Cluster-Growth Model for Branched Polymers That Are "Chemically Linear"

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We propose a new cluster-growth model for branched polymers which are highly unusual in that they are "chemically linear." The cluster grows by adding a constant number of sites in each successive "chemical shell." We find that these *chemically* linear clusters (where branches and loops are allowed) are in the same universality class as *geometrically* linear chains (where loops and branches are not allowed). We argue that this result is general in that for any chemically linear cluster, loops and branches can be neglected.

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Considerable attention has focused recently on cluster-growth models.[1-5] These models not only are of relevance in describing real systems in nature but also are useful in their own right in seeking to isolate the key features of a disordered system that determine transport properties. Until recently, the main parameter used to describe cluster models was the fractal dimension d_f that describes the fashion in which the cluster mass M scales with the cluster radius R, $M \sim R^{d_f}$. There is, however, a *second* parameter—the chemical dimension d_l—which describes how cluster mass depends on the "chemical length" l, $M \sim l^{d_l}$; here the chemical length between two sites is the minimum number of bonds connecting these sites.[6]

While static critical exponents—if suitably normalized—can be expressed in terms of the *geometrical* exponent d_f, it is believed that transport properties (such as the diffusion and resistivity exponents d_w and $\tilde{\zeta}$) are related in some way to *topological* properties of the fractal.[7] In order to better understand the role played by the chemical dimension d_l, it is of interest to construct well-defined fractal models which can be studied exhaustively. To this end, we introduce here a family of growth models for which $d_l = 1$ by construction. We find that these *chemically* linear clusters (where branches and loops are allowed) are in the same universality class as *geometrically* linear chains (where loops and branches are not allowed). We argue that this result is general in that for any chemically linear cluster, loops and branches can be neglected.

The clusters are grown by the following mechanism. At time $t = 0$, we place a seed particle at the origin of a lattice of coordination number z_1. At $t = 1$, we randomly choose B of the z_1 neighbors of the origin and occupy them; these sites constitute the first "shell," and have a chemical distance $l = 1$ from the origin. The remaining $z_1 - B$ sites will be regarded as "blocked" for the duration of the growth process. At $t = 2$ we consider the z_2 nonoccupied unblocked neighbors of the sites belonging to the first shell; we randomly occupy B of these, and block the remainder. This process is continued until a cluster with $l_{\max}$ chemical shells has been generated.[8]

Figure 1 shows typical clusters grown with $B = 1$,

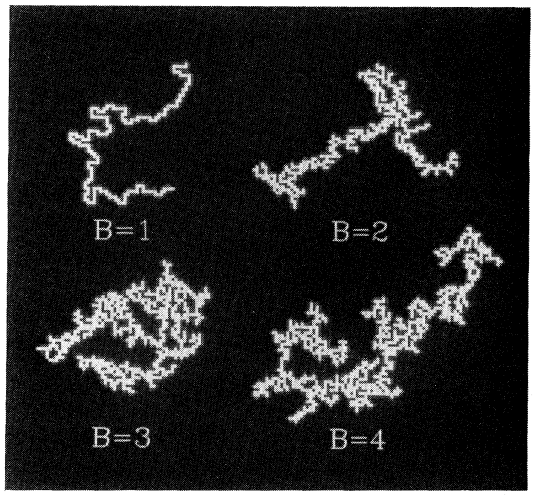

FIG. 1. Examples of branched polymers that are chemically linear: (a) $B = 1$; (b) $B = 2$; (c) $B = 3$; and (d) $B = 4$. One main point of this Letter is that all chemically linear clusters belong to the same universality class as linear polymers. This result is certainly surprising at first sight, in view of the seemingly different structures present in Fig. 1.

2, 3, and 4 on a square lattice; each cluster has $l_{max}=200$. Clearly the case $B=1$ cannot have branching or loops and is, of course, geometrically linear. The cases $B=2$, 3, 4 have branching and loops but are *chemically* linear, since the cluster mass increases linearly with the chemical distance from the origin:

$$M \sim Bl. \tag{1}$$

We found that loops were extremely rare, which is surprising at first because there is certainly nothing in the algorithm that would seem to eliminate loops. We will argue below that loops and branching *do* occur, but are irrelevant since they occur only on small scales.

