Diffusion-limited growth of polymer chains

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A new self-avoiding walk (SAW) which grows without terminating is introduced as a model of the diffusion-limited growth of linear polymers. The model is in a different universality class than the equilibrum SAW and previously considered kinetic SAW's, with $\nu = 0.774 \pm 0.006$ in two dimensions and $\nu = 0.56 \pm 0.02$ in three dimensions. The "indefinitely growing SAW" is shown to emerge as a particular limit of our model.

The seminal work of Witten and Sander[1,2] on diffusion-limited aggregation (DLA) has generated considerable interest in growth processes in which the clusters are fractals. The interest has spread into the realm of self-avoiding walks (SAW's), which are commonly used as models of polymer chains.[3] The primary problem in the study of growing SAW's has been that it is difficult to find growth rules that lead to walks which are self-avoiding and which never terminate. Amit, Parisi, and Peliti[4] introduced a walk (the "true" SAW) which grows forever, but which only prefers not to revisit a site. A walk which is strictly self-avoiding but which may terminate, the kinetic growth walk, was subsequently studied by several groups.[5] Finally, a growing walk that is both self-avoiding and unending, the indefinitely growing SAW (IGSAW), was discovered.[6-8] The walker in the IGSAW is "smart": It never steps into a *cul-de-sac* from which there is no escape. If several smart moves are possible, they are given equal weight.

The subject of this Rapid Communication is a new kinetic walk which grows without terminating and which is strictly self-avoiding, the diffusion-limited SAW (DLSAW). In this model, bifunctional monomers diffuse to the growing tip of a linear polymer from faraway, so there must always be a path from the tip to infinity that does not touch the polymer. Thus, the model explicitly contains a physical mechanism leading to "smartness." The problem is also an interesting cross between growing SAW's and DLA. The DLSAW should apply to the diffusion-limited growth of a polymer chain in a dilute solution of monomers, provided that the characteristic diffusion time is much shorter than the time characterizing the relaxational dynamics of the chain.

Our Monte Carlo studies in two dimensions (2D) show that the DLSAW is in an entirely different universality class than the IGSAW. In particular, if α is the probability that a diffusing monomer adheres to the tip on contact, then for $\alpha = 1$ the fractal dimension is $D = 1.29 \pm 0.01$. A simple, heuristic explanation for why this is smaller than the IGSAW value[7] $D = 1.76 \pm 0.01$ will be given. To gain some insight into the scaling behavior for $0 < \alpha < 1$, we first show that the DLSAW reduces to the IGSAW in the $\alpha \rightarrow 0$ limit. We then argue that for any $\alpha > 0$ the scaling behavior seen in the IGSAW is present only up to a length $l_c(\alpha)$, and that on longer length scales, crossover to the

$\alpha = 1$ DLSAW scaling behavior must occur.

So far, work on the IGSAW has been restricted to 2D.[6-8] The DLSAW, however, can be simulated for general dimensions d using essentially the same procedure as in $d = 2$. We obtain $D = 1.79 \pm 0.06$ for the DLSAW on the simple cubic lattice with $\alpha = 1$, so the upper critical dimension d_c is greater than 3.

In the DLSAW a dimer is initially placed on an arbitrary pair of nearest-neighbor points on a d-dimensional Euclidean lattice and is held fixed there. One of the ends of this polymer is considered to be the growing tip, and the other the "root." A hypersphere Σ of radius R_0 is drawn about the root; R_0 is to be large compared to the lattice constants. A point on Σ is chosen at random and a particle is released there. The diffusing particle then moves as follows: At each time step one of the particle's nearest-neighbor sites is chosen at random. If this site is not occupied, the particle moves there; otherwise, it temporarily remains where it is. For each time step the particle spends at a nearest-neighbor site of the tip, there is a probability α that it sticks there. Once the particle has struck, it moves no further and so becomes the new tip of the polymer. A second particle is then released on Σ, and it diffuses until it adheres to the new tip. This process continues with the addition of the third particle, the fourth particle, and so on. If any particle wanders too far away from the polymer, it is discarded and another diffusing particle is released on Σ. (We discarded the particle it it reached a point $2R_0$ away from the root.)

