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LETTER TO THE EDITOR

The growing self avoiding walk

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Abstract. We introduce a new self avoiding walk with one step probabilities which depend on the local environment. As a consequence this walk is irreversible and models the growth process of a linear polymer in a good solvent. To calculate its properties we have performed exact enumerations up to 22 steps on the square lattice and on the diamond lattice. This gives for the critical indices the values $\nu = 0.68$, $\gamma = 1.16$ in two dimensions and $\nu = 0.525$ and $\gamma > 1$ in three dimensions.

Recently there has been considerable interest in a new type of self avoiding walk (SAW), the so-called true self avoiding walk (TSAW) (Amit *et al* 1983). This walk differs from the usual polymer SAW in that it tries to avoid places it has visited already. The usual SAW is used to study the excluded-volume effects of linear polymers. The statistics of such a walk are then obtained by putting a new bond at the end of the chain with equal probability in every direction (see figure 1). If the chain, generated in this way, tries to visit a site for the second time, the walk is discontinued. For the TSAW, the probability p_i to proceed in a certain direction depends on how many times the new site has been visited already. This can be written as

$$p_i = \exp(-gn_i) \Big/ \sum_j \exp(-gn_j). \tag{1}$$

Here the sum runs over all nearest-neighbour (NN) sites and g is a dimensionless interaction energy. Although this type of walk has generated great interest amongst theoreticians, up to now no physical realisation for the walk has been found. The reason for this can be best illustrated for the $g \to \infty$ limit. On the square lattice this

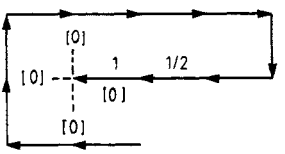

Figure 1. Example of a walk which is terminated. When the one-step probabilities differ from the SAW value $1/q_0$, it is indicated. For the TSAW termination does not occur and the walk proceeds with probability $\frac{1}{4}$ in one of the directions which have probability 0 for the GSAW.

walk has probability $\frac{1}{3}$ if no NN site is visited before, $\frac{1}{2}$ is one NN site is already visited and 1 if two NN sites are visited before (see figure 1). The trouble starts if all three NN sites are already visited, then the probability to proceed to a NN site is $\frac{1}{4}$. This property means that the walk can travel through a densely packed cluster of occupied sites without losing energy. This same disadvantage, of course, also is true for general g.

We introduce a new SAW which is a combination of the above described TSAW in the $g \to \infty$ limit and the usual SAW. For this purpose, we add the self avoiding property to the TSAW. That means that the walk is terminated when it reaches a configuration where all NN sites are visited before (see figure 1). At this point it should be noted, that for this new growing SAW (GSAW) *exactly* the same configurations occur as for the usual SAW, the only differences come from the changed weight definition. Now the various bonds (steps) have different weights whereas for the SAW all steps carry the same weight. As a consequence of the dependence of the transition probabilities on the local environment this GSAW is irreversible, that is the local probability of a chain depends on the direction along the walk in which one measures (see figure 2). This testing of the NN sites before a step is performed also means that the GSAW lives longer. The first termination occurs at the 8th step for two dimensions on the square lattice, while one needs 14 steps in three dimensions on the diamond lattice.

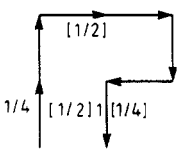

Figure 2. Example of a short GSAW, which shows its irreversibility. When the one-step probabilities differ from $\frac{1}{3}$ it is indicated. The numbers in brackets give the probabilities for the inverse direction.

