CARLO SIMULATION OF TETRAHEDRAL CHAINS II: PROPERTIES OF "FIRST SELF-AVOIDING WALKS" AND THEIR USABILITY AS STARTING CONFIGURATIONS FOR DYNAMIC RELAXATION MECHANISMS

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Very long model chains may be produced in a highly efficient manner using dynamic Monte Carlo methods. As any dynamic Monte Carlo procedure transforms one chain into another one, some starting configuration is necessary. This might be an unbiased self-avoiding walk (SAW) obtained by any static method, or an arbitrary configuration, e.g. a rodlike chain, equilibrated by a sufficiently large number of relaxations, the corresponding chains not being used for data sampling. An alternative method is to start with a non reversal random walk (NRRW) and to apply a dynamic Monte Carlo procedure under the constraint that the new chain must have a smaller (or at least an equal) number of double occupancies than the old one. The properties of those chains that are free of overlaps for the first time (FSAWs) are strongly dependent on the relaxation mechanism chosen. Whereas FSAWs obtained by local motions are very similar to the (initial) NRRWs on a macroscopic scale, pivot algorithms and reptation yield configurations with properties comparable to unbiased self-avoiding chains. When reptation is used and the relaxation is continued until each bond of the initial NRRW is replaced by a new bond (if the chain is self-avoiding earlier) no further equilibration is necessary prior to data sampling.

KEY WORDS: Dynamic Monte Carlo, random walks, first self-avoiding walks

INTRODUCTION

In very dilute solutions, the average distances between dissolved molecules are rather large. Therefore, the intermolecular interactions may be neglected and the properties of single (isolated) molecules should suffice to describe such systems. Depending on the quality of the solvent, the dimensions of **macromolecules** are more or less expanded. This is reflected in the macroscopic structure represented by global dimensions, e.g. the mean square radius of gyration $\langle s^2 \rangle$ or the mean square end-to-end distance $\langle h^2 \rangle$, and influences also the microscopic structure which may be represented by local properties such as the average fraction of trans units $\langle T \rangle$. Due to the regular succession of chain-segments in space and due to the large number of internal degrees of freedom in chain molecules, the special form of intramolecular interactions is of secondary interest only. In many cases, therefore, it is not necessary to take into consideration the details of the local design, the arrangement of the skeleton segments of the molecule being sufficient to describe the configuration. In those cases it is favourable to substitute a real polymer by a model chain and to simulate the system

by Molecular Dynamics or Monte Carlo methods. In the latter case both, model chains embedded in some lattice and off-lattice chains are widely in use. Due to economic reasons with respect to computer time lattice chains often are preferred to off-lattice chains. Usually, they consist of segments covering lattice points under the restriction that each lattice point may be occupied only once in order to comply to the excluded volume effect exercised by each individual segment (self-avoiding walks SAWs). Monte Carlo algorithms for generating such chains — a comprehensive review can be found in Reference [1] — may be grouped into static and dynamic methods. Dynamic Monte Carlo methods, especially the pivot algorithm [2,3] have proved most valuable for constructing very long model chains [4,5]. Each dynamic algorithm transfers one chain into another chain. Therefore, an initial configuration is necessary, e.g. an unbiased self-avoiding walk obtained by an appropriate static method. This might be a simple step-by-step procedure [6] for short chains. However, because the number of self-avoiding walks decreases exponentially with chain length, more sophisticated methods have to be used for longer chains. A very popular approach is Alexandrowicz dimerization method [7], where a chain is obtained from two chains of half length, the acceptance fraction decreasing with some (small) power of chain length only. Alternatively, one can start with an arbitrary configuration, e.g. a rodlike chain (all-trans configuration), and discard a "sufficiently large" number of initial relaxations.

In this paper an alternative approach is examined. Instead of starting with an arbitrary **self-avoiding** walk (SAW) a non reversal **random** walk (NRRW) — this is a random walk for which overlaps due to ring formation are allowed, but backfolding on itself is forbidden — is chosen. Then, relaxations are performed under the constraint that the number of overlaps of the new chain must be less than or equal to the number of double occupancies of the old one. This algorithm was used by Kremer for dense systems (in order to overcome the problem of filling the lattice with the desired number of chains) using local (3–4 bond) motions [8]. Here, the properties of the first configuration which is free of overlaps ("first self-avoiding walk", FSAW) are calculated for various dynamic algorithms and are compared to the average properties of true, i.e. unbiased, self-avoiding walks (SAWs). The reason for this procedure is to find an algorithm which produces FSAWs which are as similar to SAWs as possible, expecting to attain an equilibrium configuration in a more efficient (less computer-time consuming) way than with the methods hitherto used.

SIMULATION METHOD

General Considerations

The coordinates of the segments — covering N tetrahedral lattice points (numbered from 1 to N and connected by $n = (N - 1)$ bonds) are stored. In addition, the directions of the bonds (numbered from $i = 1$ to $i = n$, bond i joining segment i and segment $(i + 1)$ the bond length being $3^{1/2}$ lattice units) are stored in form of code numbers c_i. In the tetrahedral lattice, having a coordination number of 4, actually 8 different bond-vectors are involved, but they fall into two groups [6]: For bonds with an odd bond number the codes 0,1,2 and 3 correspond to the bond vectors $(+1,+1,+1)$, $(-1,+1,-1)$, $(-1,-1,+1)$ and $(+1,-1,-1)$ and for bonds with even bond numbers to the respective opposite directions $(-1,-1,-1)$, $(+1,-1,+1)$, $(+1,+1,-1)$ and $(-1,+1,+1)$. Inspection of the sequence of code numbers immediately determines the local structure of the chain: A three-bond unit

may be either a trans conformation (t), the code of the first bond of the unit being equal to the code of the third one, or one of two gauche conformations (+) or (−) where all three codes are different numbers. Two equal numbers in sequence do not occur because backfolding is not allowed in any case. For a four-bond unit nine different conformations are possible which may be arranged into 4 groups. (1) A sequence (tt) with a squared end-to-end distance $h^2 = 32$, (2) ($t+$), ($t-$), ($+t$), ($-t$) with $h^2 = 24$, (3) ($+-$) and ($-+$) with $h^2 = 16$ and (4) ($++$) and ($--$) with $h^2 = 8$. After making the arbitrary choice that some sequence (e.g. $0-1-2$) should correspond to gauche$^+$ (+) and, therefore, $0-1-3$ to gauche$^-$ (−), inspection of the sequences of code numbers leading to conformations of group (3) and (4) allows a definite assignment to (+) or (−) for all gauche sequences. Thus, a lookup table $\zeta(c_i, c_{i+1}, c_{i+2})$ can be established which yields a specific code for a given three-bond unit. This is very helpful for relaxation using local motions (see below) as well as for determining the local structure of the chain. Each k-bond unit can be split into $k-2$ three-bond units and, therefore, assigned to one of 3^{k-2} possible configurations by an appropriate linear combination ξ of the structure codes $\zeta(c_i, c_{i+1}, c_{i+2})$ specifying the conformation of the three-bond units

