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Efficient Dynamical Monte Carlo Method for Dense Polymer Systems

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ABSTRACT: A new dynamical Monte Carlo (MC) procedure for chains with excluded volume (EV) is suggested and applied to single-chain models on a simple cubic lattice. In each MC step of our procedure we select at random three neighbor "beads" and calculate for them the entire group of *allowed* local conformations (ALCs); an ALC is a conformational change of the three beads, which does not violate the EV condition. A new ALC is then randomly selected out of the group of ALCs. This new procedure differs from the conventional one (e.g., Verdier and Stockmayer), in which a trial local conformation (not necessarily an *allowed* one) is first selected and becomes the new ALC only if the EV condition is satisfied. For a single chain without EV our method leads to the expected Rouse-like dynamics, i.e., $\tau \sim N^2$ and $D \sim N^{-1}$, where τ, N, and D are the longest relaxation time, the number of beads, and the diffusion coefficient, respectively. For chains with EV we obtain $\tau \sim N^{2+\epsilon}$, where ϵ is close to the theoretical value 0.2. The use of our method for dense polymer systems is expected to be more efficient than the conventional one where most of the trial local conformations will be forbidden. To demonstrate this, the two methods have been applied to a single chain on a lattice which is partially filled with "obstacles" (i.e., a lattice site with an obstacle is also excluded for the chain). Indeed, our method has always led to significantly larger values of D than the conventional method and has been found to be significantly more efficient.

1. Introduction

The dynamics of polymer chain models with excluded volume (EV) is a difficult analytical problem and has therefore been studied mainly with computer simulation.[1-12] To make the simulation of long chains tractable, highly simplified models have been employed, in which the chain is represented by N connected nonintersecting "beads" constrained to lie on a lattice.[1-12] These models have been conveniently simulated with the Monte Carlo (MC) method using various types of bead movement.[1-12] In all of these studies the repeated MC step consists of the following two stages: (1) a small group of beads is selected at random; (2) a trial conformational change of these beads (which we call here a local conformation) is randomly selected and the EV condition is checked; if it is not violated the trial local conformation is accepted and the beads are moved to their new positions. In the other case, no conformational change is performed. This procedure has been found to be efficient for single-chain models in which the EV effect is relatively weak. However, it is expected to be highly inefficient for dense, many-chain systems where most of the trial local conformations will be forbidden. In this article we, therefore, suggest modifying the "blind" selection of local conformations (described in stage 2) by first calculating the entire group of *allowed* local conformations (ALCs), i.e., those which do not violate the EV restriction, and then selecting at random from this group a new ALC. In what follows the new method is described in detail and tested on single-chain models with and without EV on a simple cubic lattice. We are mainly interested in the dependence of the longest relaxation time, τ, on chain length, where τ is extracted from the autocorrelation functions of global properties of the chain, such as the end-to-end distance and the radius of gyration.

For a chain without EV, τ is expected to behave like in the Rouse model,[1,3,6,11,12,17-19] i.e.

$$\tau \sim N^2 \tag{1}$$

However, when the EV interaction is taken into account, one would expect the relaxation to slow down

$$\tau \sim N^{2+\epsilon} \tag{2}$$

de Gennes[20] has predicted (on the basis of phenomenological scaling arguments) $\epsilon = 0.2$ in three dimensions, which is consistent with ϵ expansion obtained by Jasnow and Moore.[21] It should be pointed out that this result has been derived for the Rouse model[17] but one would expect it to be universal, i.e., independent of the details of the model and of the particular mechanism of relaxation used.[11,13-15,23] However, MC studies carried out by Verdier's group[1-6] have all led to $\epsilon \sim 1$. Hilhorst and Deutch[22,23] have argued that this unexpected strong slowing down is due to the lattice restriction and can be removed by using, in addition to Verdier's one-bead flip, also a 90° crankshaft motion. Indeed, simulations based on these types of motion have led to values of ϵ close to 0.2.[8-12] Since our method also includes these bead movements, we expect it to also lead to the expected value $\epsilon = 0.2$. It should be pointed out that $\epsilon \sim 0.2$ has also been obtained for a nonlattice model by Ceperley et al.[14] On the other hand, a molecular dynamics study of Bishop et al [13] yielded $\epsilon \sim -1$ but for very short chains.

We compare the efficiency of our MC method with that of the conventional one, which is based on a one-bead flip and a 90° crankshaft motion. In order to demonstrate the advantage of using the new method for dense, many-chain systems, we are also studying by both methods a similar model, of a single chain with EV moving on a lattice, which

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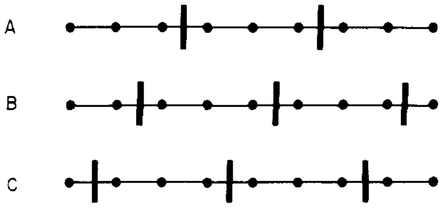

Figure 1. Schematic illustration of the three sets of segments for a chain of nine beads. Set A consists of three (n) equal segments of three beads, whereas sets B and C have four (n + 1) segments with end segments of one and two beads.