DLSAW's and IGSAW's are both formed in an inherently kinetic and irreversible way, and both are unending and strictly self-avoiding. However, smart moves need not be weighted equally in the DLSAW, and this is what leads to different scaling behavior in the two problems. The differences in weighting are best illustrated by a simple example. In the conformation on the 2D triangular lattice shown in Fig. 1, the probability of growth into the *cul-de-sac* at C is zero in both the DLSAW and the IGSAW. It is also easy to evaluate the probability that the next particle joins the polymer at A (p_A) or at B (p_B). By definition, $p_A = p_B = \frac{1}{2}$ in the IGSAW. Now consider the DLSAW. Each time the diffuser arrives at A, it adheres with probability α. (Recall that the move $A \rightarrow A$ is considered to be a new arrival at A.) Given arrival at A, the probability of the particle adhering at B before returning
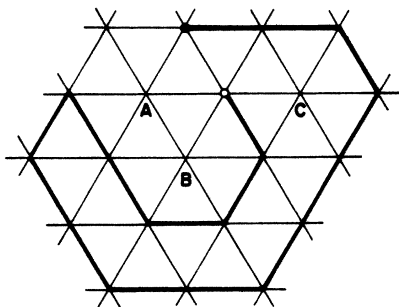
FIG. 1. A conformation on the triangular lattice. The polymer is shown as a bold line, and the root and the tip are shown as a closed and an open circle, respectively.
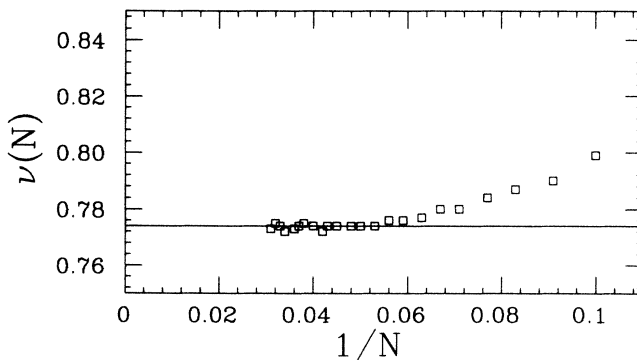

FIG. 2. Plot of $v(N)$ vs N^{-1} for the DLSAW on the square lattice with $\alpha = 1$. The solid line gives the linear extrapolation to $N = \infty$.

to A is

$$\tfrac{1}{6}\alpha(1-\alpha) \sum_{n=0}^{\infty} [\tfrac{5}{6}(1-\alpha)]^n = \alpha(1-\alpha)(1+5\alpha)^{-1} .$$

Since the walker can only reach B via A, $p_B/p_A = (1-\alpha)/(1+5\alpha)$ and, hence, $p_B < p_A$ for $0 < \alpha \le 1$. Also note that $p_A - p_B = O(\alpha)$ for $\alpha \ll 1$, so p_A and p_B converge to their IGSAW values as $\alpha \to 0$.

In our Monte Carlo studies of the DLSAW, we generated a large number of relatively short DLSAW's and assumed that the mean-square radius of gyration $\langle R^2 \rangle$ has the scaling form[9]

$$\langle R^2(N) \rangle = AN^{2v}(1 + BN^{-1} + CN^{-\Delta} + \cdots) , \qquad (1)$$

where N is the number of particles in the chain and $v \equiv D^{-1}$. A value for v was then obtained from the expansion[9]

$$v(N) \equiv \tfrac{1}{2} \ln[\langle R^2(N+1) \rangle / \langle R^2(N) \rangle] / \ln[(N+1)/N]$$

$$= v - \tfrac{1}{2}BN^{-1} - \tfrac{1}{2}\Delta CN^{-\Delta} + \cdots . \qquad (2)$$

To study the DLSAW in 2D, we generated 10000 chains of length $N = 32$ on the square lattice with $\alpha = 1$. Two optimization techniques introduced in Monte Carlo studies[2,10] of DLA were employed. (i) Rather than keeping the release radius R_0 fixed, we took R_0 to be $R_{max}+2$, where R_{max} is the distance from the root to the furthest point in the polymer. This is permissible because the first passage probability of the diffusing particle is isotropic.[2] (ii) If the diffusing particle was further than $R_{max}+4$ from the root, the step size was increased to 2. The step size was further increased at progressively longer distances from the root. This technique has been tested in DLA, and has been shown to significantly reduce computing time without compromising accuracy.[10] Figure 2 shows our results for $v(N)$ plotted versus N^{-1}. The curve becomes quite flat as N grows, and accordingly the value of B must be rather small. Moreover, there is no evidence of any curvature after a transient at small N, so it appears that $\Delta > 1$. Thus, v can be determined by linear extrapolation. We obtain the value $v = 0.774 \pm 0.006$ for $d = 2$.

The exponent v for the DLSAW with $\alpha = 1$ is substantially larger than the value $v = 0.567 \pm 0.003$ obtained[7] for the IGSAW in 2D. There is a simple argument for why this must be. In our example (Fig. 1), the site A in effect

screens B from the incident particle flux, and adhesion at B (which leads to a more compact chain) is less likely than adhesion at A. Screening is also present in the DLSAW in much more general circumstances. If the tip is approaching another part of the polymer—so that a loop is nearing completion—the growth sites outside the partially formed loop shield the growth sites inside. This shielding favors those smart moves which lead to the most rapid growth toward infinity and, hence, to less compact polymers.

Nienhuis[11] has argued that the Flory value[12] $v = \tfrac{3}{4}$ is exact for equilibrium SAW's in 2D, and this is in agreement with most of the numerical evidence.[13] Our result is sufficiently accurate to exclude the possibility that v is exactly equal to $\tfrac{3}{4}$ in our problem, so the DLSAW is in a different universality class than the equilibrium SAW. Our model is also in a different universality class from the kinetic growth walk[5] (which is in the same class as the equilibrium SAW[14]) and the "true" SAW (which has $v = \tfrac{1}{2}$ in two dimensions[4]).

