A novel growing self-avoiding walk in three dimensions

LETTER TO THE EDITOR

A novel growing self-avoiding walk in three dimensions

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Abstract. We introduce a growing self-avoiding walk in three dimensions (3D) that can terminate only by returning to its point of origin. This 'symmetric tricolour walk' (STW) is a direct generalization of the smart kinetic walk to 3D, and yet is readily simulated. Our Monte Carlo simulations strongly suggest that the fractal dimension of the STW is exactly 2. This conclusion is supported by a mapping of the STW onto a self-attracting self-avoiding walk at its collapse transition.

The equilibrium behaviour of long polymer chains in a good solvent has been the subject of much research over the last four decades and is now quite well understood [1]. Chains of this kind are commonly modelled as self-avoiding walks (SAWs). In most studies, the process of polymerization (if present at all) is so slow that it may be neglected on time scales characterizing chain fluctuations. Recently, however, there has been a great deal of interest in the opposite, far-from-equilibrium limit of rapid polymerization [2–10]. This interest has centred on the properties of growing SAWs. Although at first there were difficulties in finding growing walks that grow indefinitely and that are strictly self-avoiding [2, 3], several such walks are now known in two dimensions (2D) [4–9]. The most extensively studied and simplest of these walks is the smart kinetic walk (SKW) [4–6]. The SKW on the hexagonal lattice depends on a single parameter p. At the critical point $p = \frac{1}{2}$, the walks have fractal dimension $D_{SKW} = \frac{7}{4}$ [11]. A second indefinitely growing SAW, the diffusion-limited self-avoiding walk (DLSAW), was introduced by Bradley and Kung [7] and by Debierre and Turban [8] as a model of the diffusion-limited growth of a polymer chain in a dilute solution of monomers [12]. Their Monte Carlo studies in 2D yielded the fractal dimension $D_{DLSAW} = 1.29 \pm 0.01$ [13]. Both these results differ from the fractal dimension of the equilibrium SAW in its high temperature phase [14], $D_{EQSAW} = \frac{4}{3}$.

Growing SAWs in three dimensions (3D) have received much less attention, even though they are of greater physical interest. The kinetic growth walk does not grow indefinitely, and is believed to slowly cross over to a regime in which it has the same scaling behaviour as the equilibrium SAW in 3D [15]. The SKW has not been simulated in 3D, since it has not been clear how to generalize the growth algorithm to dimensions d higher than 2. The algorithm used to generate the DLSAW is readily extended to $d > 2$, on the other hand, and simulations of the model have been performed in three and four dimensions [7, 10]. Finally, Lyklema introduced the growing self-avoiding

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trail (GSAT) and studied it in 2D and 3D by Monte Carlo [16]. Self-avoiding trails are walks that may revisit sites but not bonds, and so display a kind of partial self-avoidance. In 3D, Lyklema finds a fractal dimension very close to 2 for the GSAT.

In addition to being important in the theory of growing polymer chains, the study of the SKW in 2D is relevant to several other topics of current theoretical interest [17–20]. For $p = \frac{1}{2}$, right and left turns are equally probable in the SKW on the hexagonal lattice, and the model can be mapped onto a certain self-attracting SAW at its collapse transition [18, 19]. This correspondence has engendered considerable progress in the understanding of the 2D θ point [18–20].

There are two ways in which the SKW can be generalized to 3D. Recently, we discussed one of the possible generalizations: the smart kinetic surface (SKS) [21]. The SKS is a growing self-avoiding surface that directly generates the hull of a percolation cluster in 3D. The SKS was employed in [21] to determine the scaling properties of 3D percolation hulls with much greater precision than in previous studies.

In this letter we introduce a new growing SAW in 3D, the tricolour walk. The tricolour walk is the second direct generalization of the SKW to three dimensions, and depends on two parameters, p and q. The tricolour walk is 'smart'—it cannot self-trap—and yet it is readily simulated. An important special case of the model is the symmetric tricolour walk (STW), in which all allowed moves for the walker are equally weighted and $p = q = \frac{1}{3}$. Our extensive Monte Carlo simulations of the STW strongly suggest that its fractal dimension is 2. We show that the STW is equivalent to a self-attracting SAW in equilibrium, and then use this equivalence to argue that its fractal dimension must be *exactly* 2. As a by-product, we obtain the exact θ temperature for a self-attracting SAW in 3D.

In the present letter, we shall confine our attention to the symmetric tricolour walk. Asymmetric tricolour walks will be considered in forthcoming publications [22].