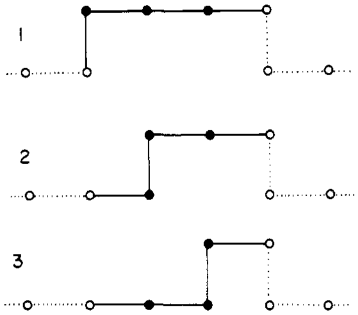

Figure 2. 1 is an example of a current local conformation of a segment of three beads (full circles) and their four connecting bonds (full lines). The open circles and the dotted lines represent the rest of the chain, which is held fixed. Because of the EV restriction only two additional allowed local conformations (ALCs) exist (2 and 3). Each of the three ALCs can be selected with probability $^1/_3$.

is partially occupied by "obstacles".

2. Theory

2.1. The Model and the MC Procedure.

The model of a polymer chain may be thought of as a chain of N connected beads lying on the lattice points of a simple cubic lattice with the bonds between adjacent beads lying along cube edges. The EV restriction does not allow the multiple occupancy of beads on a lattice site. For our procedure it is convenient to divide the chain into n constant segments of three beads each (i.e., $N = 3n$) (see Figure 1A). The MC step consists of three stages: (1) A segment of three beads is selected at random out of the n segments. (2) For this segment the computer calculates and stores the entire group of what we have previously defined as the allowed local conformations (ALCs). In detail, an ALC is a conformation of the three beads and their four connecting bonds (see Figure 2) which preserves chain connectivity and does not violate the EV restriction. Also, transition of the current local conformation (which is also an ALC) to any other ALC must not violate contour noncrossability, which can occur in only two cases, described in Figure 3. In the third stage of the process, an ALC is selected at random from the entire group of ALCs; if it is different from the current one, it becomes the new ALC of the chain and the three beads are moved to their new positions. In the other case, no conformational change is carried out. Obviously, this procedure is a Markov chain which satisfies the detailed balance condition. Notice that the number of ALCs for the end segments is considerably larger than for the inner ones; this should significantly decrease the relaxation time of the shorter chains. However, one would expect this chain end effect to vanish with increasing chain length. It should also be pointed out that, in order to simplify the calculations, we allow the chain ends to violate contour noncrossability, which is physically reasonable.

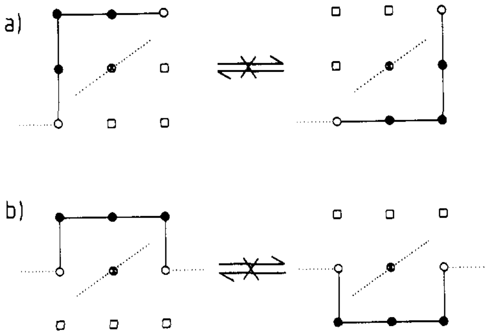

Figure 3. (a) and (b) are the only examples in which contour noncrossability can be violated. Such transitions are not allowed in the present MC procedure. The full and open circles are defined in the caption for Figure 2. The crossed circles denote a bead which belongs to another part of the chain. The squares indicate empty lattice sites.

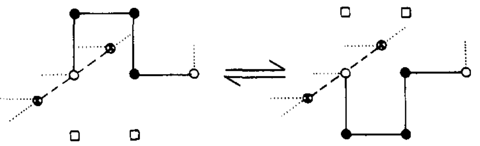

Figure 4. Local conformation where two of its neighbor sites are occupied by beads which belong to other parts of the chain. With the present MC procedure a 180° crankshaft motion is allowed, even though the two 90° crankshaft motions are forbidden since they violate the EV restriction.

Most of the former MC studies were based on the one-bead flip of Verdier and Stockmayer,[1-4] alone or together with a two-bead crankshaft motion.[8-12] Recently, Kranbuehl and Verdier[6] have used a larger set of motions, which consists of the one-bead flip and most of the possible two-bead motions, including the 180° crankshaft movement but not the 90° one. Hence, our MC procedure is based on a larger set of ALCs than has been previously used and therefore is expected to lead to smaller relaxation times. In fact, the present set of ALCs includes the one-bead flip as well as the two-bead 90° crankshaft motion, which have been argued to be essential for a correct relaxation of a chain with EV on a simple cubic lattice.[22,23] All the other ALCs (such as a three-bead 180° crankshaft motion, for example) are combinations of these two elementary motions; however, in our MC procedure they all have the same probability. Moreover, we assume that a transition from one ALC to another is always possible (provided that contour noncrossability is satisfied), even in cases where performing the transition by successive elementary motions would be violated by the EV restriction (see example in Figure 4). However, the basic difference between our method and the conventional ones is in the selection procedure for an ALC: they choose an ALC blindly, whereas we first scan the future in order to eliminate the forbidden local conformations. (In this sense the present method resembles the scanning method, which is another computer simulation technique for real chains suggested recently.[24,25]) As has been already pointed out, for dense, many-chain systems our approach is expected to be more efficient than the conventional one,[1,6,10] where the blind search for ALCs will be unsuccessful for most MC steps.