$$\xi = \sum_{i=m}^{m+k-3} \zeta(c_i, c_{i+1}, c_{i+2}) \cdot 3^{(i-m)}$$

where a $k-$bond unit starting at segment m is analyzed and $\zeta(c_i, c_{i+1}, c_{i+2}) = 0$ for trans, 1 for gauche$^+$ (+) and 2 for gauche$^-$ (−). At the end of the simulation run symmetric sequences are combined.

Non Reversal Random Walks and Self-Avoiding Walks

As a basis of comparison properties of large ensembles of non reversal random walks and self-avoiding walks of length $N = 50$, 500 and 1000 segments were generated. The non reversal random walks (NRRWs) were prepared by use of a simple step-by-step procedure: Starting with the first segment fixed in the origin and the second segment being one of the four neighbours of the first one, further segments are chosen from the particular remaining **three** neighbours — thus preventing the chain from immediately backfolding on itself — until the desired chain length is reached. Self-avoiding walks (SAWs) may be built-up in an analogous way, but — contrary to NRRWs — the whole chain has to be discarded if an overlap occurs. As the number of trials leading to self-avoiding chains decreases exponentially with chain length (e.g. approximately 23% of trials are successful for $N = 50$, but only 3% for $N = 100$) this method was only used for the shortest chains examined ($N = 50$). The longer chains ($N = 500$, 1000) were prepared by use of the pivot algorithm. With this method, a new chain is obtained by rotating one part of the chain around a randomly selected bond by $\pm 120°$ (in the tetrahedral lattice). If segments of the transformed subchain overlap with segments of the unmoved part, the new chain is rejected and the old one retained. The acceptance fraction f of this process decreases only slightly with chain length ($f \sim n^{-0.115}$) leading to still fairly high f-values for very long chains ($f = 0.64$, 0.59, and 0.45 for $N = 500$, 1000 and 10000, respectively) [5].

First Self-Avoiding Walks

Starting with a non reversal random walk, the chain was transformed by use of (1) local motions, i.e. three- and four-bond motions [9,10], (2) the pivot algorithm

[2,3,4,5] and (3) the reptation ("slithering snake") mechanism [11,12]. If the number of overlaps has increased due to the transformation, the new chain is discarded and a new trial performed; the mechanism corresponds to a Metropolis–Rosenbluth Monte Carlo process [13] defining intramolecular interactions on the basis of overlaps instead of contacts (sometimes called "soft potential" [14]) and using an interaction energy profile which is positive indefinite for vanishing segment-segment separation and zero otherwise.

First Self-Avoiding Walks by Local Motions

Except for movements of end-segments, in the tetrahedral lattice at least two segments (three bonds) are moved by one elementary motion, i.e. a gauche (+) conformation is transformed into a gauche (−) conformation or vice versa. During this process two bond vectors are exchanged, but no new bond vector is created (e.g. (1,3)-0-1-2-(1,3) ⇒ (1,3)-2-1-0-(1,3), the numbers in parentheses being allowed codes for the preceding and following bond of the unit). One-bond moves (e.g. (0)-1 ⇒ (0)-2 or (0)-3) and two-bond moves (e.g. (0)-1-2 ⇒ (0)-3-2, (0)-1-0 ⇒ (0)-2-0 or (0)-3-0) of chain ends create new bonds which may be shifted into the interior of the chain by further movements. Creation of new bond vectors may be enhanced by use of four-bond moves. There are two classes of four-bond moves available. The first one transforms a (+ −) (or (− +)) conformation into another one and may be realized by two successive three-bond moves (e.g. (1,3)−0−1−2−3−(0,2) ⇒ (1,3)-2-1-0-3-(0,2) ⇒ (1,3)-2-3-0-1-(0,2)). Thus, bond vectors are exchanged only. This mechanism is not used for relaxation. The second four-bond move transfers a (+ +) conformation into a (− −) conformation and vice versa, creating two new bond vectors (e.g.(1,2)-0-1-2-0-(1,2) ⇒ (1,2)-3-1-2-3-(1,2)). A three-bond move at the chain end may be realized as described above or may be regarded as a degenerated four-bond move changing the penpenultimate vector, thus creating a new bond vector (e.g. (1,2)-0-1-2 ⇒ (1,2)-3-1-2). Similarly, a one-bond move and two bond move may be regarded as a degenerated three-bond or four-bond move. Therefore, the chain is divided into $n+2$ "three"-bond units (c_1, c_1-c_2, c_1-c_2-c_3, c_2-c_3-c_4,...,c_{n-2}-c_{n-1}-c_n, c_{n-1}-c_n, c_n) and into $n+3$ "four"-bond units (c_1, c_1-c_2, c_1-c_2-c_3, c_1-c_2-c_3-c_4, c_2-c_3-c_4-c_5,...,c_{n-3}-c_{n-2}-c_{n-1}-c_n, c_{n-2}-c_{n-1}-c_n, c_{n-1}-c_n, c_n) including the degenerated cases. One of these $2n+5$ units is selected at random and the movement performed if the configuration of the unit fits the conditions specified above.

First Self-Avoiding Walks by Pivot-algorithm

The same algorithm was used as applied to the relaxation of self-avoiding walks. Clearly, in this case the trial is not rejected at any rate if (new) double occupancies occur. Due to the restriction stated above, the new chain is discarded only if the number of overlaps between the new and the unmoved part is larger than the number of overlaps between the old and the unmoved part.

