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LETTERS

Kinetic Growth Walk: A New Model for Linear Polymers

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To describe the irreversible growth of linear polymers, we introduce a new type of correlated walk, related to the zero–initiator-concentration limit of the kinetic gelation model. Our model simulates real polymer growth by permitting the walker to form the next bond from the unsaturated monomers at the neighboring sites of its present location. A heuristic kinetic argument of the Flory type suggests a fractal dimension $d_f = (d + 1)/2$, in agreement with our Monte Carlo and series expansion results (including a logarithmic correction at the upper critical dimension $d_c = 3$).

How to describe the configuration of a long polymer chain has been the focus of attention for some time. The classic self-repelling chain or "self-avoiding walk" (SAW) has for decades been used to model the *equilibrium* statistics of linear polymers in dilute solutions; in this model, one enumerates all possible configurations of an N-step walk subject to the constraint that the walk will not intersect itself. The numerical predictions differ considerably from those of the Gaussian chain (or random walk) which is permitted to intersect itself freely.

Recently considerable attention has been focused on the question of how statistical laws are changed when one considers *kinetic* or "growth" phenomena. For example, kinetic gelation has been seen to belong to a different universality class than percolation or equilibrium gelation.[1] Similarly, the Witten-Sander model of diffusion-limited aggregation[2] has a different fractal dimension than other equilibrium models of polyfunctional condensation. Also, the cluster-cluster *dynamic* aggregation model of polyfunctional condensation differs from *static* models.[3,4]

Thus far there is no kinetic model for linear polymers. Amit, Parisi, and Peliti recently proposed a clever variation of the SAW in which the walk can grow; it can intersect itself, but tries to avoid doing so by being attracted to "less visited" regions.[5] This model they call the true self-avoiding walk (TSAW). Since the TSAW is a true kinetic model, one might be tempted to suppose that it describes the essential physics of growing polymer chains. In this paper we propose a somewhat different growth model, which we argue is more appropriate for this

purpose.

To explain our kinetic growth walk (KGW) model, we refer to Fig. 1. In an SAW one randomly chooses the next step from among the nearest-neighbor sites (excluding the previous one); if it happens that one chooses an already visited site, the walk stops. In the KGW one instead randomly chooses the next step among the nearest-neighbor *unvisited* sites and stops growing only when none are available. Therefore the KGW is much less sensitive to attrition than the SAW as the walker will always escape whenever an avenue exists; on the other hand, it is not as free as the TSAW since the walker may be trapped when all its surrounding neighbors have already been visited. The justification for such a model is that polymer growth is only possible through the movement of a single initiator to any of the nearest-neighbor sites with *unsaturated* bifunctional monomers.

We now describe a self-consistent Flory-type theory for the generalized KGW that builds on that for the TSAW and SAW.[6] The basic idea is that the walker is described as a Brownian particle in a viscous fluid under the influence of a radial force which causes an effective radial drift velocity,[7]

$$\partial R/\partial N \sim N^{\nu-1}. \tag{1}$$

In the steady-state regime, this velocity scales with N in the same fashion as the effective radial force $F = F_1 + F_k$. Here $F_1 \sim \partial \rho/\partial R$ ($\rho = N/R^d$) is the force present in the TSAW[6] arising from the preference of the walk to avoid previously visited sites; $F_k \sim \partial U_k/\partial R$ arises from the possibility of trapping where $U_k \sim \int d^d r \, \rho^k$. In the SAW a minimum of two occupied sites are needed for the possibility of trapping, so that $k = 2$. For the KGW we make the reasonable assumption $k = 3$, suggesting that the dominant contribution comes from the three-body interaction,

$$U_3 \sim \int d^d r \, \rho^3. \tag{2}$$
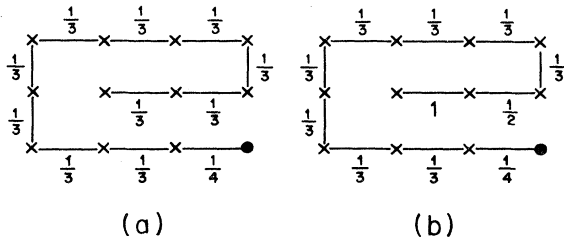

(a)   (b)

FIG. 1. Two identical configurations are shown, with appropriate weights at each step, for (a) an SAW and (b) a KGW. The starting point is denoted by the filled circle.

