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Paradoxal Diffusion in Chemical Space for Nearest-Neighbor Walks over Polymer Chains

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We consider random walks over polymer chains (modeled as simple random walks or self-avoiding walks) and allow from each polymer site jumps to all Euclidean (not necessarily chemical) neighboring sites. For frozen chain configurations the distribution of displacements (DD) of a walker along the chain shows a paradoxal behavior: The DD's width (interquartile distance) grows with time as $\Lambda \propto t^{\alpha}$, with $\alpha \approx 0.5$, but the DD displays large power-law tails. For annealed configurations the DD is a Lévy distribution and its width is strongly superdiffusive. [S0031-9007(97)03619-3]

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Random walks in random environments occur in many fields of modern statistical physics and have won major attention in the last two decades; see Refs. [1–3]. Many situations lead to random walks on random walks (RW) or on self-avoiding random walks (SAW), see Refs. [4–12]; in the polymer case such structures depict chains in θ solvents (RW) or in good solvents (SAW). The problem arises very naturally in the analysis of energy or exciton transport over polymer chains. For simplicity we view a moving entity (say electron, exciton, or enzyme) which performs steps of length a from one neighboring site (monomer) to another one. A triplet exciton, for instance, can move from one donor to another one close by, not necessarily sequentially placed along the chain. Hence not only steps along the chain but also steps between monomers which are close to each other in (Euclidean) space are involved, even if they are far apart in chemical space (where the distance l_{ch} between two points is defined through the number of monomers n between them along the chain's backbone $l_{\mathrm{ch}} = n + 1$). Viewed in terms of the regular Euclidean distance some properties of random walks on SAW chains (e.g., the spectral dimension and the anomalous diffusion exponent) were evaluated in Refs. [4–12]. To our knowledge up to now, no particular attention was paid to the corresponding properties from the viewpoint of the chemical distance; here we show that this viewpoint leads to highly unusual behaviors.

We start from the findings for frozen chain configurations in an experimentally relevant 3D situation, where we simulate nearest-neighbor random walks over RW and over SAW chains embedded in a simple cubic lattice. We first generate and save 100 chain configurations. The RW chains are generated as trajectories of a random walker on a simple cubic lattice, and their length is $L = 30\,000$. The SAW chains, of length $L = 10\,000$, were obtained using the pivot algorithm [13], as described in Ref. [14]. Each of the different realizations was created from an independent initial configuration to which the pivot transformation was applied 2000 times. Then for each configuration we start the walk at a random position and check at each step how many moves are possible from the actual position of the walker. The moves allowed are jumps to all monomers occupying nearest-neighbor positions (either along the chain or across it) and (for the simple RW chain) also to other monomers occupying the same site. The next step of the walk is chosen at random, with equal probability, from this set of allowed moves, and the value of time is increased by 1. Note that in this way large jumps (in terms of the chemical distance) occur. We then analyze the DDs of the random walker after time t, by averaging over 100 different chain configurations, over each of which 10 000 random walk realizations are performed.

The DD is given by the probability density $P(l, t)$ of the (chemical) displacement l of a random walker at time t. The DDs are evidently symmetric, and we first characterize them by their width, determined through the interquartile distance $\Lambda = Q_{3/4} - Q_{1/4}$. The time dependence of this width is shown in Fig. 1, where values of Λ determined at different times are plotted on double logarithmic scales. From Fig. 1 it is evident that both for the RW and for the SAW chains Λ follows a power law, $\Lambda(t) \propto t^{\alpha}$; here α

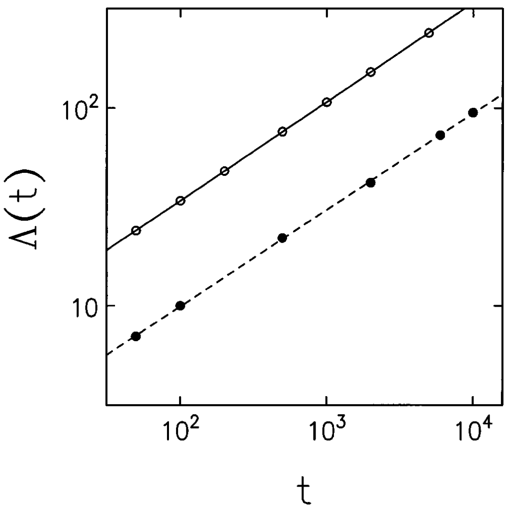

FIG. 1. Time dependence of the distribution's width $\Lambda(t)$ for random walks over RW chains (empty circles) and over SAW chains (full circles). Note the double logarithmic scales. The full line has the slope 0.499, the dashed line the slope 0.490.

