Self-avoiding Lévy walk: A model for very stiff polymers

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We propose a non-Markovian extension of the Lévy walk model of Shlesinger *et al.* [Statistical Physics, edited by H. E. Stanley (North-Holland, Amsterdam, 1986), p. 212], termed self-avoiding Lévy walk, to study a polymer configuration having a broad persistence length distribution. We use the Flory-type argument in a manner analogous to the self-avoiding walk and the self-avoiding Lévy flight schemes to include the excluded-volume effect and find that the Flory exponent ν_F varies continuously from the flexible limit [$\nu_F = 3/(d+2)$] to the stiff limit ($\nu_F = 1$), when the spatial dimension d and the Lévy index μ are varied. We also discuss the fractal dimensions and the morphology of Lévy walks in comparison with the Lévy flights.

Various random-walk models have been studied to describe equilibrium polymer configurations (for a review see de Gennes[1]) as well as nonequilibrium growth and transport phenomena.[2,3] In dealing with the former it is necessary to include the excluded-volume effect, which renders the problem non-Markovian. In such cases, the Flory argument[4] has often served as a good approximation to obtain the exponent ν defined by

$$R_N \sim N^{\nu}, \tag{1}$$

where R_N is the characteristic size of a polymer with N monomers.

In this paper, we propose a model of a long-range self-avoiding walk and apply a Flory approach. Consider polymer configurations whose segment-size distribution in the absence of the excluded-volume effect would be of Lévy type[5]

$$P(l) \sim l^{-1-\mu}, \tag{2}$$

where $\mu > 0$ is called the Lévy index and l is the segment size or the persistence length [proportional to the average number of consecutive *trans* steps in the language of the persistent random walks (PRW)].[6]

A relevant nonexcluded-volume walk model named the (*random*) Lévy walk (RLW) has been proposed by Shlesinger, Klafter, and West[7] to study certain transport phenomena[8] in the framework of the continuous-time random walk (CTRW).[9] In the Lévy walk model, the walker starting at the origin makes l correlated steps, with each step size being fixed, in a straight line in a time proportional to l and then makes the next step in a randomly chosen direction without waiting, where l has the Lévy distribution, Eq. (2). This can be expressed by $\Psi(t,\mathbf{l})$, the probability density (in both the time and space variables) to make a transition of displacement $\mathbf{l}$ in time t, as

$$\Psi(t,\mathbf{l}) = \psi(t|\mathbf{l})p(\mathbf{l}), \tag{3}$$

where $p(\mathbf{l})$ is proportional to $l^{-(d+\mu)}$ for arbitrary dimensionality d and $l \equiv |\mathbf{l}|$, so that the angular integration of $p(\mathbf{l})$ reduces to Eq. (2). $\psi(t|\mathbf{l}) = \delta(t-l)$ is the conditional probability distribution to make the transition in time t given a displacement of l. This particular choice of the coupled memory kernel[10] $\psi(t|\mathbf{l})$ ensures the mean-square displacement to be finite for finite time. Moreover, since t is directly proportional to l, t can be considered as the number of individual steps in a segment in the Lévy walk model.

Thus their results for the mean-square displacement $\langle [R_0(t)]^2 \rangle$ as a function of time in the Lévy walk[7,8] can be viewed as that of the number of monomers ($R_0 \sim N^{\nu_0}$) in the polymer case in the nonexcluded-volume limit:[11]

$$R_0 \sim \begin{cases} N, \quad 0 < \mu \le 1, \quad \langle l \rangle = \infty \\ N^{(3-\mu)/2}, \quad 1 < \mu < 2, \quad \langle l \rangle < \infty, \ \langle l^2 \rangle = \infty \\ (N \ln N)^{1/2}, \quad \mu = 2, \quad \langle l^2 \rangle \text{ log divergent} \\ N^{1/2}, \quad \mu > 2, \quad \langle l^2 \rangle < \infty, \end{cases} \tag{4}$$

where $\langle l \rangle (\langle l^2 \rangle)$ is the mean (square) persistence length. Note that for $0 < \mu \le 1$, the exponent ν takes on its absolute maximum value, namely 1, and one may consider this case as the *stiff* regime. It should also be noted that these results manifestly differ from those of the Lévy flight[12-14] for which $\langle R^x \rangle^{1/x} \sim N_s^{1/\mu}$ with $x \to 0$, $0 < \mu < 2$, and N_s being the number of segments. In fact, the statistics of the Lévy walk is that of the Lévy flight as a function of the contour length of the Lévy trajectory.