This GSAW should be able to describe the growth process of a linear polymer in a good solvent, provided that the relaxation of the chain is much slower than the growth process itself. To study this GSAW we have used an enumeration technique similar to the one described by Grassberger (1982) to count all possible walks on the square lattice and the diamond lattice up to 22 steps. From this we calculated the number of walks, the partition function Z (the sum over all products of the one-step probabilities of each configuration), the mean square end-to-end distance $\langle R^2(N)\rangle$ and the fourth moment $\langle R^4(N)\rangle$. For the scaling behaviour of $\langle R^2(N)\rangle$ we assume (Djordjevic *et al* 1983, Majid *et al* 1983)

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

with a similar expression for $\langle R^4(N)\rangle$. Using this we can estimate ν from

$$\nu^1(N) = \tfrac{1}{2} \ln [R^2(N+i)/R^2(N)]/\ln [(N+i)/N]^{1=1} = \nu - \tfrac{1}{2}\Delta BN^{-\Delta} - \tfrac{1}{2}CN^{-1} \ldots . \tag{3}$$

Thus a plot of $\nu(N)$ against $1/N$ will give us an estimate for ν provided that the correction to scaling exponent Δ is larger than one. This is tested by plotting $\ln|\nu(N) - \nu_{est}|$ against $\ln N$ where ν_{est} is the estimated asymptotic value. An alternative way to

estimate ν is given by Watts (1974)

$$\nu^{II}(N) = \tfrac{1}{2}\frac{[\langle R^2(N+i)\rangle - \langle R^2(N)][\langle R^2(N)\rangle - \langle R^2(N-i)\rangle]}{[\langle R^2(N)\rangle^2 - \langle R^2(N+i)\rangle\langle R^2(N-i)\rangle]}$$

$$i=1$$

$$= \nu + (2\nu-1)\Delta B N^{-\Delta} + (2\nu-1)CN^{-1} \ldots . \tag{4}$$

Here the analytic correction does not vanish as wrongly assumed by Djordjevic *et al* (1983) and Majid *et al* (1983). In a similar way as for method I one gets an estimate for ν. However, the convergence to the asymptotic value may be different. Also from (4) it is clear that only when $\Delta > 1$ can one expect good results from this procedure. The value of the correction exponent Δ can be estimated in a similar way as described for method I. The exponent γ is calculated from the partition function which for a finite number of steps (N) is defined as

$$Z(N) = \sum_{C_N} \prod_{i=1}^{N} p(i, C_N), \tag{5}$$

$p(i, C_N)$ is the one step probability for the ith step of an N-step walk with configuration C_N.

For the SAW the $p(i, C_N)$ are constant, independent of the configuration C_N and its position i in the sequence.

$$p(i, C_N) = K = 1/q_0. \tag{6}$$

Here q_0 equals $q-1$, being the coordination number of the lattice. For the partition function we then have for the usual SAW

$$Z(N) = a_N K^N, \tag{7}$$

where a_N denotes the number of walks of length $N(\Sigma_{C_N} 1 = a_N)$.

Using $a_N \propto K_c^{-N_N \gamma - 1}$ for large N one can write for the usual SAW (de Gennes 1979)

$$Z(N) \propto (K/K_c)^N N^{\gamma - 1}. \tag{8}$$

The value of K_c is given by

$$(K/K_c)^i = \lim_{N\to\infty} Z(N+i)/Z(N), \tag{9}$$

while the slope of a log–log plot of $Z(N+i)/Z(N)$ against $N+i/N$ gives the exponent $\gamma - 1$. For the GSAW we introduce $\Pi_{i=1}^{N} p(i, C_N)$ of (5) instead of K^N of (6). Now we assume the existence of a fixed point and a similar functional behaviour (8) of the partition function for the GSAW and calculate γ and K/K_c for the GSAW from $Z(N)$ in the above described way. Because the SAW and the GSAW are constructed from the same configurations but with different weights, it is plausible that this assumption is valid. Our results provide further justification.

Now let us turn to the result for the two-dimensional GSAW on the square lattice. The extrapolations for the exponent ν are given in figure 3. To suppress the lattice typical odd–even fluctuations we have taken $i=2$ in (3) and (4). The result from method I (figure 3(b)) at first glance suggests a value for ν of 0.65. However, the plot to estimate Δ^1 does not give a very convincing straight line. Also the minimum of $\nu^I(N)$ around $N \sim 12$ means that the two correction terms in (3) have opposite sign. This cancellation still plays a role at $N \sim 20$ and makes an accurate estimate for $\nu^I(N)$ impossible. For this reason we have studied method II.

