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The Bond Fluctuation Method: A New Effective Algorithm for the Dynamics of Polymers in All Spatial Dimensions

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ABSTRACT: We present a new effective algorithm to simulate dynamic properties of polymeric systems confined to lattices. The algorithm displays Rouse behavior for all spatial dimensions. It combines typical advantages of lattice Monte Carlo methods with those from the continuous Brownian dynamics algorithm. In addition, it allows for the simulation of branched structures and is shown to be ergodic. Detailed numerical tests for random and self-avoiding walks are performed for $d = 2$. For SAWs the power law for the mean-square displacement for inner monomers, $g(t) \propto t^{1/(1+(1/2\nu))}$ ($\propto t^{0.6}$, $d = 2$), is clearly found. Also, an anomaly in the static structure function $S(k)$, which is typical for $d = 2$ linear polymers, was found. We can also compare this ergodic algorithm with a nonergodic one, which seems to be suitable for isolated chains.

I. Introduction

Computer simulations have proven to be a very valuable tool for statistical physics for many years.[1] This happens to be true especially for the simulation of polymers.[2] Since polymers are very complicated topological objects, computer simulations often are the best tool to get precise theoretical information on the proposed model. For the subsequent discussion we confine ourselves to Monte Carlo methods. Nevertheless, molecular dynamic methods are very important for specific applications.[3] The Monte Carlo methods themselves can be separated into two major groups. The first are static or quasi-static methods. Here, chains are generated by a certain algorithm, and information on static properties is deduced. These methods provide high-accuracy data for static properties but do not allow for any dynamic interpretation.[4] Note that we here include the slithering snake algorithm of Wall and Mandell[5] and the pivot algorithm.[6]

Here we are interested in a dynamic algorithm that allows for the analysis of dynamic properties of polymers. This itself might be of no special interest since many lattice algorithms that obey Rouse dynamics[7–10] are given in the literature. The Rouse model describes the motion of a polymer by the Brownian dynamics of the monomers of a polymer chain. The monomers are connected, e.g., by springs. For random walks this model can be solved exactly.[11,12] It is a useful convention that only such algorithms can be regarded as valid for dynamical properties which reproduce (without hydrodynamic interaction) the Rouse dynamics. However, all of the dynamic Monte Carlo algorithms have several serious disadvantages. First, they do *not* allow for the simulation of two-dimensional polymers, as will be shown in the next section. This, however, would be very desirable. A polymer in a narrow slit should follow the Rouse dynamics since the hydrodynamic interaction is strongly screened by the boundary condition of the walks. In addition, the effect of the excluded volume is much stronger in $d = 2$ than in $d = 3$ (d represents dimensions). Thus it should be easier to study in $d = 2$. Secondly, the standard algorithm does *not* allow for the simulation of branched objects. There, branching points cannot move. A third difficulty was discussed more recently.[13] The lattice algorithms[8–11] are not ergodic. Although this is not a serious problem for isolated chains, it might cause difficulties for very dense systems.

Given these arguments, we think it is important to define a new dynamic Monte Carlo algorithm. It consists of single bead moves, has Rouse dynamics for all spatial dimensions, allows for dynamic simulations of linear and branched polymers (rubbers, stars, etc.), uses a lattice (which makes it very fast for computers), and is ergodic. In section II we define the algorithm and explain its basic properties. Section III displays detailed numerical tests for $d = 2$. Section IV gives a short summary and a discussion of possible applications of the method.

II. Bond Fluctuation Method

The typical situation for a dynamic Monte Carlo simulation is described in Figure 1. Especially for $d = 2$ these methods lead to an artificially slow dynamics. The reason is that new bond orientations for a self-avoiding walk (SAW) or a nonreversal random walk (NRRW) only can diffuse into the chain from the end. Kinks cannot pass through each other. (The NRRW is the random walk which obeys the SAW condition only for nearest and next-nearest neighbors along the chain.) This was already shown by Hilhorst and Deutch.[14] Therefore, standard dynamic Monte Carlo algorithms cannot be used to extract information on two-dimensional polymer dynamics. Consequently, such kink jump methods[7–11] are not effective to obtain static information as well because of their slow relaxation for $d = 2$. For $d = 3$ the situation is better; however, the simulation of branched objects still is not possible. For a general discussion we refer to ref 4.