First Self-Avoiding Walks by Reptation

The third algorithm used for preparing FSAWs was the reptation or "slithering snake" algorithm. The chain moves one lattice unit into one of three possible directions — the fourth one would lead to backfolding and, therefore, is not allowed

Table 1 Basic simulation data for $N = 50$. Mean square end-to-end distance $\langle h^2 \rangle$, mean square radius of gyration $\langle s^2 \rangle$, shape factors sf_i, average number of contacts $\langle$ NN $\rangle$ and the frequencies of 3-bond, 4-bond and 5-bond configurations of non reversal random walks (NRRW), self-avoiding walks (SAW), first self-avoiding walks by local motions ($FSAW_L$), by pivot algorithm ($FSAW_P$) and by reptation ($FSAW_R$) and of configurations obtained by reptation starting with a NRRW and replacing at least n bonds (SAW_R).

	NRRW	$FSAW_L$	$FSAW_P$	$FSAW_R$	SAW_R	*SAW*
$\langle h^2 \rangle$	289.586	297.153	374.929	356.355	415.839	409.198
$\langle s^2 \rangle$	47.829	49.126	59.163	61.101	64.123	64.148
sf_1	0.07185	0.07710	0.06539	0.06213	0.06284	0.06216
sf_2	0.19336	0.19834	0.18624	0.18255	0.18373	0.18264
sf_3	0.73479	0.72456	0.74837	0.75532	0.75343	0.75520
$\langle$ NN $\rangle$	13.22537	4.95910	3.18360	3.65900	2.63040	2.65351
$\langle T \rangle$	0.333318	0.352100	0.349030	0.351206	0.367587	0.367410
$\langle G \rangle$	0.666682	0.647900	0.650970	0.648794	0.632413	0.632590
$\langle TT \rangle$	0.111093	0.119857	0.115285	0.119813	0.126611	0.127035
$\langle TG \rangle$	0.444452	0.464735	0.468172	0.467163	0.482511	0.481907
$\langle Gg \rangle$	0.222211	0.226693	0.231604	0.223183	0.223002	0.222446
$\langle GG \rangle$	0.222244	0.188715	0.184939	0.189841	0.167876	0.168612
$\langle TTT \rangle$	0.037031	0.039249	0.038922	0.041742	0.045251	0.045150
$\langle TGT \rangle$	0.074091	0.078651	0.081209	0.083667	0.089720	0.089315
$\langle TTG \rangle$	0.148127	0.161371	0.152853	0.157887	0.162864	0.164239
$\langle GTg \rangle$	0.074077	0.073533	0.080498	0.079673	0.083596	0.082766
$\langle GTG \rangle$	0.074085	0.078200	0.077453	0.076378	0.076447	0.076437
$\langle TGg \rangle$	0.148127	0.160220	0.156193	0.156144	0.159113	0.159377
$\langle GgG \rangle$	0.074071	0.074093	0.084229	0.078333	0.081464	0.080687
$\langle TGG \rangle$	0.148141	0.147113	0.149664	0.146640	0.144273	0.144304
$\langle GGg \rangle$	0.148158	0.145687	0.138947	0.135091	0.123978	0.124140
$\langle GGG \rangle$	0.074092	0.041882	0.040031	0.044444	0.033293	0.033585

Table 2 Basic simulation data for $N = 500$. Mean square end-to-end distance $\langle h^2 \rangle$, mean square radius of gyration $\langle s^2 \rangle$, shape factors sf_i, average number of contacts $\langle$ NN $\rangle$ and the frequencies of 3-bond, 4-bond and 5-bond configurations of non reversal random walks (NRRW), self-avoiding walks (SAW), first self-avoiding walks by local motions ($FSAW_L$), by pivot algorithm ($FSAW_P$) and by reptation ($FSAW_R$), and of configurations obtained by reptation starting with a NRRW and replacing at least n bonds (SAW_R).

	NRRW	$FSAW_L$	$FSAW_P$	$FSAW_R$	SAW_R	*SAW*
$\langle h^2 \rangle$	2988.163	3043.655	6447.711	6156.304	6339.430	6430.284
$\langle s^2 \rangle$	497.595	504.701	1022.147	983.464	988.309	1021.709
sf_1	0.07616	0.08090	0.06425	0.06628	0.06642	0.06515
sf_2	0.19642	0.19927	0.18426	0.18675	0.18822	0.18552
sf_3	0.72742	0.71983	0.75149	0.74697	0.74537	0.74934
$\langle$ NN $\rangle$	233.19355	62.50160	32.58410	32.86410	31.38800	30.68393
$\langle T \rangle$	0.333339	0.366703	0.361153	0.368712	0.370656	0.371386
$\langle G \rangle$	0.666661	0.633297	0.638847	0.631288	0.629344	0.628614
$\langle TT \rangle$	0.111107	0.128617	0.122293	0.127733	0.128418	0.128956
$\langle TG \rangle$	0.444467	0.476293	0.477801	0.482543	0.484525	0.484977
$\langle Gg \rangle$	0.222192	0.220154	0.228298	0.221873	0.222117	0.221801
$\langle GG \rangle$	0.222234	0.174936	0.171608	0.167851	0.164941	0.164266
$\langle TTT \rangle$	0.037037	0.044324	0.042975	0.045721	0.046127	0.046453
$\langle TGT \rangle$	0.074085	0.085370	0.087337	0.090279	0.091139	0.091451
$\langle TTG \rangle$	0.148143	0.168633	0.158681	0.164252	0.164593	0.165056
$\langle GTg \rangle$	0.074083	0.077364	0.083539	0.083317	0.083899	0.083951
$\langle GTG \rangle$	0.074079	0.076502	0.076039	0.076008	0.076085	0.076043
$\langle TGg \rangle$	0.148126	0.159329	0.158472	0.158650	0.159206	0.159391
$\langle GgG \rangle$	0.074062	0.074947	0.084768	0.081051	0.081573	0.081451
$\langle TGG \rangle$	0.148171	0.146221	0.144689	0.143693	0.143057	0.142731
$\langle GGg \rangle$	0.148132	0.131097	0.128606	0.123175	0.121875	0.121315
$\langle GGG \rangle$	0.074082	0.036213	0.034895	0.033854	0.032444	0.032159

Table 3 Basic simulation data for $N = 1000$. Mean square end-to-end distances $\langle h^2 \rangle$, mean square radius of gyration $\langle s^2 \rangle$, shape factors sf_i, average number of contacts $\langle$ NN $\rangle$ and the frequencies of 3-bond, 4-bond and 5-bond configurations of non reversal random walks (NRRW), self-avoiding walks (SAW), first self-avoiding walks by local motions ($FSAW_L$), by pivot algorithm ($FSAW_P$) and by reptation ($FSAW_R$), and of configurations obtained by reptation starting with a NRRW and replacing at least n bonds (SAW_R).