The tricolour walk is defined on the lattice dual to the body-centred cubic (bcc) lattice. The Wigner–Seitz (WS) cell of the bcc lattice is a truncated octahedron, which is a regular polyhedron with eight hexagonal faces and six square faces. The dual (or WS) lattice is constructed by packing truncated octahedra to fill space and is four-fold coordinated (figure 1). A site of the original lattice resides at the centre of each WS cell. Note that each bond in the WS lattice belongs to three WS cells. Accordingly, we can label a particular bond by the unordered triplet (S_1, S_2, S_3), where sites S_1, S_2 and S_3 are the sites at the centre of the three WS cells that contain the bond. We will also say that the sites S_1, S_2 and S_3 are adjacent to the bond (S_1, S_2, S_3).

The tricolour walk is a random walk on the WS lattice. As the walk moves through the lattice, the sites of the original lattice adjacent to the walk are coloured black, white or grey. Initially all sites in the original lattice are uncoloured, and the bonds in the WS lattice are all unoccupied. At the first time step, the walk traverses a bond labelled (S_1^0, S_2^0, S_3^0). Sites S_1^0, S_2^0 and S_3^0 are now coloured black, white and grey, respectively. Now consider the growth of the walk an arbitrary length of time later, and suppose that the walk has just travelled along the bond (S_1, S_2, S_3). We may assume that sites S_1, S_2 and S_3 are coloured black, white and grey, respectively. The point on the WS lattice that has just been reached belongs to four WS cells. Sites S_1, S_2 and S_3 lie at the centres of three of these cells. Let site S_4—the 'target site'—be the site at the centre of the fourth WS cell. If S_4 is uncoloured, it is coloured black with probability p, white with probability q, and grey with probability $r = 1 - p - q$. If the target site is already coloured, its colouring is left unchanged. The next step of the walk is now made. If S_4 is black, the walk traverses the bond (S_4, S_2, S_3). If S_4 is
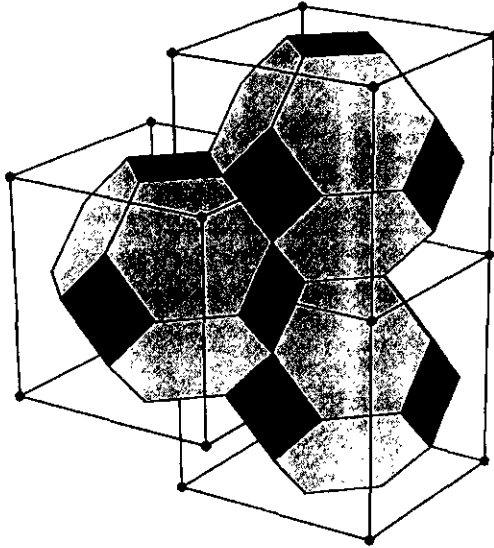
Figure 1. Wigner–Seitz lattice for the bcc lattice. The sites of the bcc lattice (solid circles) form two interpenetrating simple cubic lattices. The Wigner–Seitz lattice is a space-filling packing of truncated octahedra (shaded solids). A site of the bcc lattice resides at the centre of each truncated octahedron.

white, the walk travels along the bond (S_1, S_4, S_3). Finally, if S_4 is grey, the bond (S_1, S_2, S_4) is occupied. In each case, the sites adjacent to the newly occupied bond have three different colours. The walk terminates if it returns to its point of origin. Walks with $p = q = r = 1/3$ will be called symmetric, while walks with different values of p, q and r will be referred to as asymmetric.

The tricolour walk is a natural generalization of the smart kinetic walk from 2D to 3D. Like the SKW, the tricolour walk is strictly self-avoiding. The SKW is called 'smart' because it may terminate only by returning to its point of origin—it cannot make a move that would prevent its future return to its starting point. The same is true of the tricolour walk, since each site in a completed walk must belong to precisely two occupied bonds.

We will begin our study of the symmetric tricolour walk by attempting to anticipate its behaviour, based on the analogy with the SKW on the hexagonal lattice. The resulting conjectures on the behaviour of the STW will then be tested by Monte Carlo simulations.

First, consider the SKW for $p = \frac{1}{2}$. For this value of p, all allowed moves are equally probable. The walks generated are scale invariant [4] with a fractal dimension of $\frac{7}{4}$ [11]. Thus, $p = \frac{1}{2}$ is a critical point for the SKW. Now consider the symmetric tricolour walk. When $p = q = r = \frac{1}{3}$, the three colours black, white and grey are equally probable, and hence all allowed moves are equally weighted. By analogy with the behaviour of the SKW, we expect $p = q = \frac{1}{3}$ to be a critical point for the tricolour walk. If this is so, we expect that STWs will be scale invariant with a non-trivial fractal dimension D_3. We shall determine D_3 in what follows.

