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LETTER TO THE EDITOR

Random walk on self-avoiding walk: a model for conductivity of linear polymers

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Abstract. Random walks on self-avoiding walks (SAWs) are studied here using Monte Carlo techniques on a square lattice (with nearest-neighbour hopping along the chain and between SAW points which are nearest neighbours on the embedding lattice). The average of the square of the end-to-end distance for random walks of t steps on SAWs of length N is fitted to the scaling forms $\langle R_t^2 \rangle \propto N^{\delta} t^{k}$ (for $t \ll N^{\theta}$) and $\langle R_t^2 \rangle \propto N^{2\nu_s}$ (for $t \gg N^{\theta}$), where $\theta \simeq 2\nu_s/k$; ν_s being the average end-to-end distance exponent for SAWs. The observed value of the exponent δ is supported by our real space renormalisation group result for the conductivity of SAW chains. The exponent k has been related to the 'effective' fractal dimension of the SAW chain.

The phenomenon of diffusion (i.e., random walk (RW)) on Euclidean lattices is quite well understood (see e.g., Weiss and Rubin 1983). However, diffusion on fractal lattices is now an active field of research. So far most of the attention has been focused on diffusion on percolation clusters (see, e.g., Stauffer (1985) and the references therein, Havlin 1984, Stanley *et al* 1984). The latter is an example of the so-called statistical fractals (Rammal 1984). In this letter we shall study diffusion on another statistical fractal, namely the self-avoiding walk (SAW).

It is well known that the SAW is a good model for linear polymers in dilute solution (de Gennes 1979). Therefore, the diffusion on SAWs is expected to throw light on the nature of the electrical conduction in linear polymers (Etemad *et al* 1982). Some aspects of such investigations are directly related to the phonon density of states of some proteins, e.g., haemoproteins (Helman *et al* 1984). In fact, a numerical study of this aspect of the RW on SAWs has already been attempted (Yang *et al* 1985). Some other aspects of this study lead to the molecular weight dependence of the conductance of polymer chains (Ball and Cates 1984). In this letter we investigate the detailed scaling form for the RW on SAWs, which incorporates both the aspects mentioned above. Also, the static and dynamic critical behaviour of Ising and Heisenberg spins, with nearest-neighbour interaction, on such SAW chains have been studied recently (Bhattacharya and Chakrabarti 1984a,b, Chakrabarti *et al* 1985). The problem of diffusion on such SAW chains should also throw light on the critical dynamics of various (diffusive) modes in such systems.

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First of all let us clarify that the diffusion problem considered here is non-trivial. Indeed, it is much more complicated than diffusion on an ordered one-dimensional lattice. Consider, for example, the SAW configuration shown in figure 1(a). Each of the segments between nearest neighbours along the SAW will be called a 'street'. If we allow a RW only along the streets, it would, of course, be equivalent to a RW on an ordered one-dimensional lattice. However, in addition to hop along the 'streets' (full line in figure 1(a)) we shall also allow the random walker to hop along the 'bridges' (broken lines in figure 1(a)), the latter being the bonds between the sites which are not nearest neighbours along the SAW but nearest neighbours on the embedding lattice (in figure 1(a), for example, on the square lattice). For the sake of simplicity we shall assume that the hopping probability along the streets and along the bridges are identical. In real physical systems, e.g., in haemoproteins, of course, the physical bonding along the streets and across the bridges may be of different character giving rise to differences in the corresponding hopping probabilities for the random walker (cf Helman *et al* 1984).

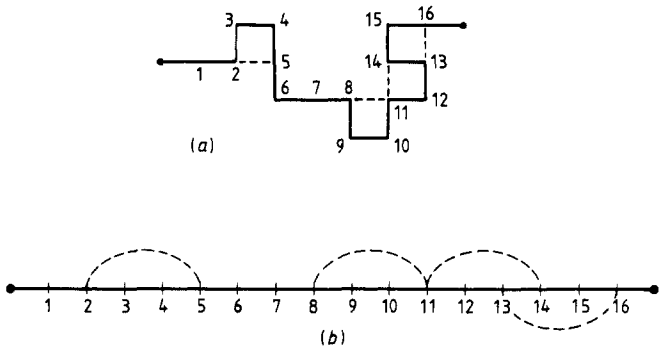

Figure 1. (a) A section of a typical SAW configuration. The full line denotes the 'streets' and the broken lines denote the 'bridges'. (b) The equivalent one-dimensional chain. Along the full line nearest-neighbour hoppings and along the broken lines Levy-like flights are allowed for the random walker.