	NRRW	$FSAW_L$	$FSAW_P$	$FSAW_R$	SAW_R	*SAW*
$\langle h^2 \rangle$	5992.204	5994.079	14985.144	14024.554	14230.086	14657.163
$\langle s^2 \rangle$	997.674	1006.794	2364.404	2227.618	2231.309	2330.497
sf_1	0.07646	0.08035	0.06424	0.06648	0.06735	0.06553
sf_2	0.19645	0.19830	0.18406	0.18785	0.18801	0.18568
sf_3	0.72709	0.72135	0.75170	0.74566	0.74464	0.74879
$\langle$ NN $\rangle$	499.50403	122.13070	64.66510	64.51770	63.23510	61.81532
$\langle T \rangle$	0.333349	0.368617	0.363290	0.369858	0.370866	0.371603
$\langle G \rangle$	0.666651	0.631383	0.636710	0.630142	0.629134	0.628397
$\langle TT \rangle$	0.111122	0.129228	0.123572	0.128114	0.128710	0.129107
$\langle TG \rangle$	0.444453	0.478841	0.479465	0.483776	0.484354	0.485050
$\langle Gg \rangle$	0.222209	0.219987	0.227558	0.222018	0.222100	0.221782
$\langle GG \rangle$	0.222216	0.171944	0.169405	0.166091	0.164836	0.164061
$\langle TTT \rangle$	0.037043	0.045059	0.043642	0.045998	0.046377	0.046566
$\langle TGT \rangle$	0.074083	0.087059	0.088323	0.090860	0.091100	0.091544
$\langle TTG \rangle$	0.148159	0.168364	0.159871	0.164341	0.164690	0.165102
$\langle GTg \rangle$	0.074071	0.078845	0.083898	0.083748	0.083838	0.084050
$\langle GTG \rangle$	0.074076	0.076412	0.075909	0.076060	0.076003	0.075944
$\langle TGg \rangle$	0.148141	0.159570	0.158910	0.159030	0.159148	0.159243
$\langle GgG \rangle$	0.074070	0.076097	0.084800	0.081376	0.081637	0.081631
$\langle TGG \rangle$	0.148147	0.145173	0.143951	0.143210	0.143014	0.142739
$\langle GGg \rangle$	0.148137	0.128198	0.126612	0.122340	0.121769	0.121048
$\langle GGG \rangle$	0.074074	0.035223	0.034086	0.033037	0.032423	0.032133

— along its own contour. It is some sort of a step-by-step procedure adding a segment to one end of a chain (arbitrarily designed as head) simultaneously removing the other end segment (tail) of the chain. The new chain is accepted, if the new segment does not violate the excluded volume condition. Otherwise the new chain is rejected, head and tail are interchanged and a new trial is performed.

RESULTS AND DISCUSSION

First of all, the macroscopic structure represented by global quantities and the average instantaneous shape of FSAWs, NRRWs and SAWs are compared. Then the number of nearest neighbour contacts between chain segments and the microscopic structure characterized by local quantities of the various model chains are examined. Finally, the efficiency of the use of FSAWs as starting configurations for dynamic Monte Carlo procedures is discussed.

The basic data obtained by the simulation are summarized in the Tables 1–3. For $N = 50$ (Table 1) $5 \cdot 10^6$ NRRWs and SAWs were generated in order to get highly accurate results for comparison. The statistical error (based on 95% confidence limits) is less than 0.1% for global and less than 0.02% for local quantities. For $N = 500$ (Table 2) and N = 1000 (Table 3) $1 \cdot 10^6$ NRRWs and $7.5 \cdot 10^6$ SAWs were prepared. Thus, the results of the longer chains are less accurate — notice that SAWs of length 500 to 1000 were generated by pivot algorithm, the integral correlation time being approximately $(5–10) \cdot n^{0.1}$ for global and $0.5 \cdot n^{1.1}$ for local quantities in tetrahedral lattice [5] — but the statistical error does not exceed 0.3% even in the worst case. With any algorithm used, 10000 FSAWs were generated. The statistical error is approximately 1%–1.5% for global quantities and one order of magnitude smaller for local ones.

Macroscopic Structure

The macroscopic structure of the chains may be represented by average global dimensions, e.g. the mean square end-to-end distance $\langle h^2 \rangle$ and the mean square radius of gyration $\langle s^2 \rangle$, h^2 being the squared length of the vector between the two end segments of the chain and s^2 being the average of the squared distances between the segments of the chain and its centre of gravity. The values of $\langle s^2 \rangle$ and $\langle h^2 \rangle$ of FSAWs obtained by local motions (marked by $FSAW_L$ in Tables 1–3) are very similar to those of NRRWs. The relative deviation of the data is less than 2.5%. Thus, it is expected that the dimensions of FSAWs by local motions should exhibit the same chain length dependence than ordinary random walks, i.e. their dimensions should increase proportionally with chain length n. Indeed, in a double logarithmic plot of $\langle h^2 \rangle$ or $\langle s^2 \rangle$ versus chain length n (see Figure 1, circles) no deviation of the data from straight lines can be detected by eye, the slope being 0.996 for $\langle h^2 \rangle$ and 1.000 for $\langle s^2 \rangle$.

On the other hand, both, FSAWs obtained by pivot algorithm and FSAWs generated by reptation (marked as $FSAW_P$ and $FSAW_R$ in Table 1–3) exhibit dimensions similar to those of SAWs, although different trends may be extracted from the Tables: Whereas the dimensions of FSAWs by pivot algorithm are smaller than those of SAWs for $N = 50$, coincide nearly perfectly for $N = 500$ and are larger for $N = 1000$, $\langle s^2 \rangle$ and $\langle h^2 \rangle$ of FSAWs by reptation are smaller than the dimensions

