Weak non-self-averaging behavior for diffusion in a trapping environment

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The statistics of equally weighted random paths (ideal polymer) is studied in two- and three-dimensional percolating clusters. This is equivalent to diffusion in the presence of a trapping environment. The number of step walks, N, follows a logarithmic-normal distribution with a variance growing asymptotically faster than the mean, which leads to a weak non-self-averaging behavior. Critical exponents associated with the scaling of the two-point correlation function do not obey standard scaling laws.

Diffusion of independent particles in the presence of randomly distributed traps has been studied for a variety of purposes. Besides being a prototype of a disordered system which allows for some analytical treatment [1,2], it may describe migration properties of excitons in mixed organic crystals [3] as well as the diffusion-controlled reaction of diffusing particles with immobile centers.

A much less trivial problem is the diffusion of independent particles on a percolating cluster [4] when the environment acts as a perfect trap. Specifically let us consider a lattice where a given site acts as a perfect trap for particle motion with probability $1-p$. We will consider the diffusion problem on the incipient infinite cluster at the percolation threshold, $p=p_c$, both in two (square lattice) and three (cubic lattice) dimensions, where particles can jump only between nearest-neighbor sites and are absorbed upon hitting a trap. Thus at variance with previous studies where diffusion occurs on arbitrary (finite and infinite) clusters [1], we will focus on the statistics of random paths having a common origin in the incipient infinite cluster.

This model differs from the usual kinetic random paths (random walk) on the same structure by the fact that the weight given to each path is (a constant) independent of the particular path, and that the total probability is not conserved [5,6]. Thus this model is the exact equivalent of the well-known self-avoiding-walk (SAW) problem on the same structure when self-avoidance is negligible, and is also known as the ideal-chain (IC) problem [5].

In view of the fact that the SAW problem on strongly correlated disorder (such as the incipient infinite cluster) appeared to be extremely difficult to understand [7]. It is worthwhile to first understand the simpler problem of a single polymer coupled with disorder but without excluded-volume effects.

We will follow the method developed in a previous work [6]. The basic idea of this method is that the discretized version of the master equation for the probability $P_{x_0,x}(N)$ of being at site x after N steps, having started

from x_0 on a lattice of coordination z, can be expressed as a product of random matrices (transfer matrices) containing the information about the percolating cluster $\mathcal{C}$. The number of N-step walks in $\mathcal{C}$ with extrema x_0, x is then $C_{x_0,x}(N)=z^N P_{x_0,x}(N)$, and the total number of walks with origin in x_0 is $C_N=\sum_x C_{x_0,x}(N)$, which will play a role similar to the partition function.

Let $\mathcal{P}(\mathcal{C})$ be the probability of $\mathcal{C}$. The quenched average for the $q$the moment of the end-to-end distance of an N step walk w is defined as

$$\overline{\langle R_N^q \rangle} = \sum_{\mathcal{C}} \mathcal{P}(\mathcal{C}) \left[\frac{1}{C_N} \sum_w R^q(w)\Theta(w;\mathcal{C}) \right], \tag{1}$$

where $\Theta(w:\mathcal{C})=1$ if $w \subseteq \mathcal{C}$ and 0 otherwise, and $R(w)$ is the distance between the extrema of a walk w. Similarly the probability that a surviving (not trapped) particle is at site x after an N step walk can be defined by $P(x,N) \equiv C_{x_0,x}(N)/C_N$ [which is different from the quantity $P_{x_0,x}(N) \equiv C_{x_0,x}(N)/z^N$ appearing in the master equation because it is normalized to unity, while the latter is a nonconserved quantity].

It is important to notice that the disorder average was performed only on configurations $\mathcal{C}$ that span the lattice at the percolation threshold (that is, the subset of the clusters that are infinite), each configuration counted one in sampling.

Our best estimate for the exponent associated with the end-to-end distance $\langle R_N^2 \rangle \sim N^{2\nu}$ is $\nu=0.58\pm0.03$ in $d=2$ and $\nu=0.50\pm0.03$ in $d=3$ (see Fig. 1). These values were obtained as an average of values calculated by a regression procedure, Padé techniques, and standard extrapolating methods. The errors are statistical.