We now turn on the excluded-volume effect so that the walk becomes the self-avoiding Lévy walk (SALW), where the random walker cannot revisit the previously visited sites. The Flory free energy[4] can be written as the sum of an interaction-energy term and an elastic (entropic) term:

$$F = F_{\text{int}} + F_{\text{el}}. \tag{5}$$

The identification of each term for the SALW is made in analogy to the case of self-avoiding walk[4] (SAW) and self-avoiding Lévy flights (SALF).[14–18] If the persistence length $\langle l \rangle$ is finite, then we let

$$F_{\text{int}} \sim \frac{(N/\langle l \rangle)^2 \Omega}{R^d} \sim N^2/R^d, \tag{6}$$

where $\Omega \propto \langle l \rangle^2 a^{d-2}$ is the generalized Odijk excluded volume[19] with a being the excluded volume range (or the monomer diameter). Hereafter, however, we assume isotropic monomers with diameter equal to length, and thus drop all reference to the unit of length. We restrict our discussion to the cases where $\mu > 1$ and $d \geq 2$ because otherwise either the persistence length diverges or the form of Ω is not suitable. An exception occurs at $d = 1$ where $\nu = 1$ trivially. We also take the elastic free energy as

$$F_{\text{el}} \sim \left(\frac{R}{R_0}\right)^{\sigma}, \tag{7}$$

where the nonexcluded-volume end-to-end distance R_0 is given by Eq. (4) and σ is some positive number whose values are to be discussed later.

Minimizing F with respect to R gives the Flory exponent ν_F as

$$R_F \sim N^{\nu_F}, \qquad \nu_F = \frac{2 + \sigma \nu_0}{d + \sigma}, \quad d < d_c, \tag{8}$$

where ν_0 is the non-excluded-volume exponent [Eq. (4)], and $d_c = 2/\nu_0$ at and above which $\nu_F = \nu_0$. It can easily be shown that ν_F thus obtained is always greater than ν_0 and less than unity for any finite value of σ in relevant dimensions. Thus we have for SALW, for $d \geq 2$,

$$\nu_F = \begin{cases} 1, & 0 < \mu \leq 1 \\ \dfrac{2 + \sigma(3-\mu)/2}{d + \sigma}, \quad d_c = \dfrac{4}{3-\mu}, & 1 < \mu < 2 \\ \dfrac{3}{d+2}, \quad d_c = 4, & \mu \geq 2. \end{cases} \tag{9}$$

Note that in the stiff regime $0 < \mu \leq 1$, $\nu_F = \nu_0 = 1$ because ν cannot exceed unity in any case, and the normal SAW result is recovered for $\mu \geq 2$. Note also that the d_c is independent of σ due to the choice of Flory free energies as Eqs. (6) and (7). Therefore we expect that there exist four distinct regimes for SALW in (d, μ) parameter space as shown in Fig. 1.

Despite the inherent approximate nature of the Flory argument, we can check the consistency of the above expressions using the same criteria as in Ref. 20. Requiring that the first term in the expansion of F_{int} in terms of the segment concentration and the ratio of any term to its next-higher-order term be much greater than unity, that is,

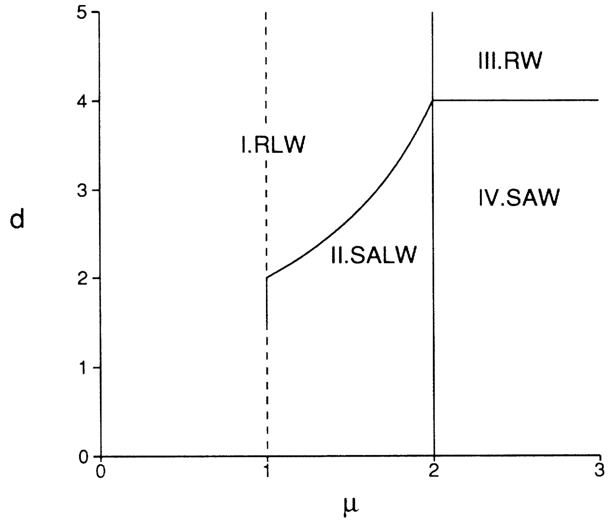

FIG. 1. Four distinct regimes of Lévy walk with the self-avoiding constraint according to the Flory argument. I, random Lévy walk (RLW); II, self-avoiding Lévy walk (SALW) for which $d_c = 4/(3-\mu)$; III, random walk (RW); IV, self-avoiding walk (SAW). The dashed line indicates the stiff regime $0 < \mu \leq 1$ where $\nu = 1$.