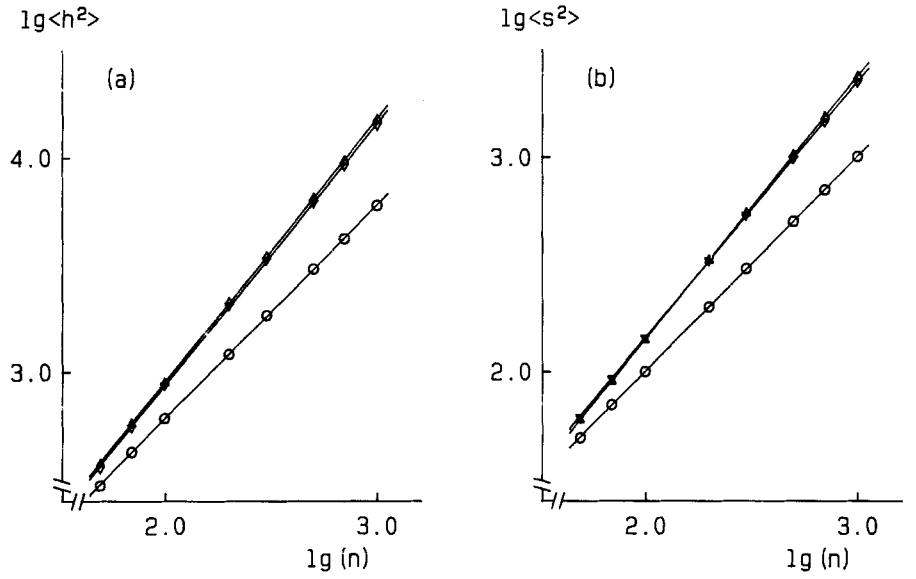

Figure 1 Double logarithmic plots of (a) mean square end-to-end distance $\langle h^2 \rangle$ and (b) mean square radius of gyration $\langle s^2 \rangle$ as a function of the number of bonds for first self-avoiding walks obtained by local motions (○), for first self-avoiding walks obtained by pivot algorithm (Δ) and for first self-avoiding walks obtained by reptation (∇).

of SAWs for all chain lengths examined. The effect of a chain length dependence of the deviations should be reflected in the power laws of $\langle h^2 \rangle$ and $\langle s^2 \rangle$. Long ago, Flory [15] calculated the chain length dependence of $\langle h^2 \rangle$ using a mean field theory and found a scaling relation $\langle h^2 \rangle \sim n^{\nu}$. More recent approaches yielded the same result in principal with different values for the exponent ν. From renormaliazation group theory [16] now a value $\nu = 1.176$ has been established which is slightly smaller than $\nu = 1.2$ predicted by Flory. Monte Carlo estimates from very long chains [4,5] are in the range 1.180-1.188. In Figure 1 double logarithmic plots of $\langle s^2 \rangle$ and $\langle h^2 \rangle$ as a function of n for FSAWs obtained by pivot algorithm (Δ) and by reptation (∇) are shown. The data nearly perfectly lie on straight lines. From linear regressions the exponents for $\langle h^2 \rangle$ and $\langle s^2 \rangle$ were estimated as 1.223 and 1.225, respectively, for FSAWs by pivot algorithm and for FSAWs by reptation the values 1.217 and 1.191, respectively, were found. Thus, in both cases the critical exponents of the scaling laws of mean square dimensions are larger than expected for SAWs.

Average Instantaneous Shape

The instantaneous shape of an individual chain may be characterized by the three specific orthogonal components of the radius of gyration taken along its principal axes of inertia [17,18]: The chain is represented by the following tensor of the second kind

$$A = \begin{vmatrix} xx & xy & xz \\ xy & yy & yz \\ xz & yz & zz \end{vmatrix}$$

with

$$xx = \frac{1}{N}\sum_{i=1}^{N} x_i^2 \qquad xy = \frac{1}{N}\sum_{i=1}^{N} x_i y_i \qquad \text{etc.}$$

N being the number of segments per chain and x_i, y_i and z_i being the coordinates of the ith segment of the chain relative to the centre of gravity of the chain.

Diagonalization ($| A - \lambda \cdot E | = 0$) yields the Eigenvalues λ corresponding to the squared length of the three axes of the "equivalent" ellipsoide L_i^2, which by definition are chosen as $L_1^2 \leq L_2^2 \leq L_3^2$.

In order to be able to compare the shape of the model chains irrespective of the chain dimensions reduced components ("shape factors") $sf_i = \langle L_i^2 \rangle / \langle s^2 \rangle$ [19] may be introduced. Comparison of the shape factors of NRRWs and SAWs reveals a slightly larger asymmetry of the latter (The reduced component of $\langle s^2 \rangle$ along the longest axis, sf_3, of SAWs is larger by $\approx 3\%$, the reduced components along the shorter axes, sf_2 and sf_1, are smaller by $\approx 5.5\%$ and $\approx 15\%$, respectively). The effect is not very pronounced, but large enough to extract — by comparison of the shape factors of SAWs and NRRWs to those of various FSAWs — the same statement as obtained from the global dimensions: Whereas the shape factors of FSAWs generated with local motions are very similar to those of NRRWs, sf_i-values of FSAWs obtained by pivot algorithm or reptation closely resemble those of SAWs.

Nearest Neighbour Contacts

Another quantity which is some intermediate between global and local quantities is the average number of nearest neighbour contacts $\langle$ NN $\rangle$. For all relaxation mechanisms used to prepare FSAWs, the number of nearest neighbour contacts is larger than that of SAWs. The difference between $\langle$ NN $\rangle$ of SAWs and FSAWs by pivot algorithm or reptation is appreciable for $N = 50$ (20% and 38%, respectively) but decreases with increasing chain length to approximate 5% for $N = 1000$. On the other hand, the number of nearest neighbour contacts of FSAWs by local motions are approximately twice the number of contacts of SAWs and ca. 1/3–1/4 of the contact number of NRRWs. Of course, in spite of the close resemblance of FSAWs by local motions and NRRWs on a macroscopic scale, their average number of nearest neighbour contacts cannot coincide, because each overlap in a NRRW is accompanied by 4 contacts. Comparing the number of overlaps $\langle Z \rangle$ (3.258 for $N = 50$, 58.233 for $N = 500$ and 124.813 for $N = 1000$) with the number of contacts (13.225, 233.194 and 499.504 for $N = 50$, 500 and 1000) shows that nearly all contacts result from overlaps ($\langle Z \rangle / \langle$ NN $\rangle \approx 4$). During the relaxation process all overlaps and contacts due to the overlaps are removed, on average producing approximately the same number of (new) contacts as the number of (removed) overlaps, $\langle$ NN $\rangle$ of FSAW by local motions being 4.959, 62.502 and 122.13 for $N = 50$, 500 and 1000.