The dynamics dictated by the constant division of the chain into segments is somewhat unphysical since a bead can only move with the other two beads of the same segment. In order to obtain a "smoother" relaxation we define two additional sets of n + 1 segments (rather than n) as described in Figure 1B,C. State 1 of our MC step is now changed as follows: first a set of segments is selected at random out of the three sets and then a segment is selected, etc. The new procedure is thus based on three

Markov chains, each satisfying the detailed balance condition. It should also be pointed out that the new sets have smaller end segments than the set initially defined, which is expected to weaken the chain end effects discussed previously.

To end this section we point out that, in principle, segments of more than three beads can be used; however, in this case the necessity to satisfy the noncrossability of contours would complicate the computer program and would require longer computer time. Our approach can be extended, with trivial modification, to chains with both EV and finite attractive or repulsive interactions; it can also be applied to off-lattice chain models.

2.2. Autocorrelation Functions and Their Relaxation Times. We calculate the autocorrelation functions $\rho(R^2,R^2,t)$, $\rho(S^2,S^2,t)$, and $\rho(\mathbf{R},\mathbf{R},t)$ of the square end-to-end distance R^2, the square radius of gyration S^2, and the end-to-end vector $\mathbf{R}$, respectively

$$\rho(R^2,R^2,t) = [\langle R^2(t_0)R^2(t_0+t)\rangle - \langle R^2\rangle^2]/(\langle R^4\rangle - \langle R^2\rangle^2) \tag{3}$$

$$\rho(S^2,S^2,t) = [\langle S^2(t_0)S^2(t_0+t)\rangle - \langle S^2\rangle^2]/(\langle S^4\rangle - \langle S^2\rangle^2) \tag{4}$$

and

$$\rho(\mathbf{R},\mathbf{R},t) = \langle \mathbf{R}(t_0)\cdot\mathbf{R}(t_0+t)\rangle/\langle R^2\rangle \tag{5}$$

In these equations the angular brackets denote ensemble averages in equilibrium; however, in the simulation, time averages are employed. We define the unit of time to be $[n + 2(n + 1)]/3 = (n + 2)/3$ MC steps, which is the average minimal number of MC steps (for the three sets of segments) required to visit all the segments of the chain. This number should be multiplied by ν_0, which symbolizes the rate at which any single bead receives collisions.[1] One can, therefore, relate the simulation time to real time by adjusting the value of ν_0, which does not affect the scaling relations for τ (eq 1 and 2). (See ref 15 and also discussion by Verdier and Stockmayer,[1] who compared the diffusion coefficient obtained in the simulation to that of the Rouse model.) The longest relaxation time of the system, τ (or a quantity proportional to τ), can be obtained by best-fitting the linear "tail" of the logarithm of the autocorrelation function to log $\rho(t)$, where $\rho(t)$ is the exponential function

$$\rho(t) = A\exp(-t/\tau) \tag{6}$$

In other words, τ^{-1} is the slope of log ρ and A is a constant, $A = \rho(0)$.[3] One can also define for $\rho(R^2,R^2,t)$ an average relaxation time $\tau_{\text{int}}(R^2)$ (which depends on τ, as well as on the shorter relaxation times) by the integral[24,25]

$$\tau_{\text{int}}(R^2) = \int_{t=0}^{\infty}\rho(R^2,R^2,t)\,\mathrm{d}t \tag{7}$$

Similar integrals also define $\tau_{\text{int}}(S^2)$ and $\tau_{\text{int}}(\mathbf{R})$. Another definition of an average relaxation time is the time required for the autocorrelation function to decrease to the value $1/e$. We denote this relaxation time by $\tau_{1/e}$. Obviously, when the decay is exponential (i.e., $A = 1$ in eq 6), the three relaxation times are equal. In the general case, however, they are expected to differ from each other but not by very much since the average relaxation time of a global property is mainly determined by the longest relaxation time τ. It should be pointed out, however, that the autocorrelation functions of long chains decay very slowly and therefore computation of their tails becomes impractical; for long chains, however, calculation of $\tau_{1/e}$ may still be feasible.

Table I
Relaxation Times and Diffusion Coefficients for Chains without Excluded Volume[a,b]

	N			
	21	33	51	72
$\tau(R^2)/N^2$	$0.0240^{7,c}$	0.025^1	0.027^1	0.026^1
$\tau_{1/e}(R^2)/N^2$	0.013^1	0.013^1	0.016^1	0.016^1
$\tau_{\text{int}}(R^2)/N^2$	0.016^1	0.016^1	0.018^1	0.018^1
$\tau(S^2)/N^2$	0.0240^1	0.025^1	0.028^1	0.027^1
$\tau_{1/e}(S^2)/N^2$	0.022^1	0.023^1	0.026^1	0.026^1
$\tau_{\text{int}}(S^2)/N^2$	0.022^1	0.024^1	0.026^1	0.025^2
$\tau(\mathbf{R})/N^2$	0.053^1	0.053^2	0.056^2	0.058^2
$\tau_{1/e}(\mathbf{R})/N^2$	0.037^1	0.040^2	0.044^1	0.044^1
$\tau_{\text{int}}(\mathbf{R})/N^2$	0.039^1	0.041^2	0.045^2	
	DN			
	0.64^2	0.58^2	0.60^2	0.57^2
$\langle R^2\rangle/(N-1)$				
present	0.996^4	0.999^4	1.010^4	0.993^5
exact	1.000	1.000	1.000	1.000
K	1, 2, 3, 6	6, 7, 9, 14	22, 30, 50	34, 42, 65

