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LETTER TO THE EDITOR

The growing self-avoiding trail

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Abstract. We introduce a new random walk which can be used as a model for the θ polymer. The walk belongs to a different universality class from the usual SAW. Extensive Monte Carlo calculations have been performed to calculate the exponents γ and ν . We find in two dimensions $\nu = 0.535$ and $\gamma = 1.025$ and in three dimensions $\nu = 0.50$ and $\gamma = 1.0$. This result strongly suggests that the upper critical dimension is equal to three.

The scaling behaviour of a linear polymer in a 'good' solvent is by now very well understood. By using the self-avoiding walk (SAW) as a model one is able to study this problem in great detail. The success of this description has stimulated several authors to study kinetic versions of the SAW which could possibly describe the non-equilibrium phenomenon of polymer growth (Majid *et al* 1984, Lyklema and Kremer 1984). In the growing version of the SAW (GSAW) the constant one step probability $1/(q-1)$, q : coordination number) for the SAW has been replaced by $1/(\text{number of free sites})$ for the GSAW. In this way the walker checks its environment and tries to avoid early termination. It was also suggested that these models could describe the θ point behaviour of linear polymers (Majid *et al* 1984), which is governed by different exponents from those of the usual SAW. A more detailed study of this model (Lyklema and Kremer 1985) shows that the different definition of the one-step probabilities does not change the critical behaviour but only shifts the asymptotic scaling regime to much larger N values. This confirmed the theoretical predictions of Peliti (1984) and Pietronero (1984) that this model should belong to the same universality class as the SAW. Thus this walk cannot serve as a model for the θ polymer.

In this letter we introduce a new model which shows a different asymptotic behaviour from that of the SAW. The model allows for self-intersection, which models the vanishing two-body interactions typical for the θ polymer (de Gennes 1979). It should however *not* be confused with the k -tuple SAW (Malakis 1976). The model is a 'growing' version of the self-avoiding trail (SAT) (Malakis 1975, 1984). In its usual form the SAT is constructed similarly to the SAW, except that each *bond* rather than each site can be occupied only once. A new bond is attached to the chain with equal probability for all bonds. If the chosen bond is occupied, the walk is terminated. From this construction one expects the same critical exponents as for the SAW, because the paths generated in this way are the same, as has been shown recently (Malakis 1984, Guttmann 1985a, b). The growing SAT (GSAT) belongs however to a different universality class, as may be anticipated from the construction process. We have the same rules as for the SAT except that we write the one-step transition probability p_i as

$$p_i = 1/\text{number of free bonds.} \quad (1)$$

For the square lattice we have $p_i = \frac{1}{3}$ if the last site has not been visited before. If a site is occupied for the second time, three bonds have been used and we have $p_i = 1$ (see figure 1(a)). This walk can only end at the origin, since this is the only site for which an odd number of bonds leading to it are occupied. After the second visit, three bonds are occupied, and only one bond remains to enter this site again (see figure 1(b)). The origin is also special, because the first bond is chosen with probability $\frac{1}{4}$ and after visiting it for the second time the one-step probability is $\frac{1}{2}$. If the walk enters a site other than the origin, there is always at least one free bond through which the walk can leave. This walk still displays an excluded volume effect in two dimensions, as can be seen from figure 2. The battlement type construction acts like a hard wall, since the area inside cannot be visited by the walker. The foregoing discussion obviously holds only for lattices where the sites are connected by an even number of bonds. For instance for the honeycomb lattice the probability to choose a bond from a site which is visited for the first time is $\frac{1}{2}$. On a second visit, however, there is no free bond leaving. The walk can terminate at every site and there is no difference from the usual SAT. Thus one cannot define a GSAT on the honeycomb lattice. On the triangular lattice and in higher dimensions we have the extra freedom of choosing the maximum number of visits M to a site. On the triangular lattice, for example, we can define two different walks e.g. $M = 2$ and $M = 3$. (The choice $M = 1$ reduces this walk to the GSAW.) The $M = 2$ case can terminate at every site. If all nearest-neighbour sites of a central site C have been visited twice and site C no more than once, this creates a trap and therefore the walk will terminate if it enters C . From the experience with the SAW-GSAW one expects that the $M = 2$ case on the triangular lattice will also be in the