To determine the fractal dimension d_f, we calculated the rms radius of gyration R of the cluster at each stage of growth (i.e., at each successive value of l). We show in Fig. 2 a log-log plot of R vs l, and we see the curves for different values of B are parallel. Since

$$R^{d_f} \sim M \sim l, \tag{2}$$

we find

$$d_f = 1.47 \pm 0.05 \quad (B=1\text{–}4). \tag{3}$$

We note in passing that the special case $B=1$ is in the same universality class as two models of *growing* linear polymers, the biased self-avoiding walk (BSAW)[9] and the kinetic growth walk (KGW).[4] Whereas the perimeter sites in the present model are blocked from growing during the growth process, they are not blocked in the BSAW and the KGW. However, this blocking is a "short-range effect" and hence does not affect the universality behavior. Indeed, our result (3) for d_f is the same as for the BSAW and the KGW. The *intriguing* feature of this new model is that even when branching and loops are allowed (i.e., $B>1$), the universality class does not change—as will be discussed next.

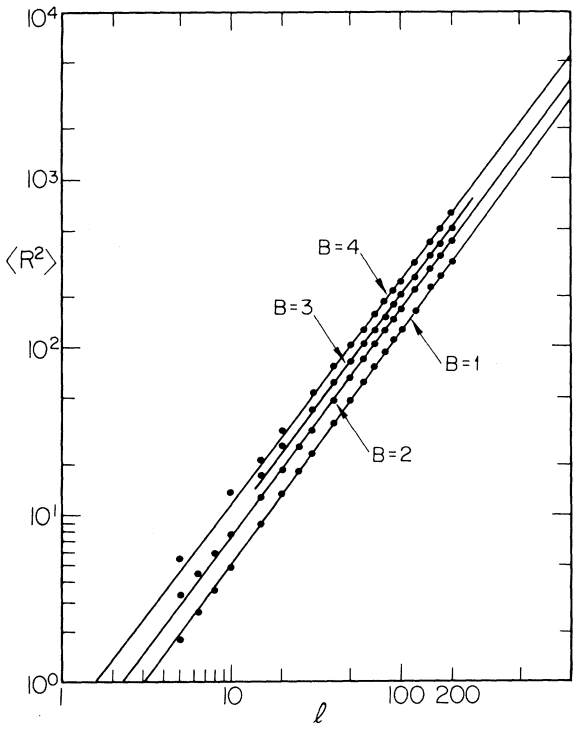

FIG. 2. Dependence of radius of gyration $\langle R^2 \rangle$ on the "chemical size" of the cluster.

The transport properties for these fractals can also be calculated. We will give two arguments. (i) The first is physically more transparent, but involves the assumption that loops (which are rare) can be neglected for finite B.[10] In this case, the chemical path is the only path connecting two sites at distance R, so that the resistivity between two sites separated by R, $\rho \sim R^{\tilde{\zeta}}$, scales in the same fashion as $l \sim R^{d_f}$. Hence

$$\tilde{\zeta} = d_f. \tag{4}$$

Using Eq. (4) and the known result[11] $d_w = \tilde{\zeta} + d_f$, we obtain $d_w = 2d_f$. These results are known for linear geometrical chains[11] without loops or branches. Hence the fracton dimensionality $d_s = 2d_f/d_w$ is *exactly* 1.

(ii) We now argue that *any* cluster with $d_l = 1$ (chemically linear) is in the same universality class as geometrically linear chains; i.e., loops and branches can be neglected. The argument is based on the following reasoning. The chemical diffusion exponent d_w^l is defined by

$$t \sim R^{d_w} \sim l^{d_w^l}, \tag{5a}$$

where l is the average *chemical* distance traveled by the random walk and t is the time. Since

$$M \sim R^{d_f} \sim l^{d_l}, \tag{5b}$$

it follows that

$$M \sim t^{(d_l/d_w^l)} \sim t^{d_f/d_w} \sim t^{d_s/2}. \tag{5c}$$

We have the following bounds: (a) $d_w^l \geq 2$ (the walk cannot be faster than when performed on Euclidean lattices); (b) $d_s \geq 1$ (from $d_w = d_f + \tilde{\zeta}$ and $\tilde{\zeta} \leq d_f$), that is $d_l/d_w^l \geq \frac{1}{2}$. Since in our case $d_l = 1$ we have $d_w^l \leq 2$. From (a) and (b) follow the equalities