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obtained by linear regression is $\alpha = 0.499 \pm 0.005$ for the RW case and $\alpha = 0.49 \pm 0.02$ for the SAW case. This may suggest that a $t^{1/2}$ dependence of $\Lambda(t)$ is exact.

As we proceed to show, the DDs scale well with $\Lambda(t)$; on the other hand, the form of the DDs is not Gaussian and shows long (power-law) tails. In Fig. 2 we display on double logarithmic scales the DDs for RW over RW chains for three different times. Plotted is the value of $\rho(\xi) = \Lambda(t)[P(l,t) + P(-l,t)]$ (the distribution of the absolute value of the displacement) vs $\xi = |l|/\Lambda(t)$ for $t = 50$, 500, and 5000. The results fall on a master curve both for the small x, flat part of the function and for the large x regime. Moreover, the large-ξ regime suggests for $l > \Lambda$ a power-law behavior $P(l,t) \propto l^{-x}$; from a least-squares fit we obtain $x \approx 1.5$. With this x value the DD lacks even its first moment. Comparison of the DD with a Lévy-stable law with the same width and power-law tail behavior shows that these two distributions differ strongly.

Figure 3 shows similar results for the case of RW over SAW chains at three different times, $t = 100$, 500, and 6000. We again find that the DD scales with $\Lambda(t)$. However, now the behavior of the DD is somewhat more complex than for RW chains: the power-law tail (if any) starts only at large values of l, such that $l \gg \Lambda$; here the statistical fluctuations (and also finite-size effects) begin to be important. Assuming that for $l > 3\Lambda$ the distribution $P(l;t)$ goes as l^{-x} we find x to lie between 2.6 and 2.9. In any case x is less than 3 and the distribution lacks its second moment. As for RW chains, the form of the DD for SAW chains differs from a Lévy distribution.

We now turn to the theoretical analysis of our findings. The overall behavior of the walk is connected to the probability distribution of the jump lengths. This distribution is the probability $p(l)$ to find two monomers separated by the chemical distance l in an a-vicinity of each other (see, e.g., Refs. [15–17] for a detailed analysis of the problem). In both cases, for RW and for SAW chains in 3D the distributions $p(l)$ show power-law tails, $p(l) \propto l^{-\zeta}$; we note, however, that the exponents ζ of these power laws are quite different.

For a Gaussian chain the probability of the monomers to be in an a vicinity is

$$p(l) \propto l^{-3/2}, \tag{1}$$

so that $\zeta_{\mathrm{RW}} = 3/2$ and the first (and *a fortiori* the second) moment of the corresponding distribution does not exist. The behavior of $p(l)$ for the case of SAW chains is different, due to the excluded-volume interaction between different parts of the chain; see Ref. [16]. In the case of an extremely large SAW chain one has

$$p(l) \propto l^{-\nu(d+\theta_2)}, \tag{2}$$

where the Flory exponent is $\nu \approx 0.588, \ldots$ [14–16] and the numerical value of θ_2 is not known accurately. Our numerical evaluation of $p(l)$ for SAW chains gives $p(l) \propto l^{-2.2}$ (i.e., $\zeta_{\mathrm{SAW}} = 2.2$), leading to the estimate $\theta_2 = 0.74 \pm 0.03$ (for $5 < l < 300$) which agrees very well with the results reported in Ref. [17].