To investigate the DLSAW in three dimensions (3D), we generated 28000 chains of length 32 on a simple cubic lattice with $\alpha = 1$. The results for $v(N)$ (obtained using 100 hours of central processing unit time on a VAX-11/780 computer) are shown in Fig. 3. A least-squares fit to the form (2) gives $B \cong 0$, $C \cong -2.6$, $\Delta \cong 1.2$, and the
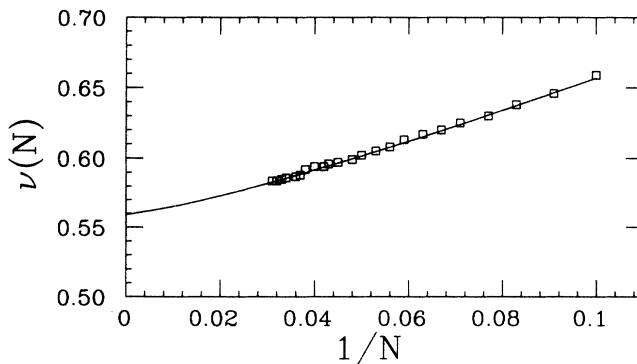

FIG. 3. Plot of $v(N)$ vs N^{-1} for the DLSAW on the simple cubic lattice with $\alpha = 1$. The solid line is the least-squares fit to the form (2).

desired exponent $v = 0.56 \pm 0.02$. This value is smaller than the theoretical,[15] experimental,[16] and Monte Carlo[17] values of v obtained for the equilibrium SAW in 3D.[18] We also see that the DLSAW must have an upper critical dimension d_c which is greater than 3, since $v(d=3) > \frac{1}{2}$. Preliminary studies of the DLSAW in $d = 4$ indicate that d_c is probably also greater than 4. This suggests that d_c may be infinite, as it is believed to be in DLA.[2,19]

Finally, let us study the α dependence of the DLSAW. First consider the behavior of the diffusion field around a polymer when $\alpha = 0$. Suppose that the site $\mathbf{r}$ is not completely surrounded by the polymer, and that k of its z nearest neighbors are occupied. In equilibrium the probability that the diffusing particle is at $\mathbf{r}$, $p(\mathbf{r})$, satisfies $zp(\mathbf{r}) = kp(\mathbf{r}) + \sum p(\mathbf{r}')$, where the sum runs over the $z - k$ vacant nearest-neighbor sites $\mathbf{r}'$. For large $\mathbf{r}$, $p(\mathbf{r})$ must approach a constant c which is determined by the normalization condition. The solution that meets this boundary condition is simply $p(\mathbf{r}) = c$ for all sites $\mathbf{r}$ that can be reached by the diffusing monomer, and $p(\mathbf{r}) = 0$ for all sites that cannot. The IGSAW then corresponds to the limit in which the diffusing particles come into equilibrium with the polymer before adhesion occurs.

For $\alpha > 0$, the diffusing particle makes an average of α^{-1} contacts with the tip before it adheres. Thus, for small α the particle wanders for a long time before adhering, and during this time it comes close to reaching equilibrium. We therefore expect the probability of growth at a particular site in the DLSAW with $\alpha \ll 1$ to differ from its IGSAW value by, at most, a term of order α. (This has been explicitly verified in our example.). Thus, the DLSAW with small α should display the same scaling behavior as the IGSAW on short length scales. Indeed,

$\ln\langle R^2(N) \rangle$ for the DLSAW on the square lattice with $\alpha = 0.1$ was found to lie within 2% of the exact IGSAW values[6] for N up to 22. The time t_c between the particle's initial contact with the tip and adhesion is proportional to $\alpha^{-1} - 1$, however. Thus, when $0 < \alpha < 1$ there is a new length scale $l_c(\alpha) \sim (Dt_c)^{1/2}$ in the problem which is not present in the $\alpha \to 0$ or $\alpha = 1$ limits. (Here D is the diffusion constant.) This suggests than the effect of a small but nonzero α accumulates as the polymer grows, and that on length scales much longer than $l_c(\alpha)$, crossover to the scaling behavior seen in the $\alpha = 1$ DLSAW will occur.

The proposed behavior of the DLSAW for $\alpha < 1$ is analogous to that displayed by DLA when there is a nonzero probability $1 - \alpha$ that the diffusing particle fails to adhere upon contact with the aggregate. In the limit $\alpha \to 0$, DLA reduces to the Eden model,[20] which has compact clusters.[21] However, it appears that for any $\alpha > 0$, crossover to the $\alpha = 1$ scaling behavior occurs once the aggregate is sufficiently large.[2,10] This nontrivial scaling behavior has been attributed to the fact that the tips of the branches shield the interior of the aggregate from the incident particle flux.[1,2] In precisely the same way, we have argued that the DLSAW scales differently than the IGSAW because the interior of an incipient loop is shielded by the growing tip of the polymer.

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