This can be clearly seen on the honeycomb lattice where at least three particles are needed for trapping. Since $\rho = N/R^d$,

$$F_1 \sim N^{1-(d+1)\nu}, \tag{3a}$$

while for (2)

$$F_k \sim N^{k-[(k-1)d+1]\nu}. \tag{3b}$$

Note that $F_k > F_1$, so that the TSAW force dominates *only if there are no interactions;* in this case, we may equate (1) and (3a) and recover the Pietronero result[6]

$$\nu = d_f^{-1} = 2/(d+2). \tag{4a}$$

If there are interactions, then the interaction with the lowest power of k dominates and we find on equating (1) and (3b)

$$\nu = d_f^{-1} = (k+1)/[(k-1)d+2]$$
$$(k \geq 2). \tag{4b}$$

For $k = 2$ this reduces to the Flory result for SAW,

$$\nu = 3/(d+2), \tag{5a}$$

while for $k = 3$ we have the KGW result (Table I)

$$\nu = 2/(d+1). \tag{5b}$$

Above a critical dimension d_c the Gaussian probability distribution dominates the asymptotic form of the walk with a radial velocity given by $\Delta R/\Delta N \sim N^{-1/2}$ (i.e., $\nu = \frac{1}{2}$ above d_c); equating (4b) to $\frac{1}{2}$, we find

$$d_c = 2k/(k-1). \tag{6}$$

The critical dimension (6) for the generalized KGW with dominant k-body repulsive interactions is the same as for the Ising model at a critical point of or-

TABLE I. Fractal dimension d_f in Flory-type theory for various values of system dimension d. Shown are the SAW ($d_c = 4$), the KGW ($d_c = 3$), and the TSAW ($d_c = 2$). Note that for all d, d_f for the KGW is intermediate between d_f for the SAW and TSAW. For $d = d_c$, all three models have $d_f = 2$, with a log correction of the form $\langle R_g^2 \rangle \sim N(\ln N)^\alpha$ with $\alpha = \frac{1}{4}$ (SAW) (Ref. 12), 0.2 (KGW), and 0.4 (TSAW) (Ref. 5).

	$d = 1$	$d = 2$	$d = 3$	$d = 4$
SAW	1	4/3	5/3	2
KGW	1	3/2	2	· · ·
TSAW	3/2	2	· · ·	· · ·

der k.[8] Thus, in particular, $d_c = 4$ for an SAW *and* an ordinary critical point, $d_c = 3$ for a KGW *and* a tricritical point, and $d_c = 2$ for the $k = \infty$ limit and for a critical point of infinite order.[9] The detailed mapping between the KGW critical point and a tricritical point will be developed in a longer paper.[10]

We have performed extensive Monte Carlo simulations on several two- and three-dimensional lattices, calculating the radius of gyration $\langle R_g^2 \rangle$ and end-to-end distance (second and fourth moments $\langle r^2 \rangle$ and $\langle r^4 \rangle$). On the honeycomb lattice, 2×10^6 walks were simulated, of maximum length 350 steps, but only 1700 survived without being trapped. For the square lattice, 2×10^6 walks were started, of which 2700 survived to 350 steps. On the triangular lattice, 2×10^6 walks were started and 3400 survived up to 350 steps. In Fig. 2(a) we show double logarithmic plots of $\langle R_g^2 \rangle$ vs N for walks on all three two-dimensional lattices. We note that the curves are parallel, and from the slopes we estimate $d_f = 1.48 \pm 0.02$; $\langle r^2 \rangle$ and $\langle r^4 \rangle$ give equivalent results.[11]

We have also calculated $\langle r^2 \rangle$ for the square lattice by *exactly* enumerating all possible walks of up to 22 steps. Employing standard ratio methods of analysis we estimate $d_f = 1.47 \pm 0.03$, which is consistent with the Monte Carlo simulations. Thus both the Monte Carlo simulations and series work are consistent with the prediction $d_f = \frac{3}{2}$ for $d = 2$.