Microscopic Structure

The microscopic structure of chains may be described by local quantities, e.g. the frequency of conformations of short units. Following the procedure outlined in chapter "Simulation Method", three-bond, four-bond and five-bond units were analyzed. For NRRWs the probability of a specific unit easily may be determined from geometric considerations: The probability of each k-bond configuration simply

reads $(k-2)^{-3}$. Making allowance for symmetry yields the following frequencies; the second entry is the squared end-to-end distance of the specific k-bond unit:

$k = 3$:							
trans:	(t)				$\langle T \rangle$	$= 1/3$	$h^2 = 19$
gauche:	$(+)$	$(-)$			$\langle G \rangle$	$= 2/3$	$h^2 = 11$
$k = 4$:							
trans-trans	(tt)				$\langle TT \rangle$	$= 1/9$	$h^2 = 32$
trans-gauche	$(t+)$	$(t-)$	$(+t)$	$(-t)$	$\langle TG \rangle$	$= 4/9$	$h^2 = 24$
gauche-gauche'	$(+-)$	$(-+)$			$\langle Gg \rangle$	$= 2/9$	$h^2 = 16$
gauche-gauche	$(++)$	$(--)$			$\langle GG \rangle$	$= 2/9$	$h^2 = 8$
$k = 5$:							
trans-trans-trans	(ttt)				$\langle TTT \rangle$	$= 1/27$	$h^2 = 51$
trans-gauche-trans	$(t+t)$	$(t-t)$			$\langle TGT \rangle$	$= 2/27$	$h^2 = 43$
trans-trans-gauche	$(tt+)$	$(tt-)$	$(+tt)$	$(-tt)$	$\langle TTG \rangle$	$= 4/27$	$h^2 = 35$
gauche-trans-gauche'	$(+t-)$	$(-t+)$			$\langle GTg \rangle$	$= 2/27$	$h^2 = 35$
gauche-trans-gauche	$(+t+)$	$(-t-)$			$\langle GTG \rangle$	$= 2/27$	$h^2 = 27$
trans-gauche-gauche'	$(t+-)$	$(t-+)$	$(+-t)$	$(-+t)$	$\langle TGg \rangle$	$= 4/27$	$h^2 = 27$
gauche-gauche'-gauche	$(+-+)$	$(-+-)$			$\langle GgG \rangle$	$= 2/27$	$h^2 = 27$
trans-gauche-gauche	$(t++)$	$(t--)$	$(++t)$	$(--t)$	$\langle TGG \rangle$	$= 4/27$	$h^2 = 19$
gauche-gauche-gauche'	$(++-)$	$(--+)$	$(+--)$	$(-++)$	$\langle GGg \rangle$	$= 4/27$	$h^2 = 11$
gauche-gauche-gauche	$(+++)$	$(---)$			$\langle GGG \rangle$	$= 2/27$	$h^2 = 3$

Comparison with numeric data of NRRWs (Tables 1–3) shows a perfect agreement. (It should be mentioned that $\langle s^2 \rangle$ and $\langle h^2 \rangle$ calculated using analytical expressions for the freely rotating chain [20] are in excellent agreement with numeric data, too. Both results serve as some test of the random generator used [21]).

Contrary to the global quantities, the local structure of NRRWs is not preserved in FSAWs by local motions (see Tables 1–3). The different behaviour of these local quantities as compared to the global ones in case of FSAWs by local motions may be unexpected at a first glance, but is simply the result of eliminating double occupancies: In Table 4, the frequencies of three-, four- and five-bond units are summarized for very short SAWs ($N = 7, 9, 11, 13, 15$) obtained by exact enumeration. Eliminating

Table 4 Frequencies of 3-bond, 4-bond and 5-bond configurations in short self-avoiding walks obtained by exact enumeration.

	$N = 7$	$N = 9$	$N = 11$	$N = 13$	$N = 15$
$\langle T \rangle$	0.341772	0.347975	0.352368	0.355327	0.357471
$\langle G \rangle$	0.658228	0.652025	0.647632	0.644673	0.642529
$\langle TT \rangle$	0.113924	0.117423	0.121453	0.122707	0.123628
$\langle TG \rangle$	0.455696	0.463836	0.472274	0.474762	0.476454
$\langle Gg \rangle$	0.227848	0.226061	0.223932	0.223486	0.223232
$\langle GG \rangle$	0.202532	0.192679	0.182342	0.179045	0.176686
$\langle TTT \rangle$	0.037975	0.039531	0.040634	0.041458	0.042081
$\langle TGT \rangle$	0.075949	0.079063	0.081267	0.082817	0.083980
$\langle TTG \rangle$	0.151899	0.156662	0.159229	0.160596	0.161433
$\langle GTg \rangle$	0.075949	0.077599	0.078646	0.079355	0.079926
$\langle GTG \rangle$	0.075949	0.077599	0.077620	0.077479	0.077330
$\langle TGg \rangle$	0.151899	0.156662	0.157976	0.158600	0.158902
$\langle GgG \rangle$	0.075949	0.077599	0.078076	0.078512	0.078876
$\langle TGG \rangle$	0.151899	0.149341	0.148743	0.148125	0.147531
$\langle GGg \rangle$	0.151899	0.142020	0.137231	0.134118	0.132156
$\langle GGG \rangle$	0.050633	0.043924	0.040577	0.038940	0.037785

Table 5 Frequencies of 3-bond, 4-bond and 5-bond configurations in 6-bond-ring erased random walks. ($N \leqslant 15$: exact enumeration; $N \geqslant 50$: Monte Carlo samples of size 10^6)