$$d_w^l = 2, \quad d_s = 1, \quad d_w = 2d_f, \tag{6}$$

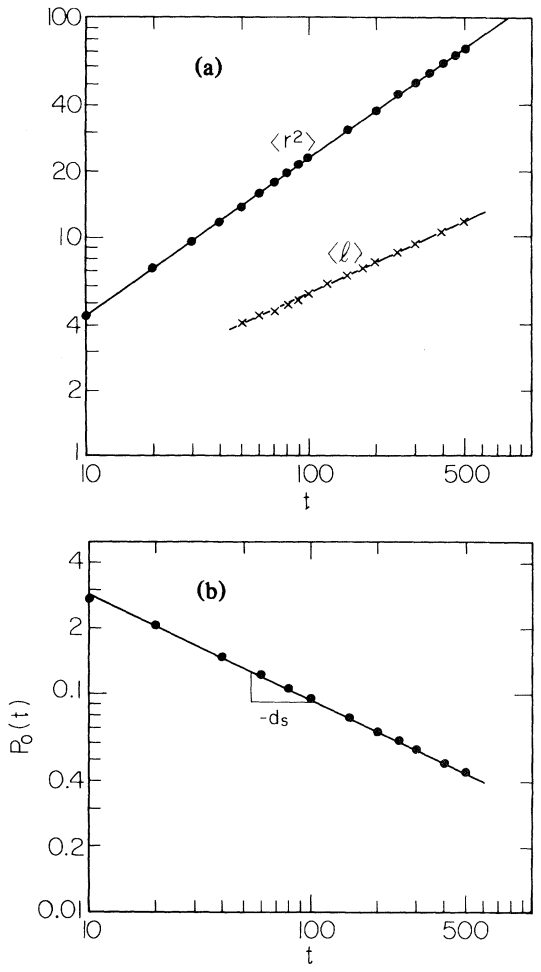

FIG. 3 Diffusion on fractals (chemically linear branched polymers) generated by our model for the case $B=3$. Dependence on time of (a) $\langle r^2\rangle$ and $\langle l\rangle$ and of (b) $P_0(t)$, the probability of returning to the origin.

for *any* chemically linear cluster.

All three expressions of Eq. (6) are identical for geometrically linear chains, and so we see that chemically linear clusters belong to the same universality class as geometrically linear chains, i.e., loops and branches can be neglected. Using (4) and (6) and the values found for d_f, we can evaluate the transport exponents; the results are summarized in Table I.[12]

In order to check our predictions $d_w=2d_f$, $d_w^l=2$, and $d_s=1$ in $d=2$ we performed exact enumerations[13] of random walks on our branched clusters with $B=2$, 3, and 4. The results shown in Fig. 3 yield $d_w=2.86\pm0.10$, $d_w^l=2.1\pm0.1$, and $\frac{1}{2}d_s=0.49\pm0.02$, confirming the predictions of Table I. Since all the static and dynamic exponents are the same as the geometrical linear chain, we argue that any chemically linear cluster is in the same universality class as geometrically linear chains; i.e., loops and branches can be neglected. In other words, the fact that the clusters are chemically linear implies that the statistical weight of closed loops and branches is going to zero in the large-system limit.

TABLE I. Fractal dimensions found for the present model of chemically linear branched polymers.

d	d_f	d_l	$\tilde{\zeta}$	d_w	$\frac{1}{2}d_s$	d_w^l
1	1	1	1	2	$\frac{1}{2}$	2
2	1.47	1	1.47	2.94	$\frac{1}{2}$	2
3	2	1	2	4	$\frac{1}{2}$	2

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[1]Apart from the Eden "cancer growth" model and the Vold-Sutherland "ballistic aggregation" models, two growth models that appear to have $d_f=d$, one can say that the modern era of growth models was initiated by the diffusion-limited aggregation (DLA) model of T. A. Witten and L. M. Sander [Phys. Rev. Lett. **47**, 1400 (1981), and Phys. Rev. B **27**, 5686 (1983)], which has $d_f=f(d)$. It appears that $d_l=d_f$ for all d (P. Meakin, I. Majid, S. Havlin, and H. E. Stanley, to be published).

[2]Addition polymerization has been developed as a growth model, termed kinetic gelation, by H. J. Herrmann, D. P. Landau, and D. Stauffer [Phys. Rev. Lett. **49**, 412 (1982), and J. Phys. A **16**, 1221 (1983)].

