

Modified Self-Avoiding Walk in a Polymerization Process

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The modified SAW (mSAW) is defined as a statistical method to treat a polymerization process in a manner similar to that used to treat chains with excluded volume statistics where no two monomers can occupy the same site in space. Unlike the chains with excluded volume statistics, the walk algorithm does not terminate when the next walk is an occupied site. Instead the walker continues along a different direction. Monte Carlo simulations of the random walk are carried out on both 2D and 3D lattices. Universality classes different from those of the chain with excluded volume statistics are found. The critical exponents of the mean-square end-to-end distance are found to be 1.437 (0.005) for 2D and 1.007 (0.004) for 3D, where the figures in the parentheses are the uncertainties of the last digit. The universality classes are determined from rigorous computer simulations.

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A self-avoiding walk (SAW) is a well accepted method used to investigate a homopolymer in a good solvent [1, 2]. This is because this simple model captures the essential physical properties of the system. The SAW has a random-walk-like feature. It also incorporates the fact that no two monomers can occupy the same spatial position. As Amit *et al.* [3] and Peliti [4] pointed out, a “true” self-avoiding walk is different from that of the SAW used in polymer problems. In addition, it is of a different universality class. The SAW has been shown to have an upper critical dimensionality of 4. Pereira [5] has presented a good review of polymer structure from the viewpoint of the SAW.

One of the fundamental geometrical properties that characterize a polymer in the polymerization process is the mean square of the end-to-end distance or the radius of gyration $\langle R^2 \rangle$ [6]. It is well established that $\langle R^2 \rangle$ is related to the number of monomers or N steps making up the chain in the asymptotic limit through the scaling relation

$$\langle R^2 \rangle = AN^{2\nu}, \quad (1)$$

where A depends on the microscopic lattice. The critical exponent 2ν is, however, universal. The critical exponent depends only on the spatial dimension D . Due to the universal character of 2ν , it has been measured to great accuracy. The theoretical results are given by the Flory formula [1]

$$\nu \approx \frac{3}{D+2} \quad \text{for} \quad (1 \leq D \leq 4) \quad (2)$$

Equations (1) and (2) have been verified for chains of different topologies in both experimental and computer simulation studies [2,6–11]. Within the SAW approach, 2ν is equal to 1.500 and 1.200 in 2D and 3D, respectively.

Since it is difficult to study the dynamic properties of the SAW model analytically, one uses computer simulation. The most versatile technique is the Monte Carlo (MC) method or statistical sampling technique [12,13]. This method can handle complicated phenomena in a straightforward fashion, provided the transition probabilities are explicitly defined. A simulation based on the previously defined SAW or on the chains with excluded volume model will be referred to in this paper as a conventional self-avoiding walk or cSAW. The shortcoming of a cSAW is that the probability of randomly generated walks being self-avoiding decreases exponen-

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tially with chain length. Narasimhan *et al.* [14] recently pointed out that this shortcoming prevents the cSAW from being used to grow maximally compact configurations. This would preclude its use for studying new problems such as the folding of a protein. To overcome this shortcoming, they introduced the interacting growth walk (IGW) model.

The present authors wish to introduce another model called the modified SAW (mSAW), which will attempt to overcome the problem of sample attrition as N increases. The mSAW is similar to the cSAW, except that the walk algorithm does not terminate when it encounters an occupied site. Instead, the mSAW continues along an unoccupied site direction. Also, unlike the “true” SAW of Amit *et al.* [3], the mSAW does not only *try* to avoid the visited site, but it *completely avoids* the visited site. The mSAW is believed to imitate a real world system better than the cSAW does. An example for which our suggested model can well be used is large proteins [15]. Proteins are considered to be macromolecules having large molecular weights. They need to be big enough to contain certain information in order to have a specific function [16]. With the cSAW, such molecules with large molecular weights are not possible because the algorithm terminates the chain before it gets big enough. However, with mSAW, such large molecular weight proteins are possible.