	N = 7	*N = 9*	*N = 11*	*N = 13*	*N = 15*	*N = 50*	*N = 500*	*N = 1000*
⟨ *T* ⟩	0.341772	0.345949	0.348300	0.349689	0.350616	0.356527	0.357868	0.357942
⟨ *G* ⟩	0.658228	0.654051	0.651700	0.650311	0.649384	0.643473	0.642132	0.642058
⟨ *TT* ⟩	0.113924	0.116739	0.119326	0.119660	0.119866	0.121862	0.122418	0.122455
⟨ *TG* ⟩	0.455696	0.461135	0.466621	0.467404	0.467887	0.470003	0.470968	0.471009
⟨ *Gg* ⟩	0.227848	0.227656	0.226959	0.227327	0.227548	0.226558	0.226429	0.226445
⟨ *GG* ⟩	0.202532	0.194469	0.187095	0.185608	0.184700	0.181577	0.180185	0.180091
⟨ *TTT* ⟩	0.037975	0.039301	0.039817	0.040085	0.040245	0.041671	0.041878	0.041895
⟨ *TGT* ⟩	0.075949	0.078603	0.079634	0.080170	0.080490	0.082349	0.082685	0.082701
⟨ *TTG* ⟩	0.151899	0.155750	0.156922	0.157505	0.157857	0.160640	0.161107	0.161133
⟨ *GTg* ⟩	0.075949	0.077147	0.077288	0.077355	0.077394	0.077438	0.077485	0.077470
⟨ *GTG* ⟩	0.075949	0.077147	0.077288	0.077355	0.077394	0.077466	0.077466	0.077479
⟨ *TGg* ⟩	0.151899	0.155750	0.156922	0.157505	0.157857	0.158747	0.159010	0.159041
⟨ *GgG* ⟩	0.075949	0.077147	0.077288	0.077355	0.077394	0.076538	0.076456	0.076463
⟨ *TGG* ⟩	0.151899	0.148472	0.147875	0.147575	0.147393	0.146779	0.146608	0.146576
⟨ *GGg* ⟩	0.151899	0.147016	0.145641	0.144934	0.144513	0.141435	0.140949	0.140930
⟨ *GGG* ⟩	0.050633	0.043668	0.041325	0.040162	0.039463	0.036937	0.036355	0.036312

the 24 cyclic structures (12 (+ + + +) and 12 (− − − −) configurations) from the $4 \cdot 3^5 = 972$ 6-bond NRRWs ($N = 7$) and averaging the data of the remaining 948 self-avoiding configurations shows increased frequencies of configurations having larger end-to-end distances and decreased frequencies of those having smaller ones as compared to NRRWs. From $4 \cdot 3^7 = 8748$ 8-bond configurations 552 are not self-avoiding, the smallest ring having 6 bonds in 504 cases and 8 bonds in 48 cases (12(+ + − − + +), 12(− − + + − −), 12(+ − − + + −), 12(− + + − − +)). Eliminating these configurations, comparison of the data with those obtained for 6-bond SAWs shows that the effect stated above is even stronger. Increasing the chain length (and hence also the size of the largest ring possible) leads to higher frequencies of more extended configurations, at least for the comparatively small range of chain lengths examined (trans units are altogether absent in rings with $n = 6$ and $n = 8$ bonds, their fraction is at least smaller than 1/3 for small rings and achieves 1/3 only at infinite chain length [22]; thus, it is expected that the effect levels off for longer chains).

Of course, the results obtained for short chains are not representative for the effect a unit of equal chain length has in a long chain, because statistical combination of these (self-avoiding) units leads to overlaps between segments of different units and, therefore, to further eliminations. Thus, it is expected that the effect of removing (small) rings should be still larger than given in Table 4. This statement may be corroborated by evaluating the properties of random walks which are not allowed for rings consisting of a given number of bonds: e.g. elimination of first-order overlaps [23, 24, 25] yields 6-bond-ring erased NRRWs. The results summarized in Table 5 (exact enumeration for $N \leq 15$, Monte Carlo data for $N \geq 50$) clearly show that the elimination of the smallest ring possible alone forces more extended structures to some extent, the effect growing stronger with increasing chain length. To conclude, removing of double occupancies — due to the simultaneous elimination of ring structures — always are accompanied by an enrichment of those units giving a SAW a "stiffer" character than a NRRW on a local scale.

Chain Length Dependence of Properties of FSAWs

The frequencies of units of FSAWs irrespective of their generation are roughly the average of the frequencies of units of NRRWs and SAWs for $N = 50$; for $N = 1000$ they coincide with those of SAWs fairly well. The reason for the comparatively large chain length dependence of the effect is based on the number of movements needed in order to attain a FSAW and hence on the number of replaced bonds. For $N = 50$ on average approximately 25 new bonds are generated using local motions and ≈ 19 using reptation. By use of pivot algorithm the NRRW is transformed into a FSAW by ≈ 10 accepted moves only. For the longer chains $N = 500$ (1000) local motions produce 1600 (5500) new bonds, reptation 460 (960) and pivot algorithm performs 370 (900) accepted moves. Therefore, for $N = 50$ more or less large parts of the initial NRRW are retained in the corresponding FSAW and hence a relatively large amount of the initial local structure. In long chains, on the other hand, all or nearly all bonds of the initial NRRW are replaced by new bonds (in order to remove overlaps) leading to a statistics of local structure similar to SAWs.

As described above in the section "Macroscopic Structure", FSAWs by a pivot algorithm or reptation look much more like SAWs than like NRRWs for all chain length examined. Nevertheless, the dimensions of short FSAWs are significantly smaller than those of SAWs — leading to exponents in the power laws of $\langle h^2 \rangle$ and

$\langle s^2 \rangle$ which are larger than expected for SAWs — because the initial structure is retained to some extent after the few relaxations needed in order to become self-avoiding. The longer the chains are the more relaxation steps are needed and the less is the correlation between the initial NRRW and the resulting FSAW. By use of reptation, after replacing n bonds a completely new chain — built up step-by-step albeit started from a NRRW — is present. Thus, its properties do not differ very much from those of SAWs. Using pivot algorithm after n accepted relaxations we have a completely new chain, too, but in this case large parts of the chain are moved by one elementary motion. Therefore, it is not unexpected that removing the last overlap on average yields a configuration which is more extended (on a global scale) than an unbiased SAW. On the contrary, using local motions a completely different situation arises: Very small parts of the chain are moved per relaxation step and contrary to reptation, the overwhelming part of (accepted) relaxations take place in the interior parts of the chain instead of chain ends. An overlap can be removed by reorientation of a very short part of the chain only, changing the microscopic structure but having no considerable effect on the macroscopic structure of the chain. A second example for this behaviour may be obtained by use of another sort of NRRWs, e.g. the 6-bond-ring erased NRRWs mentioned above. Their global dimensions are approximately 14% larger than the dimensions of (ordinary) NRRWs, e.g. $\langle s^2 \rangle = 1139$ and $\langle h^2 \rangle = 6842$ for $N = 1000$. Starting from these chains instead of starting from (ordinary) NRRWs and applying local motions yields FSAWs with $\langle s^2 \rangle = 1142$ and $\langle h^2 \rangle = 6860$, values which are very close to the mean square dimensions of the initial configurations. Clearly, the average number of overlaps of 6-bond-ring erased NRRWs is smaller than the number of cross sections of (ordinary) NRRWs, e.g. $\langle Z \rangle = 76.2$ for $N = 1000$. On the other hand, the number of contacts is larger than $4 \cdot \langle Z \rangle$ in this case, the number of contacts $\langle \mathrm{NN} \rangle = 340.8$ and $\langle \mathrm{NN} \rangle / \langle Z \rangle \approx 4.5$, respectively, for $N = 1000$. Thus, we have $76.2 \cdot 4 = 304.8$ contacts due to overlaps and 36 "true" contacts. The average number of contacts of the resulting FSAWs by local motions is ≈ 113.6. Therefore, on average each overlap of the 6-bond-ring erased NRRW has been replaced by one contact — as stated above for NRRWs — and the "true" contacts of the initial configuration have been retained. Therefore, in both cases, after the relatively small number of relaxations needed to remove all overlaps, practically no change in global dimensions is detectable; to produce a "real" SAW by local motions, a much larger number of relaxations would be necessary.