[3]Cluster-cluster aggregation, a generalization of DLA where clusters are free to diffuse laterally, was proposed independently by P. Meakin [Phys. Rev. Lett. **51**, 1119 (1983)] and by M. Kolb, R. Botet, and R. Jullien [Phys. Rev. Lett. **51**, 1123 (1983)].

[4]The kinetic growth walk is a model of a linear polymer which grows by choosing the next step from among the *available* sites [I. Majid, N. Jan, A. Coniglio, and H. E. Stanley, Phys. Rev. Lett. **52**, 1257 (1984)]. It appears to describe the configuration of a polymer in a θ solvent at the coil-globule transition (A. Coniglio, N. Jan, I. Majid, and H. E. Stanley, to be published).

[5]A growth model analogous to the Eden model but with a power-law screening has been found to have a continuously tunable *fractal* dimension, d_f (P. Meakin, F. Leyvraz, and H. E. Stanley, to be published). A

growth model analogous to the present model has been found to have a continuously tunable *chemical* dimension d_l (D. C. Hong, S. Havlin, F. Leyvraz, and H. E. Stanley to be published).

[6]S. Havlin and R. Nossal, J. Phys. A **17**, L427 (1984). See also R. Pike and H. E. Stanley [J. Phys. A **14**, L169 (1981)] for $d=2$ only (where d_l is denoted ψ_{13}); D. C. Hong and H. E. Stanley [J. Phys. A **16**, L475, L525 (1983)] and H. J. Herrmann, D. C. Hong, and H. E. Stanley [J. Phys. A **17**, L26 (1984)] for all d (where $d_l - d_f/d_{\min}$). H. J. Herrmann, D. C. Hong, and H. E. Stanley [J. Phys. A **17**, L261 (1984)] calculate d by Monte Carlo methods for $d=2,3$ to high accuracy, while A. Coniglio [J. Phys. A **15**, 3829 (1982)] finds $d_{\min}=2$, $d_l=2$ for the Cayley tree. Also see the recent calculations of J. Vannimenus, J.-P. Nadal, and J. Martin [J. Phys. A **17**, L351 (1984)] (where d_l is denoted $\hat{d}$). Applications to neural conduction are discussed by A. L. Ritzenberg and R. J. Cohen, Phys. Rev. B (to be published).

[7]In fact, for any finitely ramified fractal in which loops are irrelevant (such as lattice animals, and probably Witten-Sander clusters), it can be shown that d_l and d_f are sufficient to determine $\tilde{\zeta}$: S. Havlin, Z. Djordjevic, I. Majid, H. E. Stanley, and G. H. Weiss, Phys. Rev. Lett. **53**, 178 (1984).

[8]If at any stage there are fewer than B sites available for occupancy, then all the available sites are occupied.

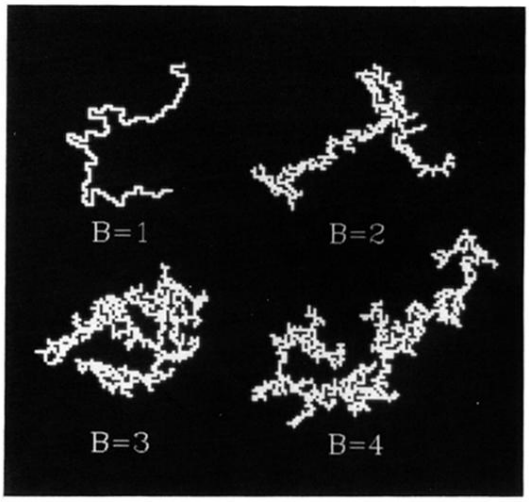
[9]C. Brender, D. Ben-Avraham, and S. Havlin, J. Stat. Phys. **31**, 661 (1983).

[10]This can be understood if one assumes that the probability of creating a loop decreases exponentially with increasing l. This implies that loops can be neglected.

[11]S. Alexander and R. Orbach, J. Phys. (Paris), Lett. **43**, L625 (1982). See also the review by H. E. Stanley, J. Stat. Phys. **36**, 815 (1984), and other articles in this issue (Proceedings of the International Conference on Fractals, Gaithersburg, 1983).

[12]Since $d_f=2$ for the BSAW and KGW for $d \geq d_c=3$ (Refs. 4 and 9) it follows that the same is true for our model for all values of B.

[13]I. Majid, D. Ben-Avraham, S. Havlin, and H. E. Stanley, Phys. Rev. B **30**, 1626 (1984).



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