$$x_F \equiv \frac{N^2}{R_F^d} \gg 1, \quad N/x_F \gg 1, \tag{10}$$

we obtain the condition

$$\frac{1}{\nu_0 + 1/\sigma} < d < 4/(3-\mu). \tag{11}$$

Since the lower limit of this conditon is always less than 2 [see Eq. (4)] but recalling that we must restrict our approach to $d \geq 2$ in addition, the final condition is $2 \leq d < 4/(3-\mu)$, which conforms to our result in Eq. (9).

It still remains to determine the σ in Eq. (9). Without any explicit form of the entropy of the Lévy walk known, but having in mind the unique characteristic of the Lévy walk that its individual step size is fixed but its moments of segment size diverge, we first propose two possible values of σ in analogy to SAW (Ref. 4) and SALF (Refs. 14, 15, and 18) for $1 < \mu < 2$, namely, $\sigma = 2$ and μ. Thus one obtains, for $1 < \mu < 2$,

$$\nu_F^{(1)} = \frac{5-\mu}{d+2} \tag{12}$$

if $\sigma = 2$ is chosen, or

$$\nu_F^{(2)} = \frac{(1+\mu)(4-\mu)}{2(d+\mu)} \tag{13}$$

if $\sigma = \mu$ is chosen. It should be noted that both choices of σ ensure the continuity of ν_F at the boundaries $\mu = 1, 2$ in Eq. (9). Even if these expressions looks quite different in their form, their numerical values are very close to each other: the maximum difference is about 0.018 at $\mu = 2(\sqrt{3} - 1)$ and $d = 2$.

On the other hand, Bouchaud and Daoud[16] used a different value of σ for the node-avoiding Lévy flight due to de Gennes's analysis[17] of a stretched flight in terms of Pincus blobs,[21] namely $\sigma = 1/(1-\nu_0)$, which in turn, when applied to the case of SALW [$\sigma = 2/(\mu-1)$], suggests yet another estimation of the Flory exponent for $1 < \mu < 2$,

$$\nu_F^{(3)} = \frac{1+\mu}{d(\mu-1)+2}. \tag{14}$$

This particular choice of σ automatically ensures a correct value of ν_F at $d = 1$ and makes the lower limit of condition (11) unity independent of ν_0. The continuity of ν_F at $\mu = 1, 2$ is again secured by $\nu_F^{(3)}$. Figure 2 provides a brief comparison of these suggested Flory exponents together with ν_0 at $d = 2, 3$.

Finally, we would like to discuss the fractal dimension $d_f \equiv 1/\nu$ of the Lévy walks in contrast to that of the Lévy flights.[5,15] The introduction of self-avoidance lowers the fractal dimensions in both cases for $d < d_c$ and both become SAW for $\mu > 2$, $d < 4$. It is interesting that the morphology of *turning points* of the SALW is exactly the same as the path-avoiding Lévy flight (PALF).[18] The difference comes only from the way in which the intermediate points in the segments are weighted: the segments of SALW can be viewed as a rigid rod with a uniform mass density, but those of PALF as an unpenetrable massless rod with a unit mass attached at the end of each segment.

Yet this simple difference leads to dramatically different behaviors especially for $0 < \mu < 1$, where $d_{f,\mathrm{SALW}} = 1$ independent of μ but $d_{f,\mathrm{PALF}}$, though not known for arbitrary d and μ, is expected to behave as the random Lévy flight for small μ ($d_{f,\mathrm{PALF}} = \mu$ exactly for $d = 1$, $0 < \mu < 1$).[18,22] This seems to suggest that the statistics of a polymer modeled by the SALW in the stiff regime is essentially characterized by the longest single segment in the whole polymer.

