Indefinitely Growing Self-Avoiding Walk

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We introduce a new random walk with the property that it is strictly self-avoiding and grows forever. It belongs to a different universality class from the usual self-avoiding walk. By definition the critical exponent γ is equal to 1. To calculate the exponent ν of the mean square end-to-end distance we have performed exact enumerations on the square lattice up to 22 steps. This gives the value $\nu = 0.57 \pm 0.01$.

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In this Letter we introduce a new self-avoiding walk (SAW) with the property that it continues forever. The construction of such a walk is of great physical interest in connection with the kinetics of irreversible growth processes[1] such as polymerization and kinetic gelation. In order to study these systems it is important to include the self-avoiding condition so that unphysical multiple occupancy of a site cannot occur. On the other hand, the model should possess the property that it can grow indefinitely in order to describe a kinetic process. Presently there is no truly kinetic walk which is completely self-avoiding and grows indefinitely. This model describes the diffusion-limited growth of a polymer in a dilute solution under the condition that the relaxational dynamics of the polymer chain is much slower than the typical growth rate of the process. The monomer diffuses from the outside to the growing end of the chain. This walk should not be confused with the recently introduced true SAW,[2] which also continues forever. However this walk is allowed to violate the self-avoiding condition in order to continue. This leads to an upper critical dimension $d_c = 2$ for the true SAW and consequently gives mean-field behavior in two and higher dimensions. This is certainly a drawback if one wishes to describe a physical process.

For the indefinitely growing SAW (IGSAW) the excluded-volume condition cannot be violated; nevertheless, the walk proceeds forever. We obtain this effect because the IGSAW recognizes cages, no matter how large. This property of the IGSAW makes it possible to generate many long self-avoiding chains very rapidly. As shown below, this enables us to study the asymptotic properties of the SAW in great detail.

To generate this walk we first search for the unoccupied nearest-neighbor (nn) sites. Secondly, we check whether any of these sites leads into a cage. If this is the case this particular site is not considered as a possible jump site. Then, we define the probability of going to one of the jump sites as

$$p = 1/(\text{number of jump sites}). \tag{1}$$

In Fig. 1 we show these features of the IGSAW. The irreversible character of this walk can also be deduced immediately from this figure. In order to recognize whether a new possible step leads into a cage it is sufficient (for $d = 2$) to analyze all the sites which form the smallest closed path in the forward direction, starting at the end of the walk. For the square lattice this path also includes two next-nearest-neighbor (nnn) sites, as illustrated in Fig. 2. On the triangular lattice only nn sites are relevant, but on the honeycomb lattice this closed path even includes a next to next-nearest-neighbor site. These considerations are only of a local nature. In addition to that we need global information about the walk, namely, the winding number. For the square lattice one simply counts the number of 90° angles along the chain. A clockwise angle corresponds to -1 and a counter-clockwise angle to $+1$ (see Fig. 2). The sum then indicates which way is outward, away from the interior of a closed loop which can be formed in the following nn or nnn step. Through this information of the conformational structure of the walk we are able to exclude nn sites which

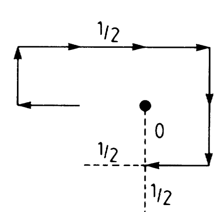

FIG. 1. One-step probabilities for the IGSAW starting from $N = 0$. The irreversibility is simply deduced by inserting the walk direction. If the one-step probabilities differ from the SAW value $\frac{1}{3}$ it is given (see also Fig. 4).

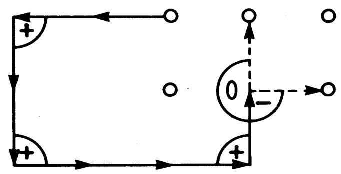

FIG. 2. A simple example illustrating the decision procedure whether a step leads into a cage or not. The circles denote the sites which are checked in the analysis. The signs denote whether the angles correspond to $+1$ or -1. The "plus loop" allows for two new configurations each with probability $\frac{1}{2}$.

give rise to trapping. Clearly this procedure is independent of the size of the loop to be formed. Usually the SAW condition, a long-range memory effect along the chain, leads to a relevant short-range interaction in space. For the IGSAW, the winding number now leads to both a long-range interaction along the chain and in space, even though only nearby sites are analyzed.