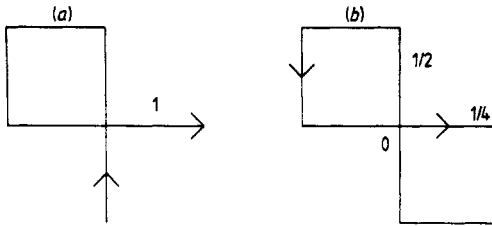


Figure 1. The one-step probabilities which are not equal to $\frac{1}{3}$ are shown for (a) an arbitrary site, (b) the origin. Note that in (b) the walk terminates at the origin.

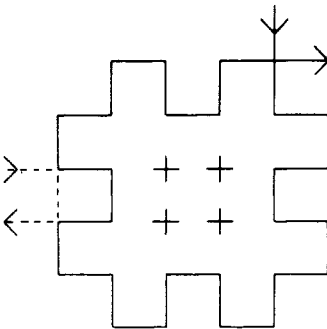


Figure 2. The battlement type construction which causes the excluded volume effect. The broken line shows the repulsive effect of this wall.

SAW universality class. However the asymptotic behaviour will probably show up only at very high N values. Thus I define the $GSAT$ to be the walk where a site can be visited $\frac{1}{2}$ times the coordination number on a lattice with an even number of bonds per site. This walk has the property that it only terminates at the origin in contrast to all other walks in the SAW universality class. Therefore one can expect that this walk will have a different asymptotic behaviour from the usual SAW.

A possible interpretation of this model is the following. Associate with every site on the square lattice a small region in continuous space which can be occupied twice by the walk. Now one can redraw any trail in such a way that no intersections occur and still have the double occupied sites visited twice (see figure 3). This represents the cancellation between the attractive and repulsive forces between different parts of the walk. This interpretation is strictly speaking not possible for the triangular lattice or in higher dimensions. However from universality considerations one expects no differences between a continuum approach or a different lattice type approach.

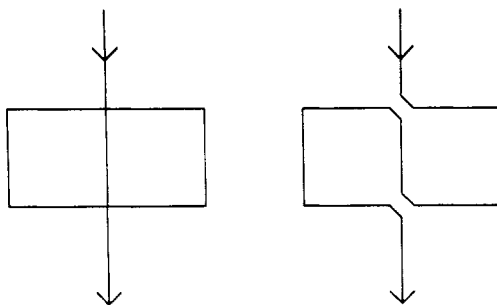


Figure 3. Interpretation of the intersections (see text).

For this walk I have performed extensive Monte Carlo simulations using the static sampling procedure (Kremer *et al* 1982). On the square lattice I have generated 48×10^6 chains of maximum length $N = 200$. The first termination occurs at the ninth step and, as expected, the acceptance rate is very high. Even at $N = 200$, 94.68% of the chains have survived. However, a considerable number of chains manage to return to the origin. The difference between the acceptance rate at $N = 198$ and 200 is 0.02%. To improve the accuracy of the analysis I have generated a smaller number of chains (5×10^6) of maximum length $N = 2000$. In this case the mean square end-to-end distance is only calculated every tenth step. At $N = 2000$ the acceptance rate is 89.52%. On the simple cubic lattice I have generated 37×10^6 chains of maximum length $N = 400$. Here the first termination occurs at step thirteen. The acceptance rate at $N = 400$ is 99.976%. In this case, the difference between the acceptance rate at $N = 398$ and 400 is of the order of 10^{-7} showing the extremely slow decrease of this function. Also in this case I have generated a small number of chains (2×10^6) with maximum length $N = 2000$. Again the mean square end-to-end distance is calculated every tenth step. The acceptance rate for $N = 2000$ is 99.969%.