[a] N is the number of beads in a chain. τ, $\tau_{1/e}$, and τ_{int} are the relaxation times obtained from the slope of log $\rho(t)$ (eq 6) (the longest relaxation time) by the $1/e$ criterion and by integration (eq 7), respectively. These relaxation times are extracted from the autocorrelation functions of R^2—the square end-to-end distance (eq 3), S^2—the square radius of gyration (eq 4), and $\mathbf{R}$—the end-to-end vector (eq 5). D is the diffusion coefficient (eq 8) and $\langle R^2\rangle$ is the average of R^2. Values for the autocorrelation functions are calculated every K MC steps. [b] The unit of time, in which the results for τ and D are expressed, is $N/3 + {}^2/_3$ MC steps (for explanation see text). [c] The statistical error is denoted by a superscript. For example, 0.0240^7 means 0.0240 ± 0.0007.

Table II
Results for the Parameter A[a,b]

	N			
	21	33	51	72
	Without Excluded Volume			
$A(R^2)$	0.60^2	0.64^1	0.65^1	0.67^1
$A(S^2)$	0.90^2	0.92^1	0.92^1	0.96^1
$A(\mathbf{R})$	0.77^2	0.78^1	0.80^1	0.78^1
	With Excluded Volume			
$A(R^2)$	0.61^1	0.62^1	0.66^1	0.69^1
$A(S^2)$	0.87^2	0.86^1	0.90^1	0.90^1
$A(\mathbf{R})$	0.78^1	0.80^1	0.80^2	0.82^1

[a] A is defined in eq 6. It is obtained by a best-fit procedure (for explanation see text). [b] N, R^2, S^2, $\mathbf{R}$, and the statistical error are explained in the caption for Table I.

Another quantity of interest is the diffusion coefficient D

$$D = \langle d^2\rangle/6t \tag{8}$$

where $\langle d^2\rangle$ is the mean square displacement of the center of mass of the chain calculated over a long period of time t. We also obtain results for the mean square end-to-end distance $\langle R^2\rangle$ and compare them to the theoretical values. This constitutes a test for the convergence of the initial relaxation of the chain to equilibrium.

3. Results and Discussion

Using our MC procedure (based on the three sets of segments; see section 2.1) we have simulated single chains of length N = 21, 33, 51, and 72 on a simple cubic lattice. The results for the relaxation times, diffusion coefficient, and the end-to-end distance are presented in Tables I and III for chains with and without EV, respectively; in Table II are presented the values obtained for A (eq 6). In Figure 5 we also provide typical semilogarithm plots of the au-