Neglecting the correlations between subsequent steps, one finds according to Lévy's limit theorem that the DDs [being the distributions of sums of independent random quantities drawn out from the same probability distribution $p(l) \propto l^{-\zeta}$] converge to a stable Lévy distribution of index $\gamma = \zeta - 1$, Refs. [1,18,19]. Because of the overall symmetry of the problem, the corresponding distribution must be symmetric and has its median value equal to zero; i.e., it is given by the characteristic function

$$f(k) = \exp(-A|k|^{\zeta-1}). \tag{3}$$

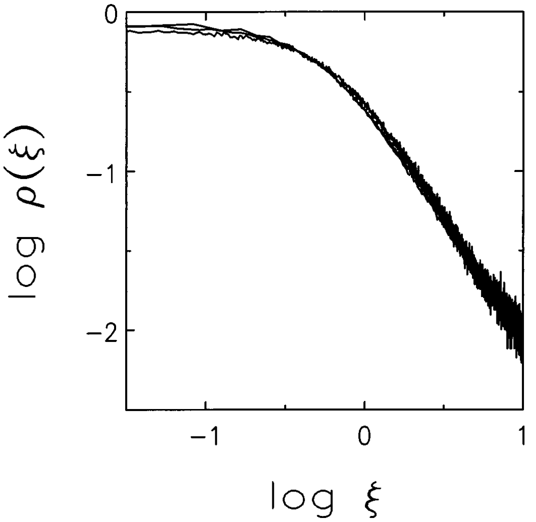

FIG. 2. Shown is the rescaled DD $\rho(\xi)$ as a function of the scaling distance $\xi = |l|/\Lambda(t)$ for random walks on a RW chain (see text for details). Note the double logarithmic scales.

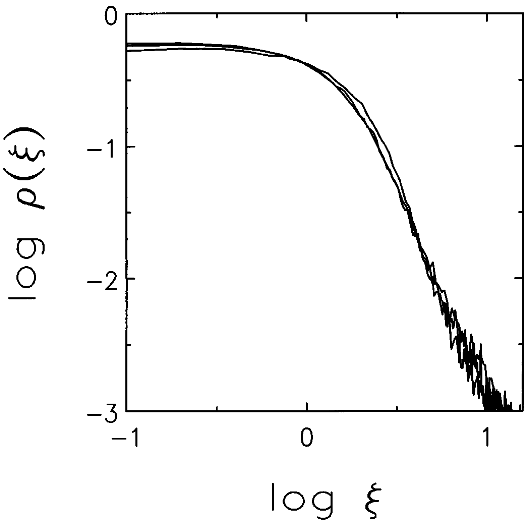

FIG. 3. Same as in Fig. 2, now for a SAW chain.

In Eq. (3) the parameter A characterizes the width of the distribution. For RW chains the corresponding distribution probability density

$$p(y) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(k)e^{-ikx}\,dk = \frac{1}{\pi}\int_{0}^{\infty}\exp(-A\sqrt{k}\,)\cos ky\,dk \qquad (4)$$

can be expressed analytically in terms of the Fresnel integrals $C(z)$ and $S(z)$; see Ref. [20],

$$p(y) = \frac{1}{\sqrt{2\pi}}A|y|^{-3/2}\left\{\cos\left(\frac{\pi z^2}{2}\right)\left[\frac{1}{2} - C(z)\right] + \sin\left(\frac{\pi z^2}{2}\right)\left[\frac{1}{2} - S(z)\right]\right\}, \qquad (5)$$

with $z = A^2/\sqrt{2\pi y}$. The distribution, Eq. (4) does not possess any moments; the positions of the lower quartile $Q_{1/4}$ and of the upper quartile $Q_{3/4}$ of the distribution correspond to $\pm 1.28A^2$.

Note that according to Lévy statistics the value of A is proportional to the number of steps, i.e., to the time $A \propto t$. The overall distribution $P(l;t)$ scales then with time as

$$P(l;t) \propto t^{-1/(\zeta-1)}P_{\zeta}(lt^{-1/(\zeta-1)}), \qquad (6)$$

where P_{ζ} is a universal, time-independent function. Therefore one has

$$\Lambda = Q_{3/4} - Q_{1/4} \propto t^{1/(\zeta-1)}, \qquad (7)$$

leading to a dependence of $\Lambda \propto t^2$ for walks over RW chains: The characteristic chemical displacement of the walker should grow strongly superdiffusively. This result contradicts our numerical findings and suggests that correlations between subsequent steps cannot be neglected. According to Eq. (7) $\Lambda(t)$ for a SAW chain should grow as $\Lambda \propto t^{0.8}$, once more in clear contradiction to the numerical findings. These facts witness in favor of strong correlations between the steps. Note that this behavior is a consequence of the three-dimensional nature of the system: in $d \geq 4$ SAW and RW have very similar properties, a fact due to the relatively small number of contacts compared to the total number of sites. Therefore the number of jumps over large chemical distances is small, and a scaling law $\Lambda \propto t^{\alpha}$ with $\alpha = 0.5$ is expected.