To appreciate the importance of this global property, we can study the number of different walks, analyzed as an IGSAW or as a SAW, without considering the different probabilities a given configuration can have. From this point of view, the IGSAW's form a subset of all SAW's. Since each IGSAW grows indefinitely, the procedure searches automatically for self-avoiding paths which can belong to an infinitely long SAW. The IGSAW's of a given length N then form from all SAW's just those configurations which occur as inner parts of an infinitely long SAW. As discussed below, the different asymptotic behavior is then a consequence of the kinetic construction algorithm, which results in different probabilities for IGSAW configurations. As mentioned above it is this property of selecting infinite self-avoiding paths which makes it possible to perform a biased Monte Carlo sampling for the usual SAW. First one generates an IGSAW of a fixed but arbitrary length N. After the completion of this path one goes back to the origin and recalculates the one-step probabilities as if it were a SAW. In this way one can study the short-range correlation between elements of an infinite polymer.[3]

One property of this IGSAW is easily derived. Let

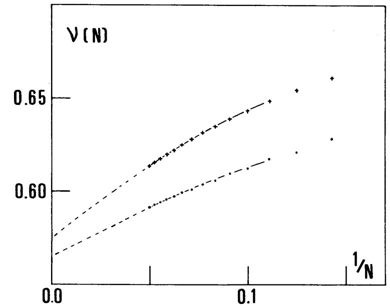

FIG. 3. Plot of $V(N)$ vs $\ln(N+2/N)$ for $\langle R^4\rangle$ (crosses) and $\langle R^2\rangle$ (dots) see Eq. (6).

$P_N(\{\mathbf{r}\})$ denote the probability of a given configuration $\{\mathbf{r}\}$ of N steps. Then because the walk never ends we have for the partition function $Z(N)$

$$Z(N)=\sum_{\{r\}}P_N\{\mathbf{r}\}=1. \qquad (2)$$

This is a consequence of Eq. (1) from which we see that

$$\sum_{\text{all jump sites}} p=1. \qquad (3)$$

Therefore, by analogy to the usual SAW one gets for the critical exponent γ

$$\gamma\equiv 1. \qquad (4)$$

The exponent ν, which describes the behavior of the mean-square end-to-end distance $\langle R^2\rangle$ cannot be found so readily. We have performed an exact enumeration[4] of up to 22 steps on the square lattice as a first attempt to calculate this property. From this enumeration we have calculated the number of chains, the partition function $Z(\equiv 1)$, the mean-square end-to-end distance $\langle R^2(N)\rangle$, and the fourth moment $\langle R^4(N)\rangle$. In a following paper[5] we will publish the detailed results of the enumeration together with a more extensive analysis of Monte Carlo data for longer chains. To calculate ν from this series we assume the scaling form[6,7]

$$\langle R^2(N)\rangle = AN^{2\nu}(1+BN^{-\Delta}+CN^{-1}\ldots) \qquad (5)$$

and a similar expression for $\langle R^4(N)\rangle$. We then find an estimate for $\nu(N)$ from[6]

$$\nu(N)=\tfrac{1}{2}\ln\{R^2(N+i)/R^2(N)\}\ln\{(N+i)/N\}=\nu-\tfrac{1}{2}\Delta BN^{-\Delta}-\tfrac{1}{2}CN^{-1}+\ldots. \qquad (6)$$

With the assumption that the correction to scaling exponent Δ is larger than unity, we find from a plot of $\nu(N)$ against $1/N$ the value for ν as the intercept with the $\nu(N)$ axis as $1/N=0$. Because of the odd-even fluctuations typical for this lattice, the best results are obtained for $i=2$. In Fig. 3 we give these extrapolations for the second and the fourth moment, the result being ($d=2$)

$$\nu=0.57\pm0.01. \qquad (7)$$

To justify this procedure one, of course, has to check if $\Delta>1$. This can be done by plotting the quantity[6] $\ln\{\nu(N)-\nu\}$ against $\ln N$. If $\Delta>1$, one gets a slope

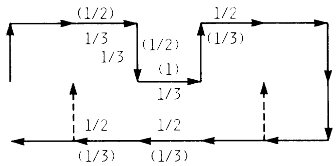

FIG. 4. Simple example showing the space-filling capability of the IGSAW compared to the SAW. The dotted bonds give directions which are allowed only for the SAW and thus increase the probability of the particular IGSAW ($P_{\rm IGSAW}(\{\mathbf{r}\}) > P_{\rm SAW}(\{\mathbf{r}\})$). The irreversibility is illustrated by the one-step probabilities. The values in brackets correspond to the inverted direction.