The data employed were obtained by averaging five different sets consisting of 1000 configurations each. The number of sites in the configurations was typically 15 000 for $d=2$ and 40 000 for $d=3$. The maximum number of steps was $N=1600$ and 600 in $d=2,3$, respectively, well
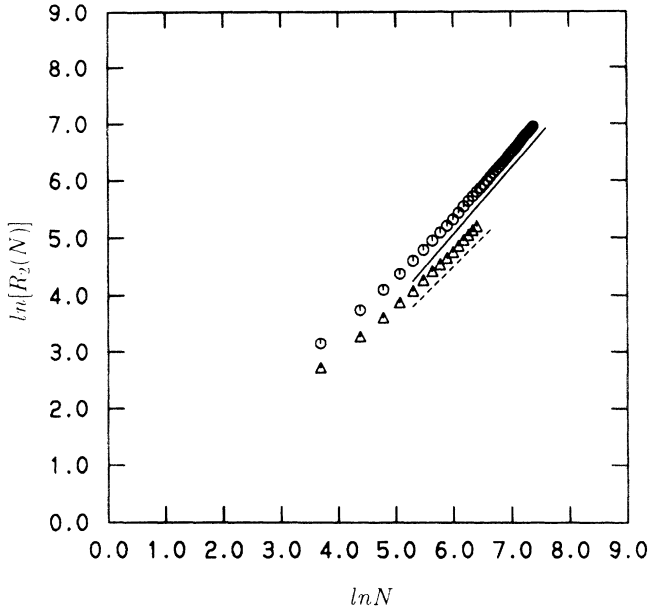
FIG. 1. Log-log plot for the quenched averaged end-to-end distance $R_2(N) \equiv \langle R_N^2 \rangle$ for $d = 2$ (○) and $d = 3$ (△). The solid line has a slope of 1.16, while the dotted line has 1.00 for $d = 2, 3$, respectively.

below the point at which finite-size effects become detectable. In $d = 3$ higher values of N do not change the previous estimate within our numerical errors. It should be noted that there seems to be a crossover between a subdiffusive regime ($\nu \le 0.5$, for both $d = 2$ and 3) to a regime where the system is superdiffusive ($\nu > 0.5$) (see Fig. 1) starting around $N = 100$. Figure 2 shows the local slope ν_N as a function of $1/N$ in $d = 2$ which gives support to the above value.
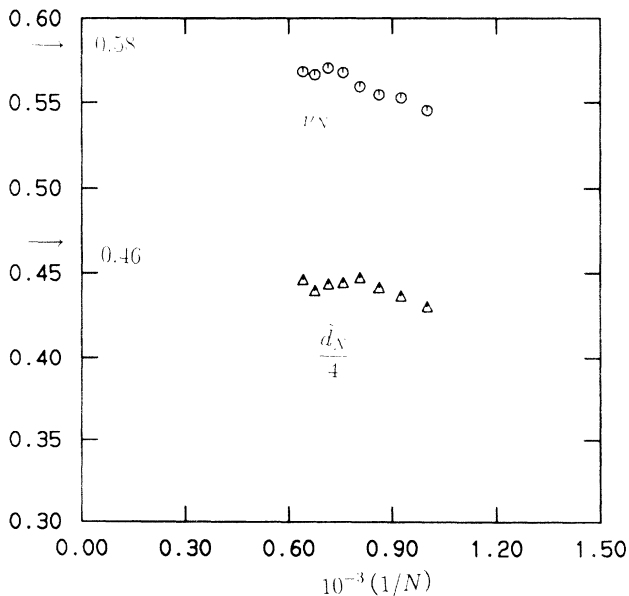
We also stress that the present problem is different from another interesting model, the freely jointed chain (with no excluded volume) in the presence of random obstacles [8], because our initial starting point is anchored. In this latter case a stretched chain is to be expected, as discussed in [9], and Flory-Lifshitz arguments do not apply.

Scaling of the quenched average of the probability density to be at site **R** at the discrete time N has been numerically investigated using the standard ansatz [10].

$$\overline{P(\mathbf{R},N)} = \frac{1}{N^{\nu d_F}} F\left[\frac{R}{N^\nu} \right] , \qquad (2)$$

where $F(x)$ is a universal function such that $F(x) \sim \exp(-x^\delta)$ for $x \gg 1$, $F(x) \sim x^g$ for $x \to 0$, and d_F is the fractal dimension of the infinite incipient cluster equal to $91/48 \sim 1.9$ and ~ 2.5 in $d = 2, 3$, respectively [4]. Note that we have normalized the probability so that $\int d^d R \rho(R) \overline{P(\mathbf{R},N)} = 1$, where the density $\rho(R)$ takes into account the fact that the support of the measure is fractal.