If our model is to be justified from a statistical physics viewpoint, the concern regarding whether it violates a detailed balance condition resulting from the “bias effect” of the ensemble average must be addressed in a way that is statistically physically relevant. However, this problem can and should be viewed differently by using a chaotic-phenomenon-like aspect. Having applied our model algorithm, we find that our mSAW has an additional feature, namely, the nonlinear feedback from the environment (its historical path or chained monomers) to keep it walking, which gets higher as time progresses. When the polymer chain gets longer or the macromolecular protein gets bigger, the path or conformation becomes more complex, increasing considerably the chance of this self (new)monomer-(old)monomer interaction between the current monomer and the past monomer in the polymer chain. This “interacting landscape” affects what the next configuration or the final conformation will be in an uncertain way. Therefore, this large nonlinear feedback of this complex chain may be a chaotic phenomenon. What and how this phenomenon occurs are typically known, but why nature adapts in this is not known. Hence, when we use the conventional non-equilibrium statistical mechanism concept via the condition of detailed balance, the condition ensures that the Markov process is the Boltzmann probability distribution that is generated after the system has come to equilibrium. This may not be the best or most suitable picture to convince the reader that this model is realistic, but it is the only one thus far.

In this paper, each monomer is represented as a circle

in 2D and a spherical ball in 3D with a constant bond length. Six spatial lattice arrangements are investigated: (1) a 2D square lattice, (2) a 2D hexagonal lattice, (3) a 3D simple cubic, (4) a 3D body-centered cubic, (5) a 3D face-centered cubic, and (6) a 3D hexagonal close-packed.

We see in Fig. 1 a square lattice (SL) of open circles representing the possible coordinates at which each new monomer can be placed during the polymerization process. The walk begins with 2 monomers. The next most recent monomer to be placed in the chain is the bricked circle labeled 2. The next position is chosen randomly from the three nearest neighbor circles as indicated by the arrows labeled 3a, 3b, and 3c. The fourth nearest neighbor, labeled 1, is a forbidden walk. The walk terminates only when the assigned N is achieved or when all the nearest neighbor sites are occupied. The *priori equal probability* is conserved because for each new step, only the unoccupied sites are being reweighed. For example, in the 2D square lattice, when there are 3 unoccupied nearest neighbors, the probabilities of walking in the three directions are equal to $1/3$. However, if the walk encounters a situation where there are only 2 unoccupied sites, the probability of each direction is $1/2$. The end-to-end distance (R) is recalculated for each walk that is added to the chain. The mean square of the end-to-end distance ($\langle R^2 \rangle$) is averaged over at least 1000 realizations. The end-to-end distance distribution ($P(R)$) is also calculated for various N in all lattices.

As mentioned earlier, the Flory theory and the cSAW predict that the scaling laws for 2D and 3D can be fit with slopes of 1.500 and 1.200, respectively [1, 2, 6–11]. Figure 2 plots $\langle R^2 \rangle$ versus N generated by using the

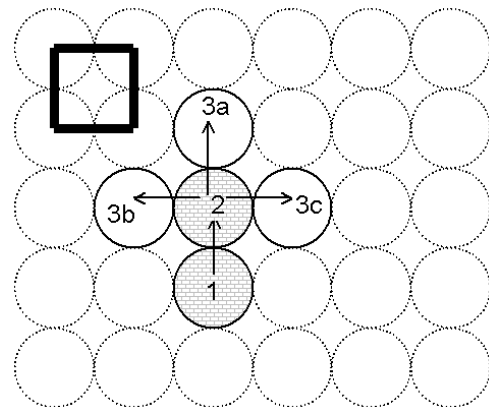


Fig. 1. **Walk on a square lattice.** The square lattice (SL) of open circles represents the possible coordinates where each new monomer can be placed during the polymerization process. The walk begins with 2 monomers. The most recent monomer to be placed in the chain is the bricked circle labeled 2. The next position is chosen randomly from the three nearest-neighbor unoccupied circles as indicated by the arrows and labeled 3a, 3b, and 3c. The fourth nearest neighbor, labeled 1, is a forbidden walk.