Let $P_n(t)$ be the probability that the diffusing particle (the random walker) is at the site n at time t. The master equation governing the motion of the particle can be written as

$$dP_n(t)/dt = \sum T_{nm}P_m(t) - \sum T_{mn}P_n(t), \tag{1}$$

where the first and second terms on the right-hand side of equation (1) correspond to the gain and loss of probability, respectively, and T_{nm} is the probability of transition from the site m to site n. In the absence of any external bias, the transition probability is supposed to be symmetric, i.e., $T_{nm} = T_{mn}$. We also assume T_{mn} to be site-independent and denote it by T. Let us now stretch out the SAW chain into a straight line segment as shown in figure 1(b). The difference between the nearest-neighbour hopping RW and the present problem is now clear; the latter allows hopping even between non-nearest neighbours on the straight line in figure 1(b), e.g., between the sites 2 and 5. It is straightforward to show that

$$d\langle P_n(t)\rangle/dt = T(1+p)(\langle P_{n+1}\rangle + \langle P_{n-1}\rangle - 2\langle P_n\rangle) \tag{2}$$

where $2p$ is the probability that an arbitrary site on the SAW has more than two nearest neighbours also lying on the SAW and the bracket $\langle\ \rangle$ denotes the average over SAW configurations. Note that equation (2) is effectively identical with a one-dimensional nearest-neighbour-hopping RW with an enhanced effective transition probability $W = T(1+p)$. One can write $Z_{\text{eff}} = 1/[T(1+p)]$ as the effective coordination number of a lattice where the RW can be looked upon as a nearest-neighbour-hopping RW. Expressing the total number G_N of SAW configurations of N steps as $G_N \propto u^N N^{\gamma-1}$ (de Gennes 1979), one can express Z_{eff} (for $N \to \infty$) as $Z_{\text{eff}} = 2 + (Z-1) - u$, where Z is the coordination number of the embedding Euclidean lattice (Bhattacharya and Chakrabarti 1984a). This, together with the link-and-blob picture of the SAW at all length scales, gives rise to its fractal nature.

The RW considered in this letter has some similarities with the random Levy walks (Mandelbrot 1983) where the random walker can occassionally make long jumps, although nearest-neighbour hoppings are more frequent. The aim of this work is, in other words, to study the effect of Levy-like flights (e.g. those between 2 and 5 in figure 1(b)) on the critical behaviour of the RW in one dimension.

The scaling law for the square of the end-to-end distance of an N-step RW, considered here, can be expressed as

$$\langle R_t^2 \rangle \propto N^{\delta} t^{k}, \qquad \text{for } t \ll N^{\theta}, \tag{3}$$

where δ and k are two critical exponents and $\theta = (2\nu_s - \delta)/k$; ν_s being the exponent for the average end-to-end distance $\langle R_{\text{SAW}} \rangle$ of SAW. The restriction $t \ll N^{\theta}$ arises from the condition $\langle R_t \rangle \ll \langle R_{\text{SAW}} \rangle$; for $t = N^{\theta}$, $\langle R_t \rangle$ becomes of the order of $\langle R_{\text{SAW}} \rangle$. According to the Einstein relation the conductivity is proportional to the diffusivity. Thus, if the total resistance r_N of a SAW chain of length N grows as N^{μ}, then we speculate that

$$\delta = 1 - \mu, \qquad k = 1,$$

when $\langle R_t^2 \rangle$ is measured along the SAW. If now $\langle R_t^2 \rangle$ is measured in the embedding Euclidean lattice

$$\delta = (1-\mu)\nu_s, \qquad k = \nu_s \tag{4}$$

where ν_s is the inverse fractal dimensionality, d_f^{-1} for SAW (Mandelbrot 1983). However, due to the hopping across the 'bridges' (Levy-like flights), the effective fractal 'seen' by the random walker will have a fractal dimensionality different from that of the SAW chain. We shall come to this point later. It may be noted that for t very large compared to N, $\langle R_t^2 \rangle$ should saturate to

$$\langle R_t^2 \rangle \propto N^{2\nu_s} \qquad \text{for } t \geqslant N^{\theta}. \tag{5}$$

In this letter we shall estimate the conductivity exponent δ by a small cell real space renormalisation group (RSRG) technique. Next, we shall measure $\langle R_t^2 \rangle$ from Monte Carlo study of RW on Monte Carlo generated SAWs. The values of the exponents δ and k, so obtained, will be compared with the RSRG results and with earlier estimates of δ (Ball and Cates 1984) and k (Helman *et al* 1984, Yang *et al* 1985). We have also studied the crossover between (3) and (5).