equal to -1; otherwise one finds a slope $-\Delta$. As one already could have guessed from the linear behavior of the plots in Fig. 3 one finds that this slope equals -1 and thus that $\Delta > 1$, confirming the validity of this approach. Also from these observations we think that our confidence estimate is justified. This is consistent with the analysis of [see Eq. (6)]

$$D(N) = \nu(N) - \nu(N-2) = \Delta^2 B N^{-(1+\Delta)} + C N^{-2}. \tag{8}$$

The linear behavior of $D(N)$ vs $1/N^2$ for $N \geqslant 14$ strongly suggests $\Delta > 1$. Note that in Eq. (8) only the corrections to scaling occur.[5]

At first glance these results might appear somewhat surprising compared with the SAW result $\nu = 0.75$.[8] One could, for instance, anticipate a larger ν due to the fact that the IGSAW can easily create larger holes. However, these holes are also present for the SAW. In addition, for those walks which start to enter a hole the IGSAW always finds a way out, creating fairly dense configurations while the SAW, as a result of its innocence, can easily end up in a trapping situation, leaving large holes. Figure 4 gives a simple example illustrating the space-filling capacity of the IGSAW. It is clear from this picture that the IGSAW can never cover the lattice completely because an empty lattice site leading to a cage will always be avoided. Thus in 2 dimensions it does not behave like a random walk and it must have a critical dimension larger than 2.

The extension of our model to higher dimensions is far from trivial and unfortunately we have not yet found a simple algorithm for it. However, it is clear that in order to define a three-dimensional cage one needs nonlocal information about the past of the chain, whereas in two dimensions the winding number is a local property of one site only. It is also very difficult for a walk to form a three-dimensional cage, since there need be only one empty site on the surface for the walk to escape. This greatly enhances the space-filling capacity compared with the two-dimensional IGSAW. The large change in the value for the exponent ν in two dimensions (SAW:0.75–IGSAW:0.57) suggests a ν value very close to $\frac{1}{2}$ (SAW: ~ 0.59) in three dimensions. This suggestion together with the result $\gamma = 1$ (by construction) leads one to speculate on the possibility of a critical dimension $d_c = 3$ for this walk. In the context of polymer physics, this is of interest for the θ-point problem, where $d_c = 3$. For $d = 2$ there exist theoretical and experimental values for ν ranging from 0.505 to 0.56.[9] It would be very interesting to check whether there is a relation between the θ point and the IGSAW in order to explore a construction scheme for a θ polymer.

After presenting this work[1] we learned that the IGSAW exactly describes the cluster-hull properties of a percolating cluster.[10] This makes it possible to study the surface properties of clusters, a subject which has attracted considerable attention recently.[11]

[1]Proceedings of the Conference on Kinetics of Aggregation and Gelation, Athens, Georgia, 1984, to be published.

[2]D. J. Amit, G. Parisi, and C. Peliti, Phys. Rev. B **27**, 1635 (1983).

[3]J. des Cloizeaux, J. Phys. (Paris) **41**, 223 (1980).

[4]P. Grassberger, Z. Phys. B **48**, 255 (1982).

[5]K. Kremer and J. W. Lyklema, to be published; J. W. Lyklema and K. Kremer, to be published.

[6]Z. V. Djordjevic, I. Majid, H. E. Stanley, and R. J. dos Santos, J. Phys. A **16**, L519 (1983).

[7]For a more general treatment, see V. Privman, Physica (Utrecht) **123A**, 428 (1984).

[8]B. Nienhuis, Phys. Rev. Lett. **49**, 1063 (1982).

[9]R. Vilanove and F. Rondelez, Phys. Rev. Lett. **45**, 1502 (1980); A. Takahashi, A. Yoshida, and M. Kawaguchi, Macromolecules **15**, 1196 (1982); A. Baumgärtner, J. Phys. (Paris) **43**, 1407 (1982); A. L. Kholodenko and K. F. Freed, J. Phys. A **17**, L191 (1984); M. J. Stephen, Phys. Lett. **53A**, 363 (1975).

[10]A. Weinrib, and S. Trugman, private communication, and to be published.

[11]See for instance, R. M. Ziff, P. T. Cummings, and G. Stell, J. Phys. A **17**, 3009 (1984); R. F. Voss, J. Phys. A **17**, L373 (1984).