From these simulations I have calculated the mean square end-to-end distance $\langle R^2(N) \rangle$ and the fourth moment $\langle R^4(N) \rangle$. To estimate the accuracy of the data, I have also calculated the mean distance in the x direction. This quantity fluctuates around zero and from its absolute value I estimate the error in $\langle R^2(N) \rangle^{1/2}$ to be less than 0.01%. To analyse these data I assume the usual asymptotic behaviour (Privman 1984,

Djordjevic *et al* 1983)

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

and a similar expression for the fourth moment. From this one can calculate ν , the leading exponent, from the following definition

$$\nu(N) = \frac{1}{2} \frac{\ln[\langle R^2(N+i) \rangle / \langle R^2(N-i) \rangle]}{\ln[(N+i)/(N-i)]}. \quad (3)$$

Inserting the expression (2) into this definition gives

$$\nu(N) = \nu - \frac{1}{2}BN^{-\Delta} - \frac{1}{2}CN^{-1} + \dots \quad (4)$$

This expression is independent of the index i , which gives us the possibility of studying larger i values without introducing a bias. The accuracy of the analysis is thereby greatly improved as shown in figure 4, where $\nu(N)$ as calculated from $\langle R^2(N) \rangle$ is plotted against $1/N$ for N values between 40 and 200 on the square lattice. The data for smaller N values fall slightly below the straight line which results from fitting the data for $N > 40$. Extrapolation of these data results in an estimate of $\nu = 0.54$. To improve the reliability of this estimate we have analysed the data for larger N values ($N_{\max} = 2000$) in a similar way. Because the accuracy in this case is not as good one has to study much larger i values. In figure 5 the data for $i = 50$ ($150 < N < 2000$) and $i = 200$ ($700 < N < 2000$) are shown. In figure 5(a) the data for the small N values extrapolate to $\nu = 0.54$, however the large N data ($N > 700$) clearly suggest a somewhat smaller value. From figure 5(b) we estimate this value at $\nu = 0.535 \pm 0.003$. The very high i value which is used in this figure still did not introduce a bias compared with $i = 10$. Thus if the asymptotic behaviour sets in at very large N values and one has to be satisfied with Monte Carlo data of lower quality, it is still possible to apply this analysis provided one takes a large i value, with the restriction that i/N cannot be too large. The linear extrapolation is justified because the $\nu(N)$ form a straight line without any observable curvature. This shows that the confluent correction exponent Δ is larger than 1, so that an extrapolation against $1/N$ is allowed. However numerically

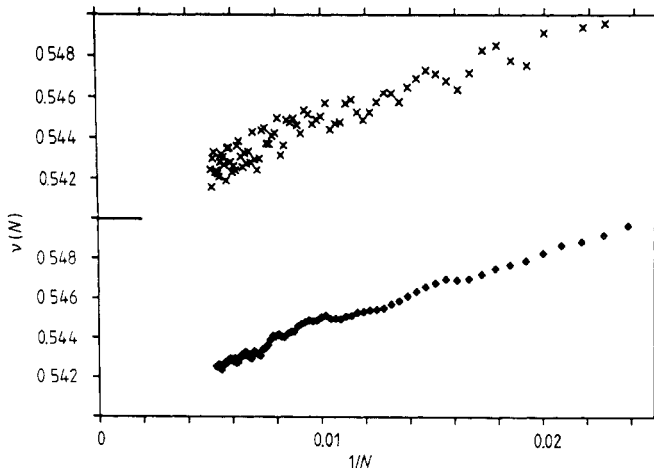


Figure 4. A plot of $\nu(N)$ calculated from $\langle R^2(N) \rangle$ against $1/N$ for N from 40 to 200 on the square lattice. The upper curve is for $i = 1$, the lower one for $i = 5$.