In our Monte Carlo simulations of the STW, each walk either closed or grew to the maximum permitted length of $N_{\max} = 2^{20} = 1048\,576$ steps. A total of 10 000 walks were constructed, which required a total of roughly 60 CPU hours on an IBM RISC System/6000 model 540.

Of the 10 000 walks generated, a total of 6269 had not closed when they reached length N_{max}. For these open chains, we computed the average squared distance $\langle R^2(\Delta)\rangle$ between sites Δ steps apart for $\Delta = 1, 2, 2^2, \ldots, 2^{20}$. For each value of Δ, we averaged over each pair of points separated by Δ steps within a chain, and then averaged over all the open chains. A log–log plot of $\langle R^2(\Delta)\rangle$ versus Δ (figure 2) reveals a linear region three decades wide, and so strongly supports our identification of $p = q = \frac{1}{3}$ as a critical point for the tricolour walk. A least-squares fit to all but the first four points gives the estimate $D_3 = 2.029 \pm 0.003$ for the fractal dimension. The error quoted here is the standard deviation obtained by a least-squares fit, and does not take into account any systematic errors present. To obtain a more reliable estimate of D_3, we computed the finite-size estimator

$$D_e(\Delta) \equiv \ln 4[\ln\langle R^2(\Delta)\rangle - \ln\langle R^2(\Delta/2)\rangle]^{-1} \qquad (1)$$

for $\Delta = 2, 2^2, \ldots, 2^{20}$. For large Δ, the estimator $D_e(\Delta)$ converges to the fractal dimension D_3. Our results are shown in figure 3. $D_e(\Delta)$ overshoots the value 2 and then decreases towards it. Based on these results, we think that it is likely that the asymptotic value of D_3 is 2.
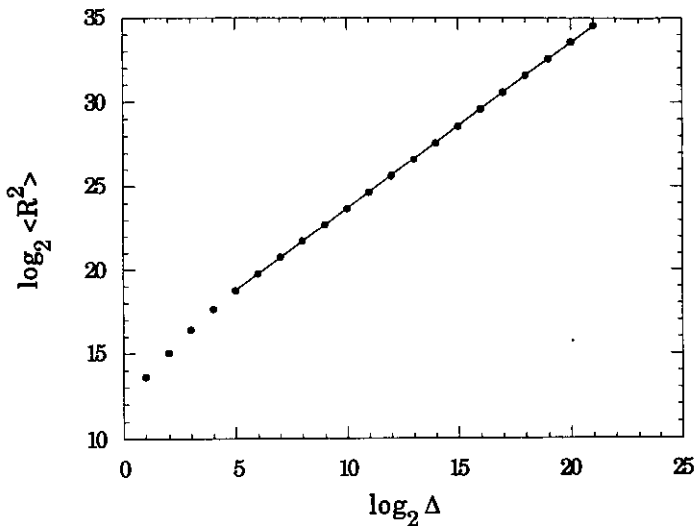

Figure 2. Log–log plot of the mean square distance $\langle R^2\rangle$ between two sites separated by Δ steps as a function of Δ for the open symmetric walks. The straight line is a linear least squares fit to the data points for $\Delta \geq 32$. This fit gives the estimate $D_3 = 2.029 \pm 0.003$ for the fractal dimension of the symmetric walks.

We now show that the STW is equivalent to a self-attracting self-avoiding loop (SASAL) that has come to equilibrium at a certain temperature. We then use this correspondence to argue that the fractal dimension of the STW is exactly 2, as suggested by our Monte Carlo results.