What is needed is a dynamic algorithm, which moves a *polymeric object* by *local jumps of the monomers*. The number of monomers (bonds) has to be fixed. Such moves have to have the property of not conserving the set of bond vectors of the object, while still conserving the number of bonds. The only way to do this is to allow for a variable bond length. Such a model can be implemented on a lattice and has all the desired features.

Definition of the Algorithm. The polymers consist of N monomers. Note that in a MC simulation one monomer always means one Kuhn's segment. They are implemented on a square lattice with lattice constant 1. Each monomer occupies four ($d = 2$) lattice sites of a unit cell. In the following text we name this model the four-site model. Each lattice site can only be part of one monomer (SAW condition). The bond length, l, has to be *smaller* than $16^{1/2}$. This condition is necessary to avoid bond cuts. To move the chain, a monomer is selected at random. Then it tries to jump at random the distance of one lattice unit into one of the four (two-dimensional) lattice direc-

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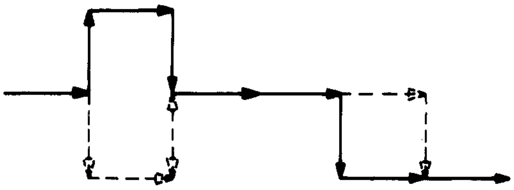

Figure 1. Two allowed moves (two-bond and three-bond moves) in a standard dynamic Monte Carlo algorithm.

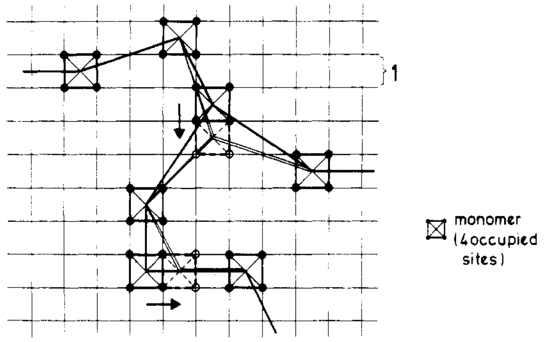

Figure 2. Typical motions for a two-dimensional branched object. The bond length is greater than or equal to $4^{1/2}$ and smaller than $16^{1/2}$. No lattice site is occupied by more than one monomer, and a monomer consists of four occupied sites (four-site model).

tions. If the move complies with both the bond length restriction and the SAW condition, it is accepted. If not, a new monomer is selected at random and so on. One can also choose another shape of the monomer. This gives only another average bond length, another bond length restriction, and another persistence length.

Figure 2 gives an example for typical motions for a two-dimensional branched object. It also clearly shows that the set of bond vectors within the polymer is not conserved and that branching points can move as well. It should be noted that a similar approach was used for the simulation of tethered surfaces.[15] They use an off-lattice algorithm, which is, by far, not as effective as the one described here.

The extension of this method to $d \neq 2$ is obvious. For $d = 3$ the monomer is given by the unit cube and occupies eight lattice sites. In the subsequent discussion, we confine ourselves to $d = 2$, since this is the most crucial test case. For the $d = 2$ version the minimal distance between two monomers is $l = 2$. The maximal allowed distance, which is less than $16^{1/2}$, is $13^{1/2}$ ($d = 2$). In between l can have the values $5^{1/2}$, $8^{1/2}$, 3, and $10^{1/2}$. In Figure 2 all typical distances are displayed. All together we have a set of 36 bond vectors. The choice of the upper limit for the bond length is governed by the information we want to gain. Since we look for dynamic properties $l^2 < 16$ guarantees that bonds never cut through each other during the course of the simulation if we start with a configuration that is self-avoiding and has no bond cuts. For $d > 2$ this has to be checked separately. This, of course, is necessary in order to obtain information which comes from the topological structure of the objects. Figure 3 displays the ability of the model to simulate branched objects. For $d = 2$ it is already possible to simulate branching points with up to eight arms. This makes this method especially suitable for the analysis of dense or highly branched polymers.

Since here the monomers move in every jump only a part of a bond length, this method for $d = 3$ typically is not as fast as the standard methods. Here monomers jump by more than a bond length. That makes it faster due to fast local motion. However, this effect is partially compensated by the smaller persistence length of the present model. It will display its advantages for dense and branched structures.