In three dimensions we were able to generate much longer walks because of the low attrition rate. On the simple cubic (sc) lattice 30 000 walks were studied, of which 2000 survived up to 10 000 steps. On the fcc lattice, 10 000 walks were studied and 8000 survived up to 10 000 steps. Figure 2(b) shows double logarithmic plots of $\langle R_g^2 \rangle$ vs N for both the sc and fcc lattices. The sc curve is parallel to the fcc curve, and both are quite linear over three decades. The inverse slope *would* correspond to $d_f = 1.93 \pm 0.02$, except that if $d_c = 3$, as suggested by Eq. (6), we expect the data to be fitted by the functional form $\langle R_g^2 \rangle \sim N(\ln N)^\alpha$. We find $\alpha \simeq 0.2$ (Fig. 3), and so the data support the prediction $d_f = 2$ with a logarithmic correction.

We observe that the KGW describes a growing polymer before it has relaxed into the self-repelling chain configuration. Such behavior may be observed in dilute polymer solutions where the relaxation time far exceeds the characteristic time to grow a sufficiently large molecule. Another physical system where such behavior may be relevant is a single polymer chain whose end points are attached to tetrafunctional units in a gel. Indeed, our model may be regarded as the zero-concentration limit of
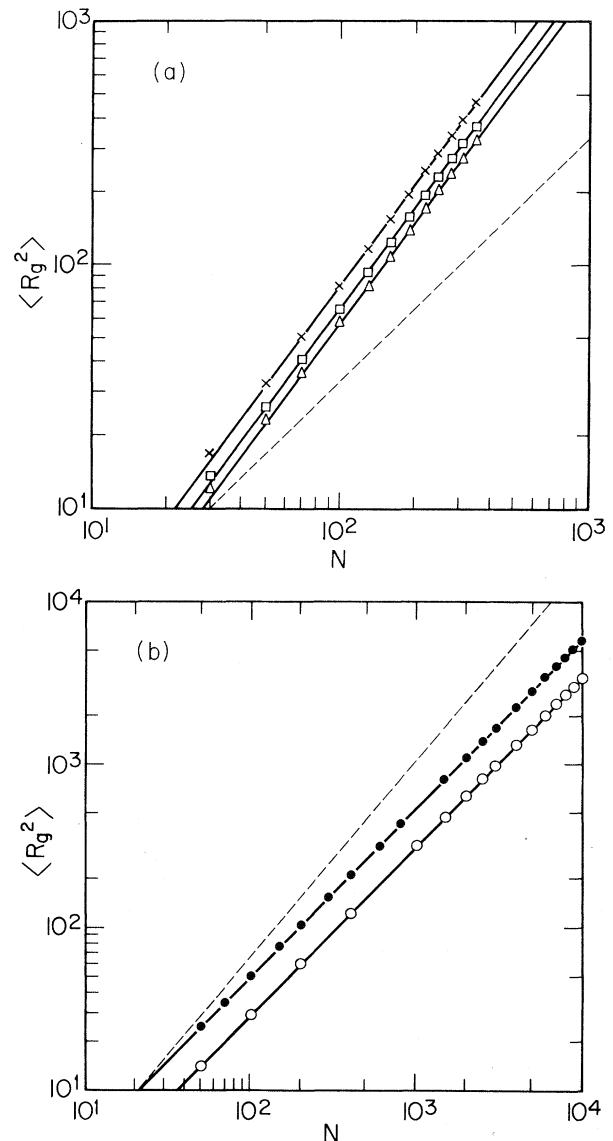
FIG. 2. Log-log plot of $\langle R_g^2 \rangle$ vs N for (a) two-dimensional lattices (triangles, triangular lattice; squares, square; and crosses, honeycomb; for comparison with TSAW, the dashed line has a slope $2\nu = \frac{1}{2}$) and (b) three-dimensional lattices (open circles, sc, and filled circles, fcc; for comparison with SAW, the dashed line has a slope $2\nu = \frac{6}{5}$.)

kinetic gelation of bifunctional monomers,[1] since in this limit a single "initiator" molecule is allowed to perform a random walk on a lattice subject only to the constraint that it not intersect itself.