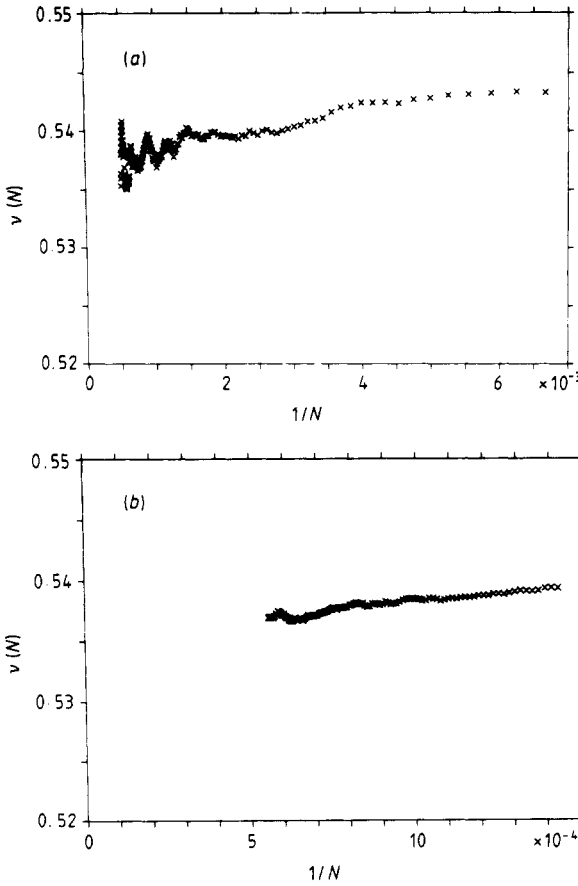


Figure 5. (a) Plot of $\nu(N)$ calculated from $\langle R^2(N) \rangle$ ($i = 50$) against $1/N$ for N between 100 and 2000. (b) Plot of $\nu(N)$ calculated from $\langle R^2(N) \rangle$ ($i = 200$) against $1/N$ for N between 500 and 2000.

one can never exclude the possibility that the prefactor B in (4) is very small and that therefore the real asymptotic behaviour only can be seen for much larger N values. The prefactor A in equation (2) is calculated from $A = N^{-1.07} \times \langle R^2(N) \rangle$. We find $A = 1.800 \pm 0.001$.

The exponent γ is calculated from the partition function, which for a finite number of steps N is defined as (Lyklema and Kremer 1984)

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

Here $p(i, C_N)$ is the one-step probability for the i th step of an N -step walk with configuration C_N . For the SAW or SAT this is a constant, $1/q_0$ with q_0 being the coordination number minus one. Thus $Z(N) = a_N q_0^{-N}$, where a_N denotes the number of walks of length N . Asymptotically this number behaves like $a_N \propto q_c^N N^{\gamma-1}$ (de Gennes 1979). This leads to the following expression for $Z(N)$

$$Z(N) \propto (q_c/q_0)^N N^{\gamma-1}. \tag{6}$$

From the slope of a log-log plot of $Z(N+i)/Z(N-i)$ against $(N+i)/(N-i)$ we find the exponent $(\gamma-1)$ and from the intercept with the y axis we obtain an estimate for q_c/q_0 . If we assume for the GSAT the same asymptotic behaviour of $Z(N)$, this analysis with $i=10$ (see figure 6) leads to $\gamma=1.025\pm 0.003$ and $q_c < 3$ but very close to it. Note that the asymptotic behaviour here also sets in at $N \approx 700$.

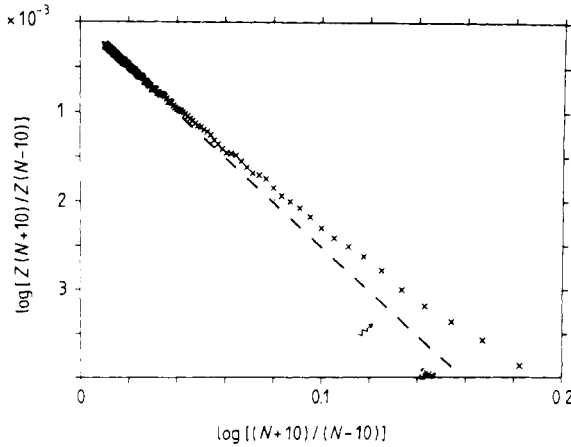


Figure 6. Plot of $\log[Z(N+10)/Z(N-10)]$ against $\log[(N+10)/(N-10)]$ for N between 100 and 2000. The slope gives $(\gamma-1)=0.025$.