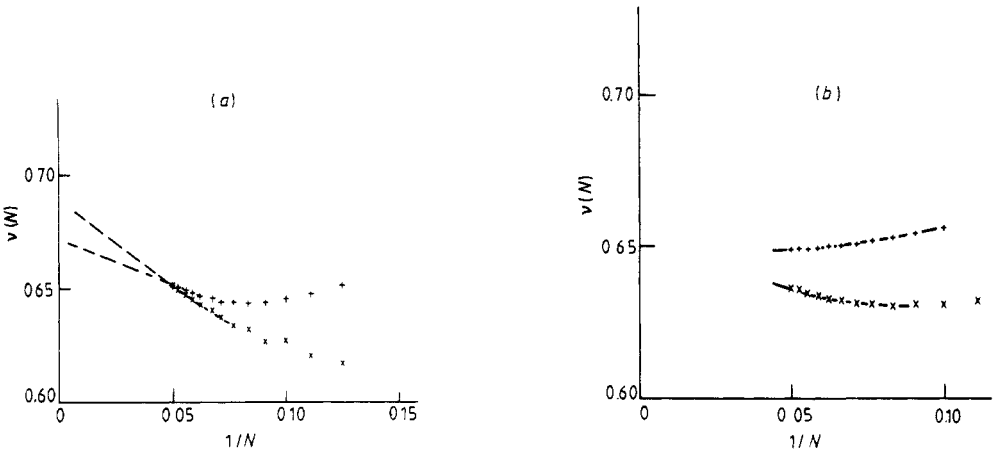

Figure 3. Plots of $\nu(N)$ by the various methods from $\langle R^2(N)\rangle$ (x) and $\langle R^4(N)\rangle$ ($+$) for $d=2$. Part (a) gives $\nu(N)$ against $1/N$ after method II, part (b) gives $\nu(N)$ against $1/N$ after method I.

Clearly the estimate has shifted considerably, now giving a value of $\nu = 0.68 \pm 0.01$. Here the plot of the estimate of Δ^{II} does give a nice straight line with $\Delta^{II} > 1$. This shows that a cancellation of correction terms does not occur here. Therefore we expect method II to give more reliable results than method I in this case. The calculation of γ and K_c appears to be much easier. From the ratio Z_{N+2}/Z_N for $N = 20$ we find $K_c = 2.94$ by multiplying (9) with $q_0 = 3$, a value which has converged already to its limiting value. From the log–log plot of Z_{N+2}/Z_N against $N+2/N$ we find for γ the value 1.16 ± 0.01, a result which also seems to have converged for $N = 20$.

In figure 4 we show the results for $\nu^I(N)$ on the diamond lattice. In this case we have also taken i equal to 2 in (3) and (4) although the odd–even oscillations are not nearly as strong as on the square lattice. In contradiction to the situation on the square lattice there is here no problem with cancellation of correction terms. Both curves clearly point to a value of $\nu = 0.525 \pm 0.010$, a result which is confirmed by method II.

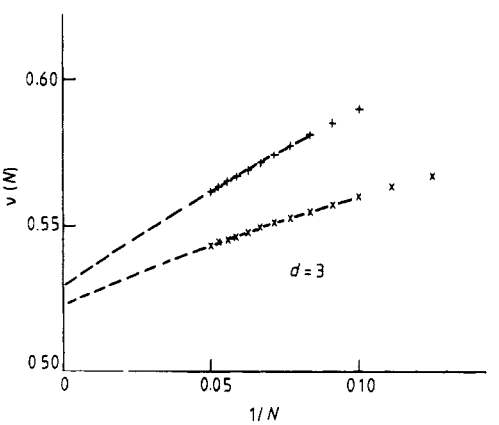

Figure 4. Plot of $\nu(N)$ against $1/N$ after method I for $\langle R^2(N)\rangle$ (x) and $\langle R^4(N)\rangle$ ($+$) for the three-dimensional GSAW on the diamond lattice.