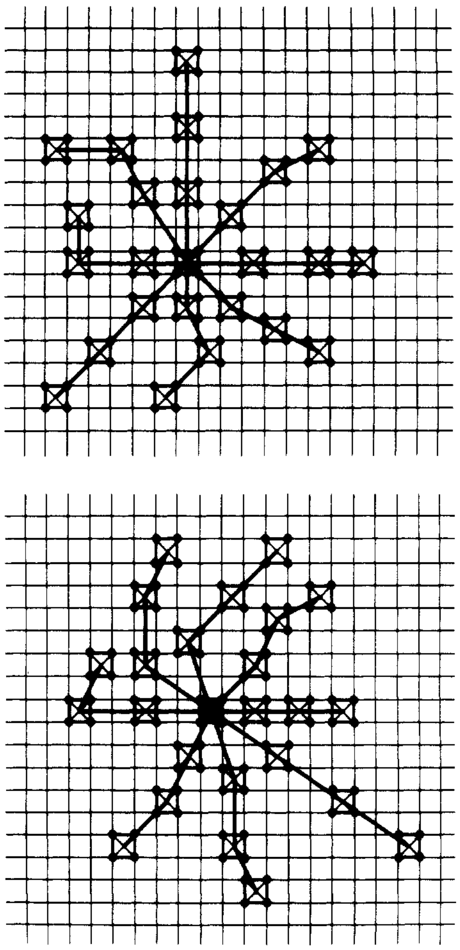

Figure 3. Two-dimensional stars with eight arms; in this case the branching point is not fixed by the neighboring monomers.

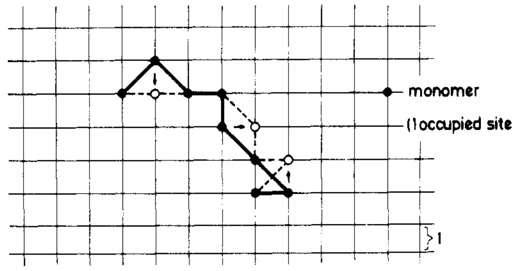

Figure 4. Typical motions for a two-dimensional linear chain. The bond length is greater than or equal to 1 and smaller than $2^{1/2}$. No lattice site is occupied by more than one monomer, and a monomer consists of one occupied site (single-site model).

For comparison, for $d = 2$ and the isolated chain we propose a nonergodic algorithm, which is suitable for a single isolated chain. In the following text we name the model the single-site model. (Branched objects are only possible with up to three branches.) Again the chain is implemented on a square lattice with lattice constant 1. Now each monomer consists of a single lattice site, and the bond length is confined to $l^2 < 4$. Here the constraint $l^2 < 4$ is necessary to avoid bond cuts. The elementary moves are the same. We now have a set of eight bond vectors with a length of $l = 1$ and $2^{1/2}$ in $d = 2$ and 1 and $2^{1/2}$ in $d = 3$. Figure 4 shows an example of such moves. The procedure of the simulation is the same as in the first case.

Figure 5a shows three configurations which are not movable. Figure 5b shows that equivalent configurations in the four-site model can move, and every knot is solvable.

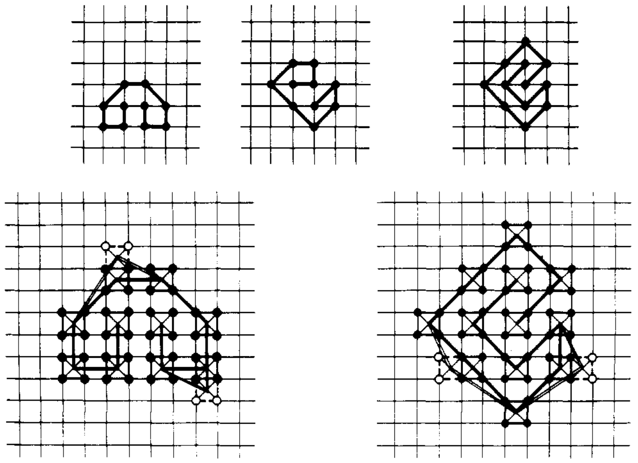

Figure 5. (a, Top) Three typical configurations in the single-site model which are not movable. (b, Bottom) Two blocked configurations in the four site-model; a possible way of moving such configurations is shown.