In Euclidean space the polymer chain is a rather loose fractal, resembling to some extent a percolative structure, Ref. [21]. The overall number of sites between which jumps are possible and therefore the number of different steps' lengths grows with time much slower than n. For example, the mean number of distinct sites visited, $S(t)$ grows as $S(t) \propto t^{D_s/2}$. We find $D_s = 1.3 \pm 0.15$ for a RW chain and $D_s = 1.02 \pm 0.08$ for a SAW chain; see Fig. 4. Here D_s is the spectral dimension of the structure, $D_s < 2$. Note that the value of D_s for SAW structures in 3D is very near to that for 2D SAWs, namely, D_s is around unity (see Refs. [6,8,11]); the value is considerably smaller than predicted theoretically, $D_s = 1.69$, in Ref. [8]. The reason for this is that due to the evident geometrical constraints, the lengths of different steps connecting the neighboring sites are correlated, so that the number of different *independent* step lengths grows even slower than $S(t)$, leading to the peculiar behavior found here.

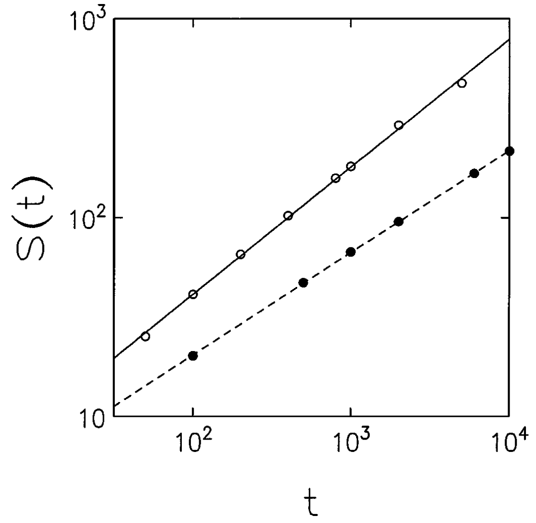

FIG. 4. Time dependence of the mean number $S(t)$ of distinct sites visited for random walks over RW chains (empty circles) and over SAW chains (full circles), plotted on double logarithmic scales. The full line has the slope 0.64, the dashed line the slope 0.51; these values correspond to the spectral dimensions $D_s = 1.28$ and $D_s = 1.02$, respectively.

To show that these numerically established behaviors are really a consequence of strong geometrical correlations we simulate "annealed" chains, in which we purposely neglect such correlations. For this we take the distribution of step lengths which we obtain from our simulations of frozen chains and compute the DD as a sum of n such steps, independently distributed. The results confirm that in this case the behavior is indeed superdiffusive: The DDs obtained scale exactly as predicted by Eq. (6).

In summary, we have numerically investigated random walks on polymer chains, where the walker can make steps from each site to its nearest neighbors in 3D. In the case of frozen chains we have found that the width of the walker's DD grows as $\Lambda \propto t^{\alpha}$, with the exponent α being close to $\frac{1}{2}$ and, moreover, that the DD scales with its width. On the other hand, the DDs show fat tails and lack the first (for RW chains) or the second (for SAW chains) moments. This paradoxal, diffusive ($\alpha \approx \frac{1}{2}$), behavior is related to the strong correlations between the lengths of subsequent jumps in chemical space. In the case of annealed chains such random walks lead to Lévy flights and to a strongly superdiffusive behavior. The extreme differences between these two cases show that transport processes on polymer chains are very sensitive to the interplay between the individual transfer steps and structural changes. Thus for random walkers which move very fast, the chain appears frozen, whereas an annealed situation is encountered if the walkers' motion is slow compared to the conformational changes of the chain. The effect could manifest itself through a strong dependence of the kinetics of luminescence on the solvent's viscosity. Monitoring transport phenomena in polymers provides thus a macroscopic means to assess the intrinsic molecular dynamics.

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