Let us first define the equilibrium SASAL. Let C be an arbitrary self-avoiding loop (SAL) of N bonds on the WS lattice. In order to assign an energy to this SAL, we walk around it, colouring the adjacent sites in the original lattice as we go. We first choose a bond in C, and let the label of the bond be (S_1^0, S_2^0, S_3^0). The sites S_1^0, S_2^0 and S_3^0 are coloured black, white and grey, respectively. Next, we traverse the bond in one of the
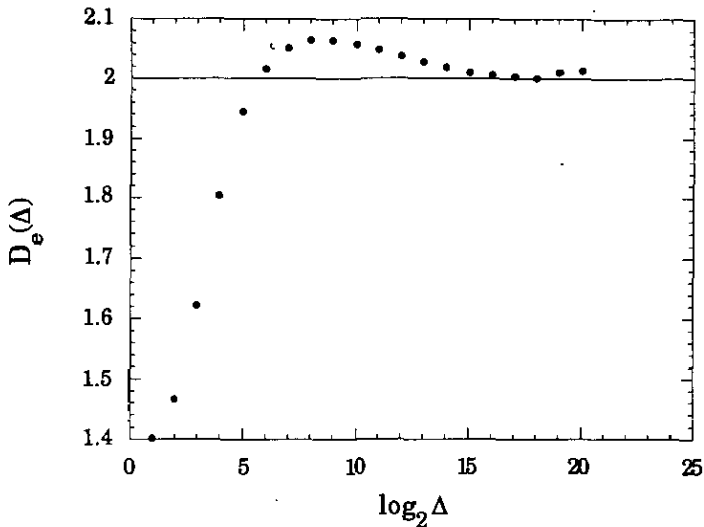
Figure 3. The finite-size estimator $D_e(\Delta)$ for the fractal dimension of the open symmetric walks as a function of $\log_2 \Delta$. $D_e(\Delta)$ appears to converge to 2 as Δ grows large.

two possible directions. The site just reached is shared by the ws cells centred on sites S_1^0, S_2^0 and S_3^0. It also belongs to a fourth ws cell centred on a site which we label S_4^0. Site S_4^0 is now coloured in such a way that the sites adjacent to the next bond in the SAL have three different colours. We continue colouring in this fashion as we follow the SAL. To see what happens in the general case, consider the situation after the colouring of the sites adjacent to the bond (S_1, S_2, S_3) has just been completed. The site just reached is shared by the three ws cells centred on sites S_1, S_2 and S_3. It also belongs to a fourth ws cell centred on a site we will label S_4. We now colour S_4 in such a way that the sites adjacent to the next bond in the SAL have three different colours. If S_4 has been coloured previously, it is recoloured. This recolouring can either change the colour of S_4 or leave it unmodified. This process continues until we return to the point of departure.

We are now ready to assign an energy to the SAL. If the colour of a site is changed at any point in the colouring process, the SAL has infinite energy—in other words, the conformation is forbidden. Otherwise, the energy of the loop is taken to be $\varepsilon s(C)$, where $s(C)$ is the number of bcc lattice sites adjacent to the loop. Thus, each coloured site is assigned an energy ε. Note that the number of times that sites are recoloured, $n(C)$, is equal to $N + 3 - s(C)$. As it ought to be, the energy assigned to the SAL is independent of the bond chosen as the starting point for the colouring process, and of the direction we travel around the SAL. The energy is also unaffected by permutations of the colours assigned to the sites S_1^0, S_2^0 and S_3^0.

The partition function of the SAL at temperature T is

$$Z_N(T) = \sum_{C'} \exp[-\beta \varepsilon s(C')] \tag{2}$$

where the sum runs over all allowed SAL configurations C' and $\beta \equiv T^{-1}$ is the inverse temperature. The Boltzmann weight of a particular allowed configuration C is

$$w(C, N, T) = \exp[-\beta \varepsilon s(C)]/Z_N(T). \tag{3}$$

The SAL we have defined has a certain set of forbidden configurations. It also has an attractive short-ranged interaction between monomers on sites in the same WS cell. This interaction has strength ε, and leads to higher Boltzmann weights for loop conformations with small numbers of adjacent sites. We expect this problem to be in the same universality class as the usual self-attracting SAW with nearest neighbour interactions alone. If this is so, the SAL will have a mean radius of gyration $\langle R \rangle$ that scales as N^ν at high temperatures, and the value of ν will be the same as that observed for the unconstrained 3D SAW in the absence of attractive monomer–monomer interactions [1]. Monte Carlo simulations of the latter problem have yielded the estimate $\nu_{SAW} = D_{SAW}^{-1} = 0.592 \pm 0.003$ [23]. As the temperature is reduced, a collapse transition occurs at some temperature $T = T_\theta$ with $T_\theta / \varepsilon = O(1)$ [1]. For temperatures $T < T_\theta$, the SAL has a non-zero density and ν assumes the value $\frac{1}{3}$. Finally, at the collapse transition temperature the value of ν is expected to be $\frac{1}{2}$, since the upper critical dimension for the θ point is 3 [1, 24].