Comparison of the results gives no difference if we restrict the polymers to movable ones; therefore, the nonergodicity of the standard dynamic lattice methods didn't cause any problems for the simulation of dilute systems. However, for very dense systems such problems (although not yet found) might be of higher importance. Then extreme care has to be taken during the construction of the initial configuration. With respect to the anticipated applications to dense systems, it is useful to show that the first method is ergodic. We do this by looking at the most crucial case, which, again, is $d = 2$. Reference 13 gives the typical configurations which cannot be reached in a simulation. If the initial state happens to sit in such a situation, it never leaves it. Here we show that such configurations do not cause a problem. As Figure 5b displays, there always is a way out of the blocked state because you have more than one bond length in every spatial direction. It should be noted that all the algorithms Madras and Sokal[13] propose as "good" ones allow only for the analysis of static properties. They thus exclude the huge class of interesting and important dynamic effects of macromolecular systems. Here we give a method which is ergodic. As will be shown in section III, it also has the required dynamics.

III. Numerical Test

To test the numerical efficiency, SAWs in two dimensions for up to 800 bonds were simulated. To test directly the Rouse dynamics also, random walks (RW) with up to $N = 100$ monomers were analyzed. RW here means that, besides the bond length restriction, the excluded volume is only taken into account between nearest neighbors along the chain. By this exactly the same set of bond vectors is allowed as in the SAW case. Since we use a lattice structure in the course of the simulation, the success of an attempted move can be easily checked by the use of occupation numbers. This makes the program fast enough to simulate two-dimensional SAWs e.g., $N = 54$ monomers, on a standard IBM-AT personal computer. The bigger systems were simulated on a Fujitsu VP-100 vector processor. A very high degree of vectorization was obtained by simultaneously running up to 250 chains independently of each other. The time factor between a 1-chain and a 250-chain run for $N = 100$ was about 15. The use of occupation numbers makes it especially fast for standard computers as well. However, by the trick described above, one can also obtain the full efficiency of modern supercomputers.

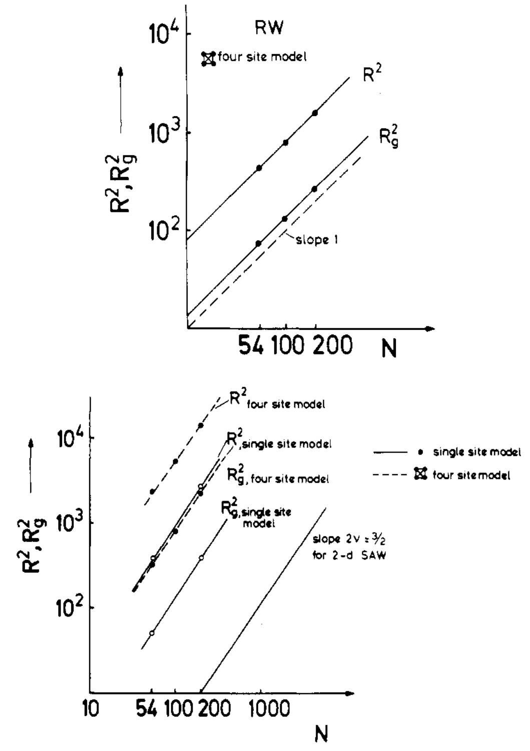

Figure 6. (a, Top) Plot of end-to-end distance $\langle R^2\rangle$ versus chain length N for RWs, done with the four-site model, $\langle R^2\rangle \propto N$, $\langle R_g^2\rangle \propto N$ ($\nu = 1/2$). (b, Bottom) Plot of end-to-end distance $\langle R^2\rangle$ and radius of gyration $\langle R_g^2\rangle$ versus chain length N for SAWs done with the four-site and the single-site model, $\langle R^2\rangle \propto N^{3/2}$, $\langle R_g^2\rangle \propto N^{3/2}$ ($\nu = 3/4$).