This point is more effectively illustrated if we particularly look at the discretized version of the random Lévy distribution[12]

$$P(l) = \frac{a-1}{a}\sum_{n=0}^{\infty}\delta_{l,b^n}a^{-n}, \quad a, b > 1, \tag{15}$$

which can be easily shown to be equivalent to Eq. (2) with $\mu = \ln a/\ln b$ when averaged into continuum as $l \to \infty$. Apart from the self-avoidance, Eq. (15) indicates that the appearance of segment size l is more likely than that of size lb by a factor of a for any $l = 1, b, b^2, \ldots$.

Let $L_{\max} = b^M$ be the largest segment just generated, then the total contour length (or the number of steps in the Lévy walk) is, on the average,

$$\begin{aligned} N &= b^M + b^{M-1}a + b^{M-2}a^2 + \cdots + a^M \\ &= L_{\max}\frac{1-\left(\frac{a}{b}\right)^{M+1}}{1-\left(\frac{a}{b}\right)} . \end{aligned} \tag{16}$$

For large N and $a/b < 1$ ($\mu < 1$),

$$N \sim \frac{L_{\max}}{1-a/b} , \tag{17}$$

which implies that the largest segment in a RLW takes a finite fraction of the contour length of the whole walk. Since even when the excluded-volume effect is included, $\nu_F = 1$ is unchanged from $\nu_0 = 1$, this discussion is consistent with the behavior of the SALW in the stiff regime. On the other hand, for large N and $a/b > 1$ ($\mu > 1$), we have

$$N \sim \frac{a^M}{1-b/a} , \tag{18}$$

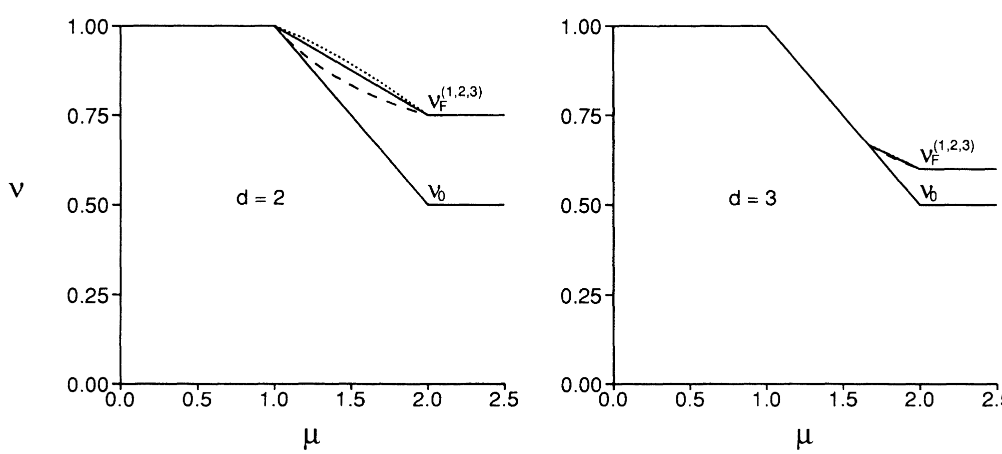

FIG. 2. The comparison of the Flory exponents obtained from various forms of the elastic-energy term suggested. The lowest solid line represents the *random* Lévy walk (RLW) exponent [see Eq. (4)] and the three upper lines the suggested Flory exponents (SALW): solid line for $\nu_F^{(1)} = (5-\mu)/(d+2)$, dotted line for $\nu_F^{(2)} = (1-\mu)(4-\mu)/2(d+\mu)$, and dashed line for $\nu_F^{(3)} = (1+\mu)/[d(\mu-1)+2]$. Note that all three Flory exponents continuously vary from $\nu = 1$ to $\nu_{\mathrm{SAW}} = 3/(d+2)$ over the region $1 \le \mu \le 2$.

which implies

$$N \sim L_{\max}^{\mu} \quad . \tag{19}$$

Although ν_F is greater than ν_0 for this region of μ, it is still expected that even in the excluded-volume case the largest segment would not dominate the behavior of the whole polymer.

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[11] This result was given in Ref. 7, for example. We note that Eq. (11) in that reference must be modified by an insertion of a factor τ in the integrand, in order to yield the quoted values. This must be obvious as Ψ is a probability density both in time and in space.

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