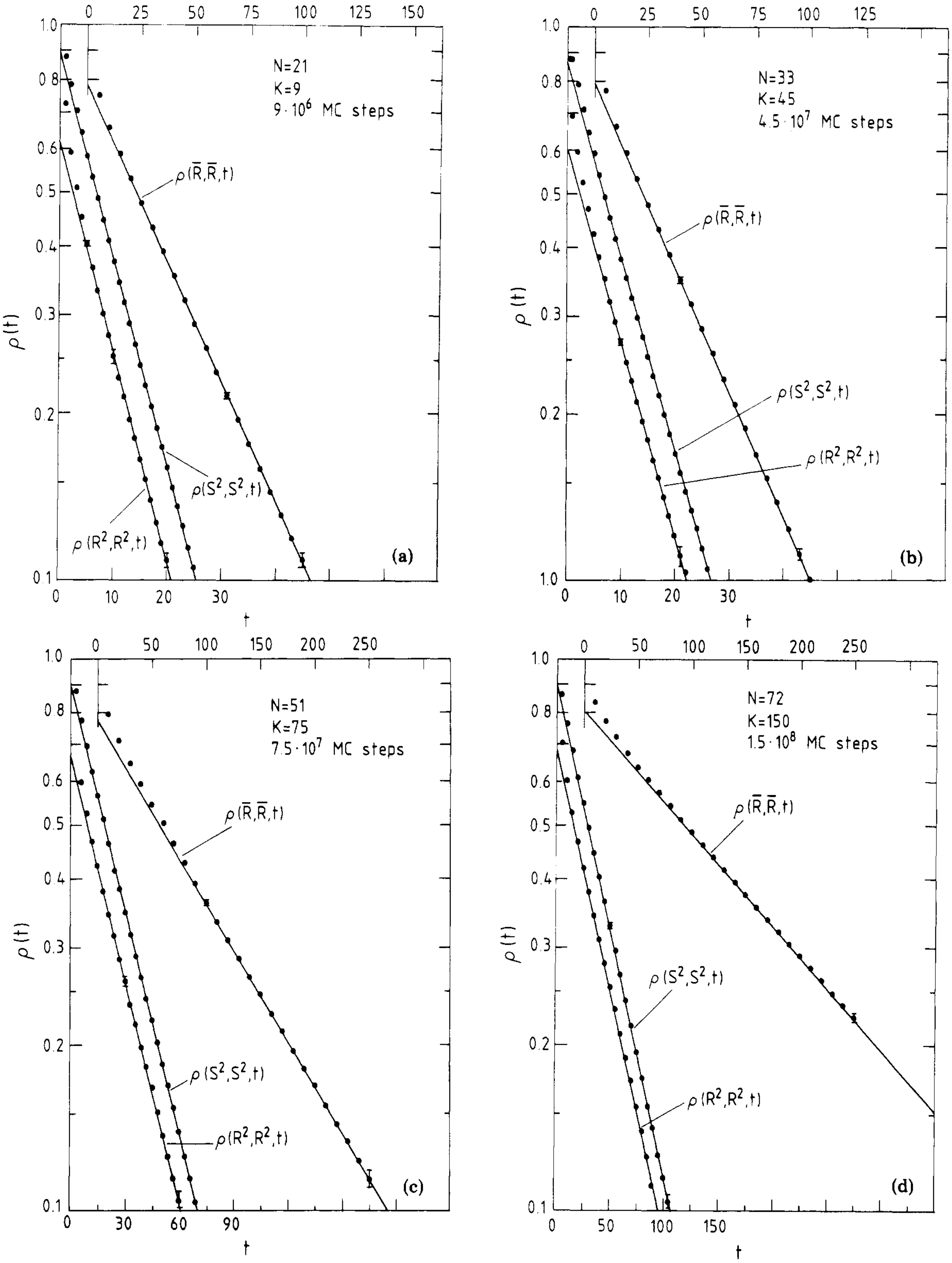

Figure 5. Semilogarithmic plots of typical autocorrelation functions $\rho(R^2,R^2,t)$, $\rho(S^2,S^2,t)$, and $\rho(\mathbf{R},\mathbf{R},t)$ for chains with EV as functions of time t. The units of t are K MC steps. The upper time scale is for $\rho(\mathbf{R},\mathbf{R},t)$ which is shifted to the right. The solid lines constitute the best fit for the "tails" of the autocorrelation functions. For each N at least two such MC runs have been performed which are based on different random number sequences. This enabled us to determine the statistical error bars. For each run the corresponding line and slope have been calculated and the results for the longest relaxation time presented in Table III are the average of these slopes.

tocorrelation functions $\rho(R^2,R^2,t)$, $\rho(S^2,S^2,t)$, and $\rho(\mathbf{R},\mathbf{R},t)$ for chains with EV. All the simulations have been started from a straight chain, which has always relaxed relatively fast to its equilibrium conformations. When equilibrium has been attained (i.e., when the results for $\langle R^2 \rangle$ have become close to the theoretical values) the current values of R^2, S^2, and $\mathbf{R}$ have been calculated every K MC steps and used for computing 250 values of the corresponding autocorrelation functions. We have also calculated every $250K$ MC steps, the value of d^2, the square displacement of the center of mass (which leads to the diffusion coefficient D, see eq 8). These values have been accumulated and averaged over the MC run. It should be pointed out that in order to simulate the tails of the autocorrelation functions a sufficiently large value of K should be chosen. Relatively large values of K are also required for defining

Table III
Relaxation Times and Diffusion Coefficients for Chains with Excluded Volume[a]

	N						
	21	33		51		72	
$\tau(R^2)/N^2$	0.0303^{6}	0.043^{1}	(0.77^{10})[b]	0.052^{1}	(0.44^{10})	0.058^{1}	(0.32^{10})
$\tau_{1/e}(R^2)/N^2$	0.017^{1}	0.025^{2}	(0.85^{30})	0.032^{1}	(0.57^{26})	0.037^{2}	(0.42^{25})
$\tau_{\text{int}}(R^2)/N^2$	0.020^{1}	0.029^{2}	(0.82^{27})	0.037^{1}	(0.56^{23})	0.042^{2}	(0.37^{21})
$\tau(S^2)/N^2$	0.0310^{6}	0.043^{1}	(0.72^{9})	0.052^{1}	(0.44^{10})	0.058^{1}	(0.32^{10})
$\tau_{1/e}(S^2)/N^2$	0.028^{1}	0.036^{2}	(0.56^{20})	0.047^{2}	(0.61^{21})	0.052^{2}	(0.29^{25})
$\tau_{\text{int}}(S^2)/N^2$	0.029^{1}	0.038^{2}	(0.60^{20})	0.049^{3}	(0.58^{26})	0.053^{3}	(0.23^{34})
$\tau(\mathbf{R})/N^2$	0.135^{1}	0.169^{2}	(0.50^{5})	0.208^{5}	(0.48^{8})	0.225^{5}	(0.23^{13})
$\tau_{1/e}(\mathbf{R})/N^2$	0.102^{1}	0.132^{3}	(0.57^{7})	0.162^{3}	(0.47^{19})	0.178^{3}	(0.27^{10})
$\tau_{\text{int}}(\mathbf{R})/N^2$	0.109^{1}	0.142^{3}	(0.59^{7})				

	DN			
	0.50^{2}	0.46^{1}	0.45^{1}	0.44^{1}
$\langle R^2\rangle/(N-1)$				
present	1.933^{4}	2.12^{1}	2.32^{2}	2.48^{2}
series[c]	1.938	2.13	2.33	2.50
K	2, 4, 6, 9	16, 40, 45	42, 50, 75	80, 120, 150