The renormalised fugacities f' (cf Stanley *et al* 1982) and renormalised resistance r' (cf Stinchcombe and Watson 1976) for the cells shown in figure 2 can be written as

$$f' = 2f^2 + 2f^3, \qquad r'f' = 4rf^2 + 2rf^3 \tag{6}$$

for the triangular lattice cell (figure 2(*a*)) with scale factor $b=\sqrt{3}$,

$$f'=f^2+2f^3+f^4$$
$$r'f'=2rf^2+6rf^3+\tfrac{7}{4}rf^4 \tag{7}$$

for the square lattice cell (figure 2(*b*)) with $b=2$, and

$$f'=f^3+3f^4+9f^5+5f^6+9f^7+2f^8+3f^9$$
$$r'f'=3rf^3+12rf^4+\tfrac{81}{2}rf^5+\tfrac{79}{4}rf^6+\tfrac{1079}{30}rf^7+\tfrac{619}{126}rf^8+\tfrac{29}{4}rf^9 \tag{8}$$

for the square lattice cell (figure 2(*c*)) with $b=3$. The non-trivial fixed point (f^*) and exponents (given by $(\partial f'/\partial f)_*=b^{1/\nu_s}$ and $(\partial r'/\partial r)_*=b^{\mu/\nu_s}$) are given in table 1. Our extrapolated RSRG result thus indicates $\mu=0.88$, giving $\delta=(1-\mu)\nu_s=0.09$ for SAWs on two-dimensional lattices.

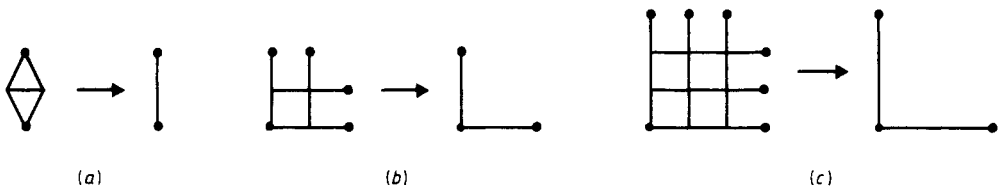

Figure 2. The original and the renormalised cells for (*a*) triangular lattice with $b=\sqrt{3}$, (*b*) square lattice with $b=2$, (*c*) square lattice with $b=3$.

Table 1. Nontrivial fixed point and exponents $\nu_s=\mu$.

Lattice	b	f^*	ν_s	μ
Triangular	$\sqrt{3}$	0.37	0.67	0.69
Square	2	0.47	0.72	0.91
Square	3	0.45	0.72	0.90

We generated SAWs of step sizes (N) from 10 to 75, on a square lattice, by the usual Monte Carlo method. In order to check the nature and also the size of the ensemble (number of configurations sufficient for reasonable average) for SAWs of various step sizes N, the average end-to-end distance exponent ν_s was computed. The value obtained agreed well with the exact value $\nu_s=0.75$ (for dimension $d=2$ of the embedding Euclidean lattice) within the limits of computational accuracy. RWs of step sizes ($t \ll N^\theta$, in practice, $t \geqslant N$ for reasons discussed later) from 7 to 70 were generated on these SAWs (also by Monte Carlo methods). Configurational averaging of the square of the end-to-end distance R_t^2 of the RW was performed by varying (a) the starting point of the RW on a given SAW configuration and then, (b) repeating procedure (a) for a large number (larger than the corresponding ensemble size mentioned earlier) of SAW configurations. The total number of RW configurations thus generated, for each given values of N and t, was 25 000 for $N \leqslant 62$ and more than 15 000 for $N>62$.

Fitting these results for $\langle R_t^2\rangle$ with the scaling equation (3) for different N and t values, the exponents k (see figure 3) and δ were determined. We get $k \simeq 0.72$ and $\delta=0.1$.