Although we are mainly interested in dynamic properties, it is necessary to control the static ones as well. Thus, during our runs we calculated the average end-to-end distance

$$\langle R^2(N)\rangle = \langle(\vec{r}_1 - \vec{r}_N)^2\rangle \tag{1}$$

where $\vec{r}_1 - \vec{r}_N$ is the distance between the first and last monomer of the chain. In addition, we checked the mean-square radius of gyration

$$\langle R_g^2(N)\rangle = \frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{\mathrm{cm}})^2 \tag{2}$$

with

$$\vec{r}_{\mathrm{cm}} = \frac{1}{N}\sum_{i=1}^{N}\vec{r}_i$$

and the structure function

$$S(k) = \frac{1}{N}\left\langle\left|\sum_{i=1}^{N} e^{i\vec{k}\vec{r}_i}\right|^2\right\rangle_{|k|} \tag{3}$$

The index $|k|$ denotes a spherical average over k-vectors of length k.

Figure 6 gives R^2 and R_g^2 for various systems. The RWs clearly give $R^2 = l^2N$, where $l = 2.87$ for the four-site model. For the SAWs the exponent $\nu = {}^3/_4$[16] is clearly exhibited for both models. With an average bond length $l_{\mathrm{FS}} = 2.89$ for the four-site model and $l_{\mathrm{SS}} = 1.21$ for the single-site version we have

$$\langle R^2(N)\rangle = l^2 l_p^2 N^{2\nu}; \quad \nu = 3/4 \tag{4}$$

where l_p is the persistence length, which yields $l_p = 0.87$ for the four-site model and $l_p = 0.76$ for the single-site model, respectively. Subsequently we always discuss the four-site model, if not stated otherwise. More complicated, however, is the static structure function. For intermediate

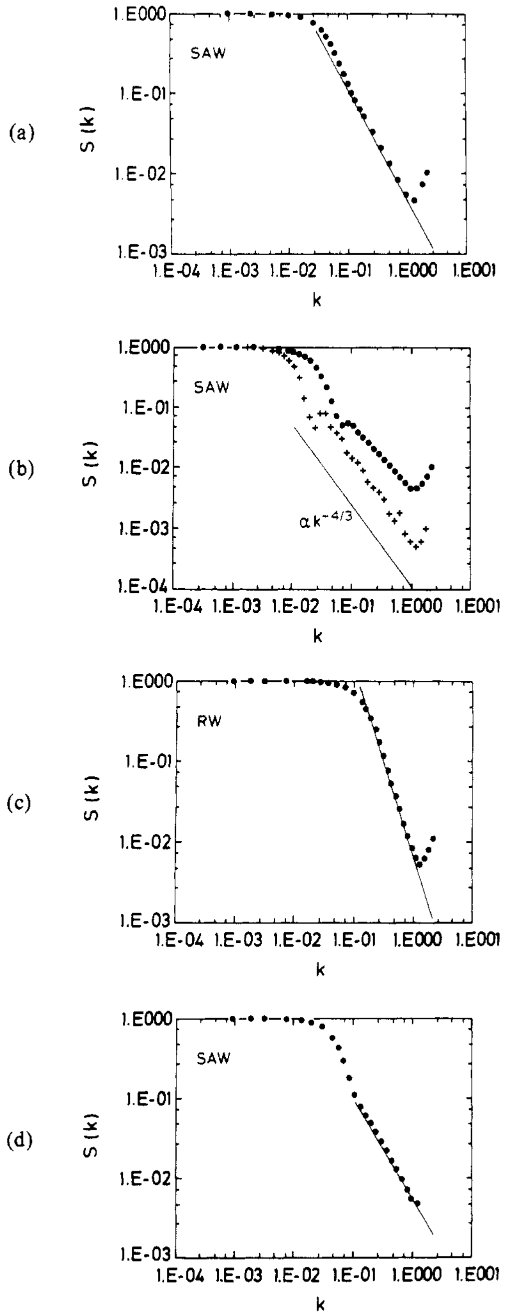

Figure 7. (a) Static structure function for SAW polymer chain with 100 monomers. One clearly sees a bump around $2\pi/R$ = 0.085. For the Kratkey plot this gives the maxima discussed in the text. The slope is around $^4/_3$. (b) Static structure function for SAW polymer ring with 800 monomers (+) and 100 monomers (●). The asympotic slope, $^4/_3$, is seen very well for the 800-monomer ring besides statistical fluctuations. (c) Static structure function for RW polymer ring with 100 monomers. The asymptotic slope is around 2; no maximum around $2\pi/R$ is seen. (d) Static structure function for a SAW two-dimensional star with three arms of 33 monomers each.

k, namely, $2\pi/R_g < k < 2\pi/l$, one expects the fractal scattering law $S(k) \propto k^{-1/\nu} \propto k^{-4/3}$.