This is consistent with the experience for the usual SAW on the diamond lattice. There Monte Carlo calculations show that, even for $N = 20$, ν displays its asymptotic value within an error of about one percent (Kremer *et al* 1982). Also the plot to estimate Δ^1 gives a straight line with slope one, indicating that $\Delta > 1$. In this case our results are accurate enough to exclude the possibility of $\nu = 0.5$, the random walk value which one expects to hold at the upper critical dimension, ignoring logarithmic corrections. Therefore, we can exclude an upper critical dimension of $d_c = 3$. To investigate this point further we have studied the second and fourth moment assuming logarithmic corrections of the form

$$\langle R^2(N)\rangle \sim N(\ln N)^{\alpha_2} \tag{10}$$

and a similar expression for $\langle R^4(N)\rangle$. From this we find values for α_2 and α_4 which differ by a factor of 1.4, whereas one expects them to be equal if (10) describes the behaviour. The calculation of $(\gamma - 1)$ and K_c from enumeration results causes some problems, because the first walk is only terminated at $N = 14$. But from then on the partition function is decreasing steadily although at a very slow rate. As a rough estimate for the fixed point we give $K_c \sim 2.9995$ but smaller than 3.0. Also the value of γ is very hard to estimate. We give $0 < (\gamma - 1) < 0.1$. To get more accurate results for the critical exponents and for the correction exponents one needs longer chains. This of course is not feasible with enumeration and one has to perform very accurate Monte Carlo calculations. This can be achieved by a precise sampling of chains up to $N = 100$. This work will be reported on in a subsequent paper (Kremer and Lyklema 1984b).

The results (see also table 1) show that the difference between the reversible SAW and the irreversible GSAW is remarkable. Although both walks are identical for all configurations, the difference in the one-step probabilities causes a significant change in their global structure and in the critical behaviour. The ability of the GSAW to look ahead and avoid, as far as possible, an early confinement by giving a zero weight to terminating NN sites and a higher weight to escaping and consequently more dense paths, results in a much smaller excluded-volume effect. However, we clearly can exclude an upper critical dimension $d_c = 3$ for GSAW, because $\gamma > 1$ and $\nu > \frac{1}{4}$. Therefore this model can not be used to study the θ-point behaviour of polymers. For the θ-point polymer one has $d_c = 3$ and $\gamma = 1$ (de Gennes (1979) and reference therein). This $\gamma = 1$ behaviour is up to now by construction only achieved for the recently introduced indefinitely growing SAW (IGSAW, Kremer and Lyklema 1984a). This walk, which is constructed in such a way that it avoids cages, still has a considerable excluded-volume

Table 1. Best available results for the four different SAW's including the exponents of the new GSAW. The exact results for the SAW in two dimensions are taken from Nienhuis (1982), in three dimensions the best known values are due to Le Guillou and Zinn Justin (1977). The results for the TSAW are from Amit *et al* (1983) and for the IGSAW from Kremer and Lyklema (1984a).

	SAW	GSAW	IGSAW	TSAW	
ν	3/4	0.68 ± 0.01	0.57 ± 0.01	1/2	$d = 2$
γ	43/32	1.16 ± 0.01	1	1	
ν	0.588	0.525 ± 0.010	—	1/2	$d = 3$
γ	1.167	> 1	—	1	

effect in two dimensions. However, the known values of the various SAW (see table 1) strongly suggest the possibility of $\nu = 0.5$ in three dimensions for the IGSAW and therefore $d_c = 3$. If this is relevant for the θ-point polymer remains to be seen.

Finally we want to remark that, after completion of this work, several preprints appeared which also study the GSAW (Hemmer and Hemmer 1984, Majid *et al* 1984 and Family 1984). The results of this work shows that the GSAW is a very interesting model which should be studied in more detail.

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