[a] For explanation see the caption for Table I. [b] In parentheses are presented the results for the exponent ϵ obtained with eq 3, using two values of τ, τ_{int}, and $\tau_{1/e}$; for example, for $N = 33$, the relaxation time values for $N = 21$ and $N = 33$ are used. [c] Result obtained with Domb's formula, based on series expansion.[28]

long time intervals ($250K$) for the calculation of d^2. Obviously, K should be increased as N increases because of the increase in the correlations. In fact, for $N = 21$ the largest values used for K are 9 and 6 for chains with and without EV, respectively; for $N = 72$ the corresponding values are 150 and 65. In order to obtain statistically reliable results, relatively long MC runs have been carried out, which, for the chains with EV, consist of 10^6K MC steps. The longest run, for $N = 72$, has $150 \times 10^6 = 1.5 \times 10^8$ MC steps, which required ~16 h computer time on the IBM 3081D computer. For each N, several runs have been performed by using different values for K and different random number sequences; the results presented in the tables are averages of results obtained for these runs. To carry out the integration (eq 7), we have defined an upper limit for t which is not smaller than the time required for the autocorrelation functions to decrease to 0.01.

3.1. Results for Chains without EV. It should first be pointed out that for chains without EV, any local conformation is also an ALC and therefore our MC procedure is equivalent to the conventional method which is based on a blind selection of local conformations. The results for $\langle R^2\rangle/(N-1)$ in Table I are equal within statistical errors of 1% and less to the exact value 1; this constitutes a verification of the convergence of our process. The results for the relaxation times (divided by N^2) are almost unchanged as functions of N: Only the results for $N = 21$ and 33 are slightly smaller than those for $N = 51$ and 72, which is due to the chain end effects discussed previously. This means that our MC procedure leads (like other MC methods)[1,2,5,6,11,12] to a Rouse-like relaxation, i.e., $\tau \sim N^2$. As one would expect, the results for the longest relaxation time τ, estimated from $\rho(R^2,R^2,t)$ (eq 3) and $\rho(S^2,S^2,t)$ (eq 4) are equal within the statistical error and are approximately two times smaller than the values of τ extracted from $\rho(\mathbf{R},\mathbf{R},t)$ (eq 5). (Similar ratios have also been obtained in ref 5 and 11.) As is also expected the results for the longest relaxation time are, in most cases, larger than the corresponding values of $\tau_{1/e}$ and τ_{int}, which both define *average* relaxation times for the corresponding global quantities. Only for $\rho(S^2,S^2,t)$ the three criteria lead approximately to the same results, which means that this function decays exponentially with $A \sim 1$ (see eq 6); in other words, the relaxation is hardly affected by the shorter relaxation times. Indeed, the values for $A(S^2)$ presented in Table II are very close to 1 and are significantly larger than those obtained for $A(R^2)$ and $A(\mathbf{R})$. It should be pointed out that the results for $A(R^2)$ and $A(S^2)$ both increase with increasing N, which means that the effect of the shorter relaxation times is less significant for the longer chains than for the shorter ones (see also a later discussion in section 3.2). It should also be stressed that the fact that the $1/e$ criterion leads to the correct N^2 dependence means that it can be used for the study of longer chains where calculating τ and τ_{int} becomes impractical (see section 2.2).

It is of interest to compare our values for τ to those obtained in former studies. One would expect the present method to lead to the smallest relaxation times and indeed our result $\tau(\mathbf{R})/N^2 \sim 0.05$ is smaller than 0.13 obtained by Gurler et al.,[12] who used the one-bead flip and a 90° crankshaft motion; it is also smaller than 0.1 obtained by Kranbuehl and Verdier[6] for the one-bead model ($p = 0$) but larger than 0.03 obtained by them for the model based on both one- and two-bead motions ($p = 1$). It should be pointed out, however, that in order to make a correct comparison, the various values of τ should be expressed in the same unit of time. Our unit of time, for example, is equivalent to N cycles of the one-bead model but is smaller than N cycles which include two-bead movements. Therefore, the values 0.13 and 0.03 appearing above, which are expressed in such units of time, should further be increased.

The results for D (eq 8), the translational diffusion coefficient (multiplied by N), are equal, within the statistical error, for $N = 33$, 51, and 72, i.e., $D \sim N^{-1}$, as in the Rouse model.[17] The higher value of D obtained for $N = 21$ stems from the stronger end effects occurring for the shortest chain studied. It should be pointed out that the relation $D \sim N^{-1}$ has been derived theoretically for the one-bead flip dynamics[2] and has also been obtained in former MC studies.[1-3,5,6,11,12] As expected, our resulted $DN \sim 0.6$ is larger than the values ~0.33 and ~0.25 obtained with the one-bead model[3,6] and with the model based on one-bead flip and a 90° crankshaft motion,[12] respectively. It is smaller than 1.2 obtained in ref 6 for the model $p = 1$. However, this result should be decreased since it has been obtained for larger units of time than ours (see former discussion in this section).