Starting Configurations For Dynamic Algorithms

Clearly, FSAWs by local motions could serve as starting configurations studying pseudoideal (theta) conditions, because the global structure of the initial non reversal random walk is nearly perfectly retained.

For athermal conditions, FSAWs by reptation or pivot algorithm only are a reasonable choice. Although there are slight differences between their properties and the properties of SAWs, fewer initial relaxations should be necessary starting from these chains than starting from e.g. an all-trans configuration in order to attain thermodynamic equilibrium.

By use of reptation, the correlation with the initial NRRW may easily be removed by slightly modifying the algorithm. Instead of stopping relaxation if the chain is free of overlaps the procedure is continued until at least n bonds are replaced. The local

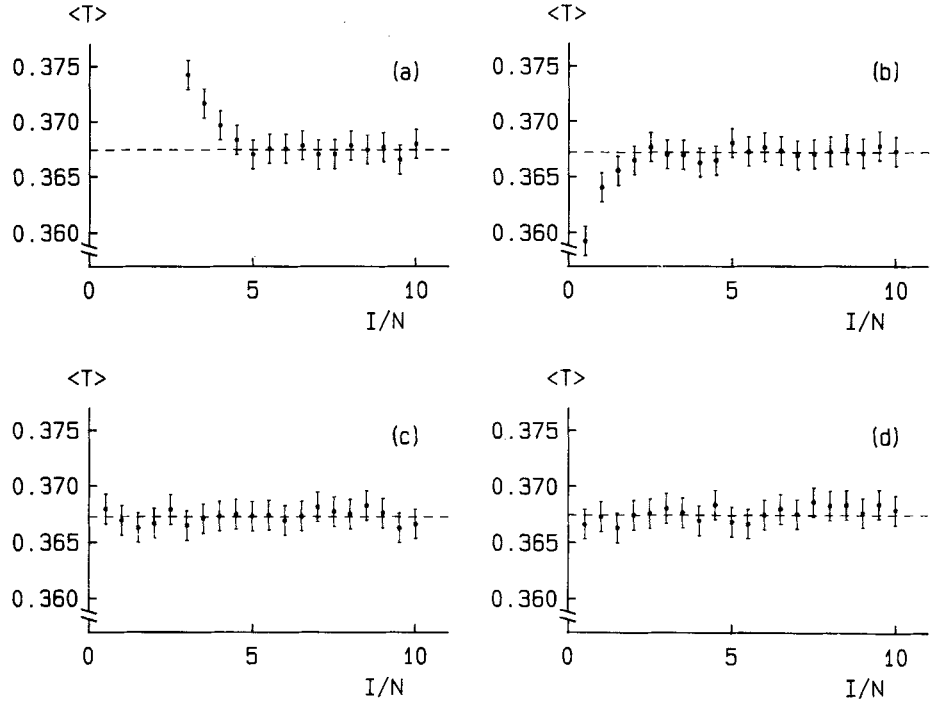

Figure 2 Average fraction of trans configurations $\langle T \rangle$ as a function of (reduced) relaxation trials I/N starting from (a) all-trans configuration, (b) FSAWs by pivot algorithm, (c) configurations obtained by reptation starting with a NRRW and replacing n bonds (SAW_R) and (d) unbiased self-avoiding walks; all for $N = 50$. Each point is the average of 10000 independent runs; the error bars are for 95% confidence limits.

and global dimensions (shown in Tables 1-3 and marked with SAW_R) now are very similar to those of SAWs irrespective of chain length.

In Figure 2 the average fraction of trans units $\langle T \rangle$ — for $N = 50$ obtained from 10000 independent runs — is shown as a function of (reduced) relaxation trials I/N (using pivot algorithm) starting from the all-trans configuration (a), from FSAWs obtained by pivot algorithm (b), from SAW_R introduced in this chapter (c) and — for comparison — from SAWs obtained by a simple step-by-step procedure (d). Starting from the all — trans configuration (a) $\langle T \rangle$ very rapidly decreases from its initial value 1 (not shown in the diagram) and reaches its average equilibrium value after ≈ 5 trials (slightly increasing with chain length) per bond; a few moves (≈ 2 trials per bond) are needed for FSAWs by pivot algorithm (b) and case (c) is very similar to case (d). Usually, one discards more data than are at least necessary in order to be absolutely sure that all initial correlations have been overcome. Therefore, using FSAWs by pivot algorithm as starting configurations does not gain much advantage over using an all-trans configuration. However, practically no data have to be discarded when a SAW_R is used as a starting configuration. In addition, replacing n bonds by reptation is much faster than performing n moves by pivot algorithm. Hence it follows that producing starting configurations by reptation is the most efficient one, at least among the algorithms discussed in this paper.

CONCLUSIONS

FSAWs are chain molecules obtained under very special and arbitrary conditions. In general, therefore, they are no appropriate models for real polymers. However, FSAWs are definite sets of chains on the path from NRRWs to (equilibrated) SAWs. Studying their properties yield a lot of information about the relaxation mechanism under consideration. In addition, careful comparison of local and global quantities of FSAWs to those of SAWs provides a very efficient method for the construction of starting configurations for dynamic Monte Carlo procedures.

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