The temperature dependence of the spin-lattice relaxation times of Fe^{3+} ions in haemoproteins and ferredoxin suggests (Helman *et al* 1984) that the phonon density

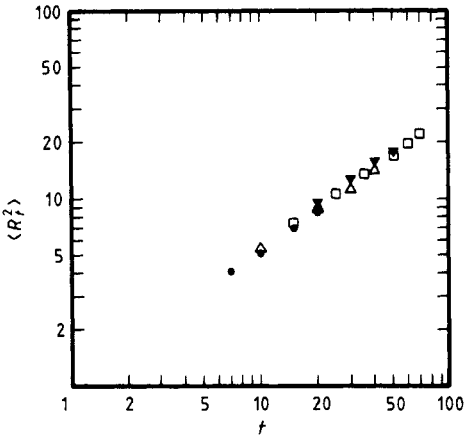

Figure 3. Log-log plot of $\langle R_t^2 \rangle$ against t for different values of N (●, $N=33$; Δ, $N=50$; ▼, $N=62$; □, $N=75$). The slope of the curve gives the exponent $k \simeq 0.72$.

of states $\rho(\omega)$ for such proteins (polymer) chains varies at low frequencies as ω^{d_s-1} where the spectral dimensionality d_s ($=2d_f/d_w$) for such SAW chains, with 'bridges', turns out to be equal to its fractal dimensionality d_f ($=\nu_s^{-1}$). Helman *et al*, therefore, concluded that due to the presence of these 'bridges' the RW might effectively 'see' the embedding Euclidean lattice, giving thereby k ($=2/d_w$) $=1$. Our Monte Carlo result $k \simeq 0.72$ does not support this speculation. Yang *et al* (1985) also reports a lower value of $k \simeq 0.75 = \nu_s$. (They did not distinguish between the N and t dependences of $\langle R_t^2 \rangle$.) We get an even lower value ($k \simeq 0.72$). This, we believe, is a definite effect of the diffusion across the 'bridges' (Levy-like flights). Due to the latter effect, RWS effectively diffuse through the shortest nearest-neighbour connecting path of a SAW chain. Knowing the length $l_N \propto N^{\varepsilon}$ for such a shortest path of an N-step SAW, where $\varepsilon = 0.98$ for $d=2$ (Bhattacharya and Chakrabarti 1984a) one can estimate k by replacing k in equation (5) by $k = \nu_s \varepsilon$ ($=0.73$ for $d=2$). This result is in good agreement with our observation.

In an earlier communication, Ball and Cates (1984) suggested that the resistance of a SAW chain grows as $r_N \propto N$ plus correction terms, so that $\mu = 1$ and $\delta = 0$. However, the plot of Monte Carlo results for fixed values of RW step size t indicates a small, yet non-zero, value of δ ($\simeq 0.1$). This value of δ compares well with our RSRG result $\delta = 0.09$. Although their field-theoretic treatment indicated that μ is slightly less than unity (for $d<4$), Ball and Cates argued that the dominant term in r_n should be linear in N. The latter arose from their 'picture' of a typical SAW configuration, which consists of distant blobs (sites on a SAW connected multiply, on a 'small' scale, by the 'bridges') connected essentially by linear (singly connected) links. However, such a picture of nearest-neighbour connected SAW is not self-similar. The self-similarity requires the blobs to be connected by links at all length scales, thereby excluding the possibility of essentially singly connected regions.

As mentioned earlier, our study was essentially restricted to the case $t \ll N$. In order to study the crossover between the behaviours (3) and (5), we plotted (see figure 4) $\langle R_t^2 \rangle$ against t for a fixed value of N ($=33$). It shows that for $t \ll N$ the asymptotic form (3) remains valid whereas for $t \gg N^{\theta}$, $\langle R_t^2 \rangle$ saturates to the limiting form (5).

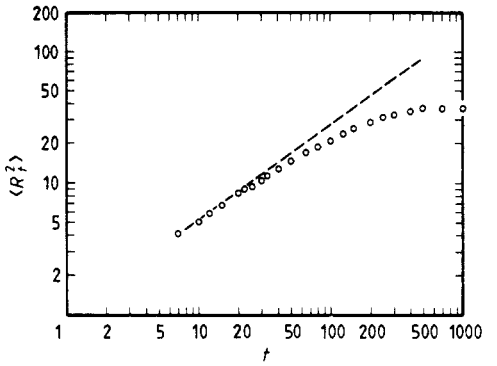

Figure 4. Log-log plot of $\langle R_t^2 \rangle$ against t for fixed N (= 33). The initial slope of the curve is 0.72 (broken straight line). The deviation, starting near $t \simeq N$, from the broken line indicates the beginning of the crossover region.

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