To summarize: For chains without EV our MC procedure, which is based on *all* local conformations of three beads, converges relatively fast to equilibrium and leads for sufficiently long chains to a Rouse-like dynamics.

3.2. Results for Chains with EV. The results for the chains with EV are summarized in Table III. It should first be noticed that the results for $\langle R^2 \rangle$ are equal, within the statistical errors 0.2–0.9%, to those obtained with Domb's formula based on series expansion;[28] this demonstrates the convergence of our MC process. The relaxation times for the chains with EV are larger than those obtained for the chains without EV (Table I): in particular, the results for the longest relaxation time $\tau(\mathbf{R})$ satisfy $\tau(\mathbf{R})/\tau(R^2) \sim 4$, as compared to the value 2 obtained for the chains without EV. Similar results for this ratio have been obtained also for the one-bead and the two-bead models of Kranbuehl and Verdier.[3,5] They have explained these unexpected high values as stemming from a process in which $\mathbf{R}$ relaxes, at least in part, by rotation of the whole chain, which one would suppose to be a slow process in the presence of EV interactions. The slow relaxation of $\mathbf{R}$ makes the numerical integration of $\rho(\mathbf{R},\mathbf{R},t)$ (eq 7) impractical for $N = 51$ and 72. However, several dynamical properties observed for the chains without EV also exist for those with EV. First, the results for $\tau(R^2)$ are equal, within the statistical error, to those of $\tau(S^2)$. This finding supports the reliability of our best-fit procedure, based on eq 6. Second, as one would also expect, the results for $\tau_{1/e}$ and τ_{int} (which constitute measures for average relaxation times) are always smaller than the corresponding values of the longest relaxation time τ. Third, the results for $\tau(S^2)$, $\tau_{\text{int}}(S^2)$, and $\tau_{1/e}(S^2)$ do not differ much from each other (even though the difference is larger than that observed for the chains without EV). This is in accord with the relatively large values obtained in Table II for $A(S^2)$, i.e., $A(S^2) \sim 1$, which means that τ is dominant already in the early stage of the relaxation. Also, like for the chains without EV, the values for $A(S^2)$ and $A(R^2)$ and $A(\mathbf{R})$ slightly increase with increasing N, which means that the effect of the shorter relaxation times on the corresponding autocorrelation functions decreases for the longer chains. This conclusion is based on the assumption that $\rho(R^2,R^2,t)$ as well as $\rho(S^2,S^2,t)$ and $\rho(\mathbf{R},\mathbf{R},t)$ can be expressed, as in the Rouse model, as a sum of exponentials

$$\rho(R^2,R^2,t) = A \exp(-t/\tau(R^2)) + \sum_i A_i \exp(-t/\tau_i) \quad (9)$$

where $\tau(R^2)$ is the longest relaxation time, the τ_i are the shorter ones, and the A_i are the corresponding prefactors. Since $A + \sum A_i = 1$, any increase in A requires a similar decrease in $\sum A_i$, which means that the effect of the shorter relaxation times weakens. The increase in the results for A (observed in Table II) probably stems from the chain end effects, which are more pronounced for the shorter chains than for the longer ones. It should be pointed out that results for $A(\mathbf{R})$ obtained in former studies showed an opposite trend for the one-bead model[3,6] but did not show any definite trend for the other models ($p > 0$).[6] However, the end effects for these models are practically negligible for the chain length studied here.

As has already been pointed out in the Introduction, for a chain with EV, τ is expected to scale like $N^{2+\epsilon}$ with $\epsilon = 0.2$.[20,21] In Table III we present in parentheses the values for ϵ obtained for only two values of the relaxation times, using the above scaling relation (eq 2). For example, for $N = 33$, the results for ϵ are based on the central values of the relaxation times for $N = 33$ and $N = 21$; for $N = 51$ ϵ is calculated with the values of the relaxation times for $N = 51$ and $N = 33$, etc. This enables one to examine the dependence of ϵ on chain length N. Because of the chain end effects, one would expect ϵ to be larger for the shorter chains and to decrease monotonically as N increases. One would also expect this change in ϵ to be more pronounced for chains with EV than for those without EV. The table reveals that in most cases these expectations are indeed borne out where ϵ drops from the maximal value 0.85 for $N = 33$, to the minimal value 0.27 for $N = 72$. On the other hand, for $\tau_{1/e}(S^2)$, $\tau_{\text{int}}(S^2)$, and $\tau(\mathbf{R})$ the results for ϵ, for $N = 33$ and $N = 51$ are unexpectedly almost equal. However, it is hard to determine the significance of this behavior in view of the relatively large statistical error in ϵ. For $N = 72$ our values for ϵ are always 0.2–0.4, which is close to de Gennes' prediction of 0.2. However, in order to obtain better estimates for ϵ, longer chains should be studied with concomitantly longer MC runs which will decrease the statistical error. Our results for ϵ are in agreement with results for ϵ obtained by the conventional MC procedure, which is based on a single-bead flip and a 90° two-bead crankshaft motion.[11,12] They are, however, different from the value $\epsilon \sim 1$ obtained by Verdier's group using MC procedures which do not include a 90° crankshaft motion. It should be pointed out that our three ways for calculating the relaxation time lead, within the statistical error, to the same values of ϵ; this is important since the $1/e$ criterion, which provides the most tractable computation of the three, can be used for studying the relaxation of longer chains with EV. It should be noted that our results for the relaxation times are significantly smaller than those obtained in former studies. For example, for $N = 33$ we have obtained $\tau(\mathbf{R})/N^2 = 0.169$ as compared to 1.799 and 0.410 obtained by Kranbuehl and Verdier[6] for the models $p = 0$ and 1, respectively, and 0.340 obtained by Gurler et al.[12] for $N = 36$. The last two results should be further increased since they are expressed in larger units of time than our results.