We next consider the tricolour walk with $p = q = \frac{1}{3}$. The probability that a particular step is made is $\frac{1}{3}$ if the target site is uncoloured, and is 1 if the target site has already been coloured. Any move that would necessitate a change in the colour of the target site is forbidden, and so each time that a previously coloured site is targeted, the next move is forced. The probability that a loop of length N is formed is

$$P(N) = \sum_{C'} 3^{-N} \exp[(\ln 3) n(C')] \tag{4}$$

where the sum runs over all allowed SAL loop configurations of length N and $n(C')$ is the number of times that forced moves are made in the walk C'. The probability of a particular allowed loop configuration C (given that the walk closes in N steps) is

$$p(C, N) = P(N)^{-1} 3^{-N} \exp[(\ln 3) n(C)]. \tag{5}$$

Let $T_0 \equiv \varepsilon / \ln 3$. Comparing (2) and (4) and using the relation $n(C) = N + 3 - s(C)$, we see that

$$Z_N(T_0) = \frac{1}{27} P(N) \tag{6}$$

while from (3) and (5) we obtain

$$w(C, N, T_0) = p(C, N). \tag{7}$$

Equations (6) and (7) show that the SASAL at temperature $T = T_0$ is equivalent to the STW. In particular, (7) establishes that the loops in these two models have the same fractal dimension. The fractal dimension of the tricolour walk at its critical point can therefore assume only one of three possible values: 2, 3 or D_{SAW}. On the basis of our Monte Carlo simulations, we can eliminate the latter two values and so conclude that the fractal dimension of the STW is exactly 2. It is interesting to note that it has been speculated that $d = 3$ is the upper critical dimension of the SKW [5, 9].

Although the equivalence we have established is exact, our argument that $D_3 = 2$ is not rigorous for several reasons. First of all, we cannot be certain that our self-attracting SAL is in the same universality class as the usual self-attracting SAW in 3D. Joining the ends of a SAW to form a SAL does not alter the value of ν in the high or low temperature phases or at the θ point. However, the attractive interactions are longer-ranged in our SAL than in the usual self-attracting SAW, and this may mean that the two collapse transitions are different universality classes. Indeed, the effect of

next-nearest-neighbour interactions on the 2D collapse transition has been debated at length [20]. The constraints on our SAL configurations may also alter the universality class. Finally, even if it is granted that our constrained, self-attracting SAL is in the same universality class as the self-attracting SAW with nearest-neighbour interactions alone, it is possible that a slow crossover occurs in the STW, and that the true asymptotic value of the fractal dimension is either 3 or D_{SAW}. This scenario strikes us as unlikely, however, since we see no evidence for such a crossover in our simulations. Moreover, it has been established rigorously that the SKW on the hexagonal lattice is critical at $p = \frac{1}{2}$ [4], and the tricolour walk is expected to be critical at the point $p = q = \frac{1}{3}$ by analogy.

If we are correct in identifying $p = q = \frac{1}{3}$ as a critical point of the tricolour walk, then $T_0 = \varepsilon / \ln 3$ is the *exact* collapse transition temperature of the SASAL. As far as we can determine, this is the first collapse transition temperature to be found exactly in 3D. This result should be quite useful in Monte Carlo studies of the collapse transition, since critical exponents can be computed much more precisely when the exact transition temperature is known. In addition, very long polymer chains at their θ point can be constructed using the STW. This may prove useful in resolving a dispute concerning the corrections to scaling at the 3D θ point [25].

In summary, in this letter we introduced the tricolour walk, a growing SAW that is a direct generalization of the smart kinetic walk to 3D. Our growing walk is readily simulated, even though it is 'smart'. In the symmetric tricolour walk, all allowed moves for the walker are equally weighted. Our Monte Carlo simulations of this walk strongly suggest that its fractal dimension is 2. We demonstrated that the STW is equivalent to a *self-attracting SAW that has come to equilibrium at a certain temperature* T_0. This equivalence is a direct analogue of a mapping [18] between the SKW on the hexagonal lattice with $p = \frac{1}{2}$ and a self-attracting SAW at its collapse transition. Our mapping was used to argue that T_0 must be the θ temperature for the self-attracting SAW, and hence that the fractal dimension of the symmetric walks is exactly 2. The STW would therefore appear to be in a different universality class than both the kinetic growth walk and the DLSAW. On the other hand, our walk may have the same asymptotic scaling behaviour as the GSAT in 3D, but this could be confirmed only by analytical work on the latter problem.

As in the case of the SKW on the 2D hexagonal lattice, the tricolour walk is intimately related to percolation. This relationship will be discussed in forthcoming publications [22], as will asymmetric tricolour walks.

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