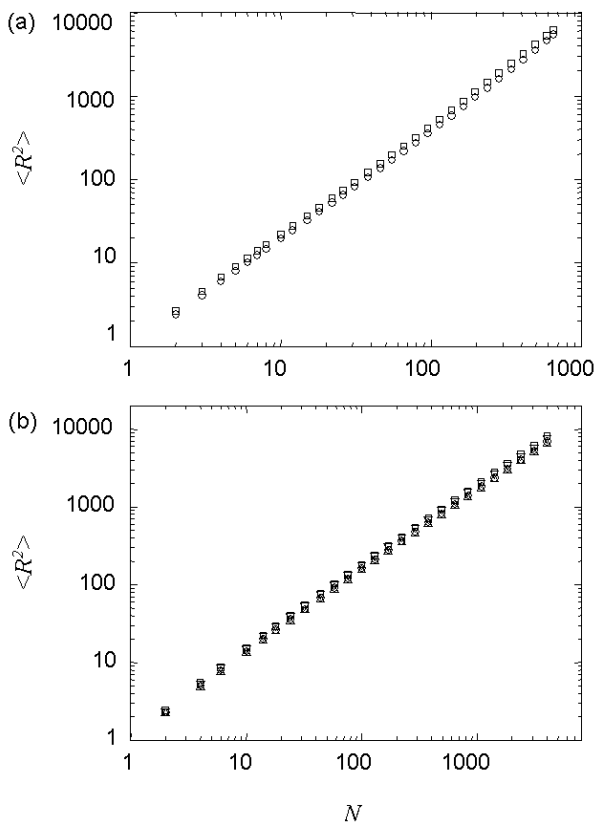


Fig. 2. **Plots of the mean square of the end-to-end distance versus the number of monomers in the chain:** (a) generated by using the mSAW for 2D lattices and (b) generated by using the mSAW for 3D model lattices. Both the 2D square lattice (\square) and hexagonal lattice (\circ) have approximately the same slope of 1.437 (0.005). All 3D simple cubic (\square), body-centered cubic (\circ), face-centered cubic (\triangle), and hexagonal close-packed (∇) lattices have approximately the same slope of 1.007 (0.004). The mSAW shows a universal scaling behavior, but deviates from that of the cSAW.

mSAW in 2D and 3D. The universality of the scaling law based on the Flory relation is found to break down. The slopes for all of the lattice structures in both 2D and 3D deviate from those of the cSAW. For 2D lattices, the slopes (Fig. 2(a)) is 1.437 (0.005) instead of 1.500. For the 3D lattices, the slopes (Fig. 2(b)) of $\langle R^2 \rangle$ versus N is 1.007 (0.004) instead of 1.200. The simulations on various lattices structure agree with the data from Domb *et al.*, Wall and Hioe, and McKenzie [17–19] that for long walks, the asymptotic behavior is independent of the lattice structure. Therefore, only a 2D square lattice and a 3D simple cubic lattice will be mentioned in this discussion.

The critical exponent 2ν in 2D is less in the mSAW than in the cSAW by approximately 0.063 (0.005). This may be due to the fact that with the mSAW, the algorithm allows the chain to be more packed than with the cSAW. The reason for this is that with the mSAW, the chain is allowed to continue until there are no more sites

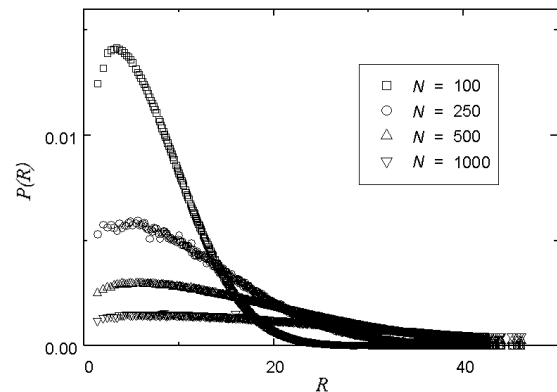


Fig. 3. **Probability distribution ($P(R)$) versus the end-to-end distance (R) for various numbers of repeating units** based on the simulations using the mSAW for the 3D simple cubic lattice. $P(R)_{max}$ is seen to decrease as the number of repeating units is increased.

available. In 3D, however, the universality class in the mSAW is much less than that of the cSAW. It is much closer to that of the random walk (RW), *i.e.*, 1.000. This results not only from the more closely packed nature of the algorithm but also from the fact that the mSAW resembles more of the RW behavior. The proposed mSAW algorithm has freedom similar to that of RW and still preserves the excluded volume principle. Here, the proposed mSAW algorithm is believed to model a real world system more closely than the cSAW does.

The probability distribution ($P(R)$) versus the end-to-end distance (R) with the mSAW on a 3D simple cubic lattice is shown in Fig. 3. The result in 2D shows a trend similar to that in 3D, so it is not shown in the paper. $P(R)_{max}$ is seen to decrease as the number of repeating units is increased. This is expected as it is observed in all random walks.

MC simulations have been used to investigate the mSAW polymerization model in 2D and 3D lattices. We measured the simulated end-to-end distance (R) and its associated probability ($P(R)$). The mSAW results suggest an asymptotic scaling relation between $\langle R^2 \rangle$ and N . $\langle R^2 \rangle$ increases with N to a power of 1.437 (0.005) in 2D and 1.007 (0.004) in 3D. The mSAW model is hypothesized to have a different universality classes; *i.e.*, it is characterized by scaling exponents different from those of the cSAW or of the chains with excluded volume.

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