Results for the diffusion coefficient D (eq 8) have been calculated for several periods of time t by changing the parameter K. This enables one to check their convergence. The values appearing in the table (multiplied by N) decrease slightly with increasing N (around $DN = 0.45$); however, it is unclear whether this is a general trend or stems only from the chain end effects. Results for D obtained in ref 12 ($DN \sim 0.25$) are also inconclusive in this respect, which means that longer chains should be studied. These findings are in contrast with the results of Kranbuehl and Verdier[6] in which the values for DN strongly decrease with increasing N, for all models $0 \leq p \leq 1$.

To summarize: For chains with EV our MC procedure defines a different mechanism of relaxation than the conventional MC procedures,[1,6,8,10–12] which leads to significantly smaller values of τ but, for sufficiently long chains, leads to the theoretically expected dependence of τ on N. This result demonstrates the universality of eq 2, discussed in the Introduction.

It is of interest to compare the efficiency of the present MC method with the conventional one. We have, therefore, simulated the chain model with EV (for $N = 21$, 33, and 51) also with the MC procedure based on a one-bead flip and a 90° crankshaft motion (for details see ref 8). We found that with this method, in order to obtain approximately the same 250 values of the autocorrelation functions as those obtained with our methods, the value of K had to be increased by a factor of ~6.5, which required (using the Fortran Q compiler), ~20% more computer time. This is not a significant difference, but one has to bear in mind that the EV effect for a single chain on the simple cubic lattice is relatively weak. In order to check the efficiency of the two methods for a system with stronger EV interactions, we have simulated a single-chain model with EV, which mimics, to some extent, a dense, many-chain system. Prior to the simulation, part of the lattice has been filled randomly with "obstacles"; i.e., in addition to the EV interaction, a bead is not allowed to lie on a lattice site which is occupied by an obstacle. The results showed that the efficiency of our method, as compared to the conventional one, increased with increasing the fraction of the obstacles on the lattice. For example, for $N = 33$ and a fraction of 0.2, calculation of a certain value for $\langle d^2 \rangle$ (eq 8) required $\sim$3 times less computer time with our method than the conventional one. When this fraction was further increased to 0.3 and 0.4, our method yielded $DN \sim 0.1$ and 0.02, respectively, whereas with the conventional method the center of mass did not move at all (i.e., $D = 0$) even for very long runs. This gives reason to believe that the present method will be more efficient also for dense, many-chain systems. In the future we intend to use our method for checking de Gennes'[29] reptation hypothesis in dense entangled many-chain systems.

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Free Energy Determination of Polypeptide Conformations Generated by Molecular Dynamics

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ABSTRACT: Molecular dynamics (MD) simulations of macromolecules are normally restricted to tens of picoseconds and do not produce statistical averages over all relevant conformational states. It is shown for the tetradecapeptide somatostatin as an example that MD at elevated temperatures can be used to generate new conformations. The statistical weight of each conformation depends on its entropy. The entropy for two conformations has been determined by analysis of the distribution functions of generalized coordinates (bond angles and dihedral angles) and by their correlations. The results show that the significant difference in internal energy of the two conformations is compensated by entropy differences, yielding comparable free energies. Effects of constraints, coordinate transformations, and quantum corrections are discussed.

1. Introduction

The method of molecular dynamics (MD), simulating the dynamical behavior of a molecular system by integrating Newton's equations of motion, has so far been successfully applied to a large variety of systems. These include small peptides in solution,[1] proteins in vacuo,[2-5] and a protein including surrounding water in a crystalline environment.[6] Up to now MD has not been applied to flexible polypeptides with a large number of conformations that may have rather different properties. Many biologically important molecules as hormones belong to this class. Although smaller, such molecules are more difficult to study with MD techniques than proteins that cover a more confined region of conformational space. The passage between different conformational states is too rapid to isolate and study the separate conformational states. Thus, the experimentally known properties of such molecules are averages over many conformations. To interpret experimental properties, a range of individual conformations with their relative probabilities has to be studied by theoretical methods. MD is generally limited to time spans in the range 10–100 ps, which is insufficient to obtain appreciable averaging over different conformations.

The purpose of this paper is twofold. First, we show that it is possible to generate new conformations by heating the system, i.e., by performing MD simulations at a temperature of 600–1200 K and subsequently cooling to room temperature. Secondly, we try to estimate thermodynamic properties of the conformational substates, with the aim of determining their statistical weight. The latter is proportional to $\exp(-\Delta G/k_B T)$, where $\Delta G = \Delta H - T\Delta S$ is the

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