This was seen for d = 3 both in experiments and in simulations.[2,17] For three-dimensional SAW rings now it is well-known that this so-called Kratky plot exhibits a maximum around $k = 2\pi/R$ ($R = \langle R^2\rangle^{1/2}$).[3,18] This typically comes from the fact that for these distances the scattered wave sees a higher density as the fractal structure of the object suggested. One measures two connected strands. For SAWs in d = 3 this does not occur.[19] Now for two-dimensional SAWs one again observes this effect *also* for *linear*, noncyclic chains. It should be noted that this is not an artifact of a new MC method. In a different context this was also found with a static algorithm.[20] Figure 7 gives the results for several SAWs and RWs. Note that this effect makes it very difficult to extract the exponent ν from $S(k)$, while for d = 3 this is one of the best methods. This enhanced density effect at $k \approx 2\pi/R$ clearly comes from the ends. For an infinite walk the ends cannot fold back and produce a higher density; thus, one always measures single-strand properties. Indeed this effect became much weaker when we analyzed only the inner half (third) of long chains. In principle one would expect a similar effect for d = 3. There, however, it is too small to observe easily.

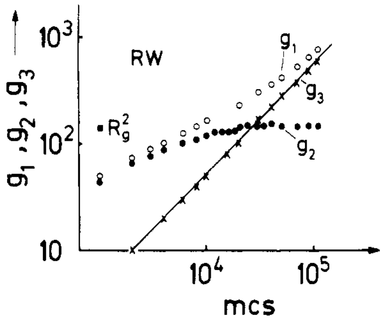

Figure 8. Plot of g_1,g_2,g_3 for a random walk; the chain length is 100. One clearly finds for short times g_1,g_2 $\propto t^{0.5}$. For calculation of these points 250 independent configurations are taken into account.

For the dynamical properties, we first look at the mean-square displacements averaged over the five inner monomers. Mainly, we are interested in three quantities:

$$g_1(t) = \frac{1}{5}\sum_{i=(N/2)-2}^{(N/2)+2} \langle(\vec{r}_i(t) - \vec{r}_i(0)^2)\rangle$$

$$g_2(t) = \frac{1}{5}\sum_{i=(N/2)-2}^{(N/2)+2} \langle[(\vec{r}_i(t) - \vec{r}_{\mathrm{cm}}(t)) - (\vec{r}_i(0) - \vec{r}_{\mathrm{cm}}(0))]^2\rangle$$

$$g_3(t) = \langle(\vec{r}_{\mathrm{cm}}(t) - \vec{r}_{\mathrm{cm}}(0))^2\rangle \qquad (5)$$

$g_3(t)$ describes the diffusion of the overall system. Following the Rouse model one expects[12]

$$\left.\begin{array}{l} g_1(t) \propto g_2(t) \propto t^{1/[1+(1/2\nu)]}\ (t^{0.5}\ \mathrm{RW},\ t^{0.6}\ \mathrm{SAW}) \\ g_3(t) \propto t \end{array}\right\} t < \tau_{\mathrm{R}}$$

$$\left.\begin{array}{l} g_1(t) \propto g_3(t) \propto t \\ g_2(t) \propto \mathrm{const} \end{array}\right\} t > \tau_{\mathrm{R}} \qquad (6)$$

τ_{R} is the Rouse relaxation time, with

$$\tau_{\mathrm{R}} \propto N^{1+2\nu}\ (N^2\ \mathrm{RW},\ N^{2.5}\ \mathrm{SAW}) \qquad (7)$$