For the simple cubic lattice I have performed a similar analysis. In figure 7 I show the $\nu(N)$ ($i=20$) calculated from $\langle R^2(N) \rangle$ and $\langle R^4(N) \rangle$ against $1/N$ for N values between 40 and 400. From this plot it is clear that the ν value is very close to $\frac{1}{2}$. A linear extrapolation from the last 200 points gives an estimate of $\nu=0.501\pm 0.002$. However this plot is also consistent with $\nu=\frac{1}{2}$ with logarithmic corrections, signalling

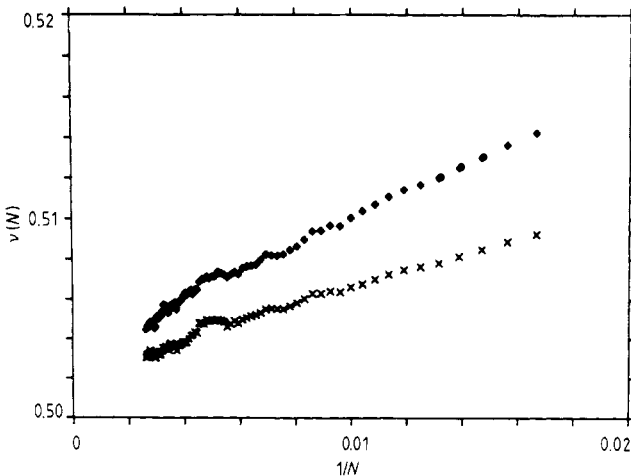


Figure 7. A plot of $\nu(N)$ ($i=20$) against $1/N$ for N between 40 and 400 on the simple cubic lattice. The lower curve is calculated from $\langle R^2(N) \rangle$, the upper one from $\langle R^4(N) \rangle$.

an upper critical dimension $d_c = 3$. If this is correct we have Gaussian behaviour which means that the ratio $\langle R^4(N) \rangle / \langle R^2(N) \rangle^2$ approaches the value $\frac{3}{2}$ for large N . This ratio is a slowly increasing function of N . For $N = 400$, the value of 1.653 is in very good agreement with a random walk behaviour. At the upper critical dimension one assumes for the mean square end-to-end distance and the fourth moment the following scaling behaviour

$$\langle R^2(N) \rangle = A_2 N (\ln N)^\alpha \quad \langle R^4(N) \rangle = A_4 N^2 (\ln N)^{2\alpha}. \quad (7)$$

A two parameter fit gives $A_2 = 1.5$, $A_4 = 3.75$ and $\alpha = 0.025$. To check the accuracy of these values we have compared the mean square end-to-end distance and the fourth moment calculated from (7) with the Monte Carlo results for the long chains ($N_{\max} = 2000$). For $\langle R^2(N > 400) \rangle$ we found that the difference is smaller than 0.1%. This difference for $\langle R^4(N > 1200) \rangle$ is smaller than 0.2%. To get an estimate for the error in the value of α we have repeated this procedure for $\alpha = 0.024$ and $\alpha = 0.026$. Now the difference between $\langle R^2(N) \rangle$ and $\langle R^4(N) \rangle$ from (7) and the Monte Carlo results has increased with a factor 8. From this we estimate the error at 0.001. The prefactor of course is not that sensitive. From a similar analysis for A_2 between 1.45 and 1.55 and $\alpha = 0.025$ one cannot draw conclusions about the value of the prefactor. However this can be estimated very accurately from $A_2 = \langle R^2(N) \rangle / N (\ln N)^{0.025}$. From $N > 400$ we find $A_2 = 1.500 \pm 0.001$. The value for A_4 is slowly increasing to 3.75 ($A_4(N = 2000) = 3.747$). This is in agreement with the slow increase of the ratio $\langle R^4(N) \rangle / \langle R^2(N) \rangle^2$ to 1.665 for $N = 2000$.