We also note that our Flory-type theory for the KGW is identical to the Flory theory for the θ point.[12] Indeed, it can be shown[10] that a polymer chain at the θ point and a KGW are in the same
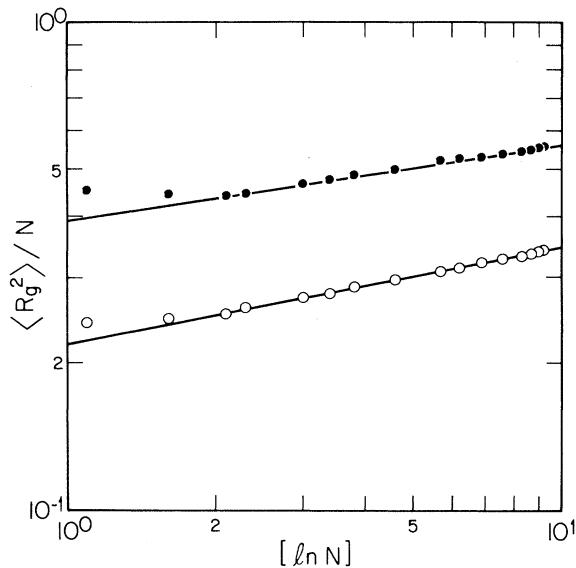
FIG. 3. Log-log plot of $\langle R_g^2 \rangle / N$ vs $\ln N$ for sc (open circles) and fcc (filled circles) lattices. The slope of the line gives $\alpha \cong 0.2$.

universality class.

In summary, we have introduced a new type of walk which is more pertinent to the growth of polymer chains. This walk has distinctive features with unique critical properties. Our simple Flory-type theory agrees to within (1–2)% with the numerical data.

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[7]One can also approach the problem from a static point of view—the conventional Flory theory—equating the energetic force to the entropic force. The same final results (4a) and (4b) are obtained from the conventional Flory theory (where the repulsive energy term is given by ρ and U_k, respectively). *For the* SAW, both static (Flory) and kinetic (Pietronero) approaches are justified and also give the same results. We somewhat prefer the Pietronero-type argument since it emphasizes the growth nature of the walk.

[8]T. S. Chang, A. Hankey, and H. E. Stanley, Phys. Rev. B **8**, 346 (1973).

[9]An open question for the TSAW problem is how to describe the $g \rightarrow \infty$ limit, which must be different than g finite (at least for $d = 1$, since $\nu = 1$ if $g = \infty$ while $\nu \cong \frac{2}{3}$ for a g finite). Here g is defined by the probability of the next step to visit site i, $P_i = \exp(-gn_i)/\sum_i \exp(-gn_i)$, where n_i is the number of times site i has previously been visted. We note that the $k \rightarrow \infty$ limit of the *generalized* KGW gives $\nu = 1/d$ for $d \leq d_c = 2$, thus reproducing the known results for the $g \rightarrow \infty$ TSAW with $d = 1$ and the numerical findings that $\nu = \frac{1}{2}$ with a log correction for $d = 2$. Indeed, it is quite plausible that our $k \rightarrow \infty$ limit has the same critical behavior as the $g \rightarrow \infty$ TSAW since as n increases, the constraint that leads to trapping becomes less significant.

[10]A. Coniglio, N. Jan, I. Majid, and H. E. Stanley, to be published.

[11]The very early results of M. N. Rosenbluth and A. W. Rosenbluth [J. Chem. Phys. **23**, 356 (1955)] are not very reliable because, as noted by them, N is not large enough to be in the asymptotic region.

[12]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979).