Figure 8 gives a plot of g_1, g_2, and g_3 for a random walk. By analyzing different chain lengths one clearly finds $\tau_{\mathrm{R}} \propto N^2$. Both display the expected behavior for g_1 and g_2. The ratio of the plateau values of g_2 for the two chain lengths considered is equal to the ratio of the chain lengths. In the Rouse model the diffusion constant D is given by $D = kT/\xi N$ with $4D = \lim_{t\to\infty} g_3(t)/t$.[12] The time unit here is one attempted move per monomer. The mean-square displacement of a free monomer then is $g_3(t,N{=}1) = t$. By checking the acceptance rate of the moves, A, we have a direct expression for kT/ξ. This gives $A = 4\ (kT/\xi)$ and

$$4D = A/N \qquad (8)$$

With A = 0.526 for the RW case we see a very good agreement to the data. Actually, D is slightly smaller than

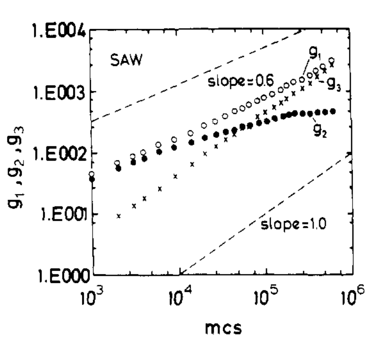

Figure 9. Plot of g_1,g_2,g_3 for a self-avoiding walk. The chain length is 100. One clearly finds for short times $g_1,g_2 \propto t^{0.6}$. For calculation of these points 1000 independent configurations are taken into account.

expected from (8): $4D \approx 5.2 \times 10^{-3}$ for $N = 100$, $4D \approx 2.3 \times 10^{-3}$ for $N = 200$. This is a consequence of averaging over all monomers along the chain and, therefore, a consequence of the connectivity.

For SAWs the situation is slightly different. Here the Rouse model cannot be solved exactly. However, from scaling considerations one expects $\tau_R \propto N^{2.5}$ (eq 7)[12] and $g_1 \propto g_2 \propto t^{0.6}$.[21] While the $N^{1+2\nu}$ dependence of τ_R has been seen quite clearly for SAWs in $d = 3$,[9,10] it is difficult to obtain the $t^{1/(1+(1/2\nu))}$ behavior of g_1 and g_2. For MD data this was seen for $d = 3$.[3] However, for $d = 3$ one has $1/(1+(1/2\nu)) \approx 0.54$, which is hard to distinguish from $^1/_2$. Therefore, we expect a much clearer signature for $d = 2$. Figure 9 shows the expected behavior. Again the plateau values of g_2 follow the $(N_1/N_2)^{2\nu}$ ratio with $\nu = {}^3/_4$. The longest relaxation times scale with $N^{1+2\nu} = N^{2.5}$. Thus the algorithm gives a consistent picture both for RWs and for SAWs. Additional checks of the autocorrelation function of the end-to-end distance are in excellent agreement. The acceptance rate for SAWs is about 47%. The diffusion constant D for a chain of 100 monomers is about 4.3×10^{-3} and for a chain of 200 monomers about 2.12×10^{-3}.

Since there was a recent discussion on the validity of the Rouse modes for SAWs[9,10] we checked this for both the RWs and SAWs. For the RWs all the requirements of the Rouse model are fulfilled, while for the SAWs the modes are strongly mixing. One clearly can say that the Rouse modes as defined for the RWs are not the normal modes for two-dimensional SAWs. Again this effect of the SAW condition for $d = 2$ is *much* stronger than for $d = 3$.[22]

IV. Conclusion

In this paper we presented and tested a new Monte Carlo algorithm for dynamical simulation of polymers. Due to the concept of fluctuating bond lengths, it has the advantage of giving realistic (Rouse) dynamics in all spatial dimensions and allowing for the simulation of branched structures. All standard dynamic MC algorithms for polymers on lattices[2,4,7-11] do not fulfill one of these two aspects. As an additional advantage, the algorithm is ergodic. Since we use a lattice structure of the background, very effective programming is possible on both scalar *and* vector computers. The tests displayed in the previous section show the wide applicability of the method. Since the elemental jumps of the monomers are smaller than a bond length, the method will become especially good for dense and/or highly branched systems. Since such systems are becoming more and more important, we think that the idea of fluctuating bond lengths on a lattice background will receive a wide application.

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