Because of the extremely high acceptance rate only very few walks are terminated and one cannot perform the analysis for the partition function $Z(N)$ as in the two-dimensional case. However the very slow decrease of $Z(N)$ is consistent with a value of one and an upper critical dimension $d_c = 3$ (see equation (6)).

To understand this asymptotic behaviour let us first consider the two-dimensional walk. Here one expects that the walker will return to the origin with probability one as in the usual random walk. Because the acceptance rate at $N = 2000$ is still $\sim 90\%$, one can argue that we have not seen the asymptotic behaviour yet, and that the 'true' asymptotic behaviour is governed by the random walk value $\nu = \frac{1}{2}$ or the SAW value $\nu = \frac{3}{4}$. Because of the already discussed excluded volume property of this walk one does not expect to find the random walk value $\nu = \frac{1}{2}$. Also the SAW value $\nu = \frac{3}{4}$ can be excluded, because the GSAT is much denser packed at every length scale. The possibility that the GSAT is in the IGSAT universality class $\nu = 0.567$ (Kremer and Lyklema 1985) can be dismissed because the IGSAT is constructed using a non-trivial long range interaction, whereas the GSAT is not. Also the value of $\gamma = 1.025$ against $\gamma(\text{IGSAT}) = 1$ by construction, excludes this possibility. In three dimensions, similar to the random walk, one does not expect that the walker always returns to the origin. Instead one expects that a large fraction of all the walkers starting at the origin will never return, and it will be this fraction which governs the asymptotic behaviour of the model. It is then reasonable to expect a value of $\nu = \frac{1}{2}$, because asymptotically fluctuations will be negligible.

From our numerical results we conclude that this new walk has an upper critical dimension of three. In three dimensions we can describe the logarithmic corrections of both the mean square end-to-end distance and the fourth moment with the same exponent. Also the ratio $\langle R^4(N) \rangle / \langle R^2(N) \rangle^2$ approaches the Gaussian result $\frac{3}{2}$. Thus we have introduced a model with $d_c = 3$, which is self-avoiding, shows an excluded volume effect and has a decreasing survival probability with increasing N . As mentioned

above this model mimics the cancellation of attractive and repulsive interactions of a polymer chain because the walker can visit a site more than once. This cancellation is responsible for the θ point behaviour ($d_c = 3$) of a polymer solution. For $d = 2$ the theoretical and experimental values for ν range from 0.505 to 0.56 (Vilanove and Rodelez 1980, Takahashi *et al* 1982, Baumgärtner 1982, Kholodenko and Freed 1984, Stephen 1975), consistent with the present result (0.535). I therefore suggest that this walk can be used as a model for the θ polymer, although a rigorous justification requires an analytical theory.

An interesting physical phenomenon which can be studied using this model is kinetic gelation (Herrmann *et al* 1982). Here one models the sol-gel transition by performing a number of random walks of the self-avoiding type simultaneously. The first occurrence of an infinite cluster marks the sol-gel transition. To study the scaling behaviour of the process in terms of the scaling properties of the underlying walks it is clearly desirable that the individual walks are long enough to show their asymptotic scaling behaviour. The GSAT has this property. Both in two and three dimensions one can describe the mean square end-to-end distance for $N > 50$ with a power law ($\nu(d=2) = 0.54$, $\nu(d=3) = 0.5$), contrary to the GSAW (κ GW) which has been proposed by Majid *et al* (1984) to describe the zero-concentration limit of kinetic gelation. Computer simulations which use the GSAT as building block are currently in progress.

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