The universal function $x^{d_F} F(x)$ can be obtained by looking at the probability that a walk is a distance R from the origin. Using the above values of ν, a rather good collapse of the data is found both in $d = 2$ and 3. In Fig. 3 the collapse of the data is shown in $d = 2$ for $N = 400$, 800, 1200, and 1600. The best fit is obtained for $\delta = 1.60 \pm 0.03$, which is not consistent with the scaling relation [11] $\delta = (1 - \nu)^{-1} = 2.38 \pm 0.17$, taking for ν the value previously given. For small values of the argument we could fit $x^{d_F} F(x) \sim x^{d_F + g}$, with $g = -0.29 \pm 0.03$.

Consistent values of g and δ have been obtained by calculating dimensionless ratios of qth moments of the end-

FIG. 2. Local slope for the two exponents ν and $\tilde{d}/4$ as function of $1/N$ in the case $d = 2$. Also shown by an arrow are the values obtained from the Padé analysis.
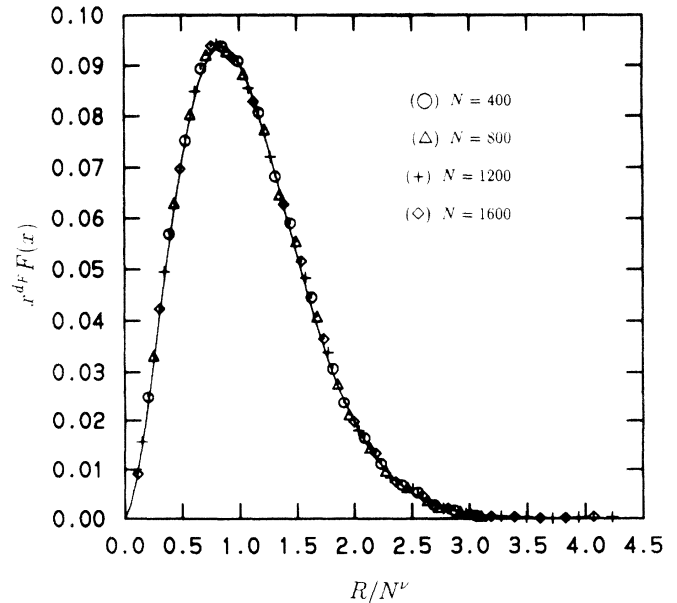

FIG. 3. Plot of the universal function $x^{d_F} F(x)$ vs the dimensionless quantity $x = R/N^\nu$, in $d = 2$. The data shown are an average over five points. The solid line is the best-fit result which gives $\delta = 1.60 \pm 0.03$ and $g = -0.29 \pm 0.03$.
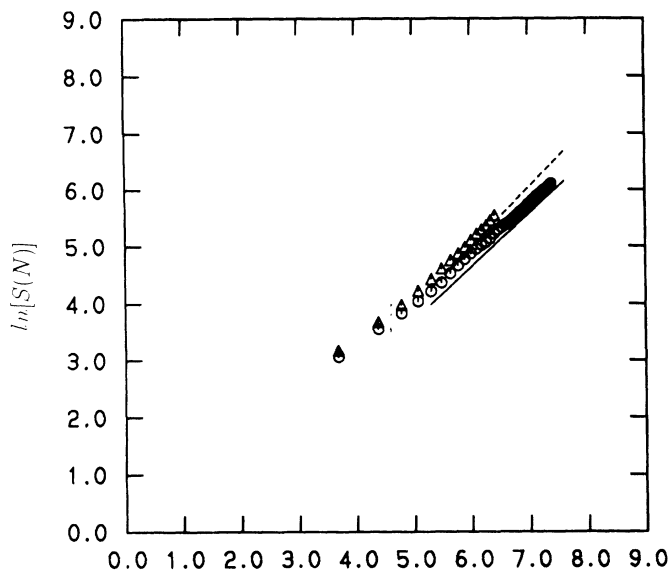
FIG. 4. Log-log plot for the quantity $S(N) \equiv 1/\overline{P(\mathbf{x}_0,N)} \sim N^{\tilde{d}/2}$ for $d=2$ (○) and $d=3$ (△). The solid line has a slope of 0.94, while the dotted line has 1.02 for $d=2,3$, respectively.
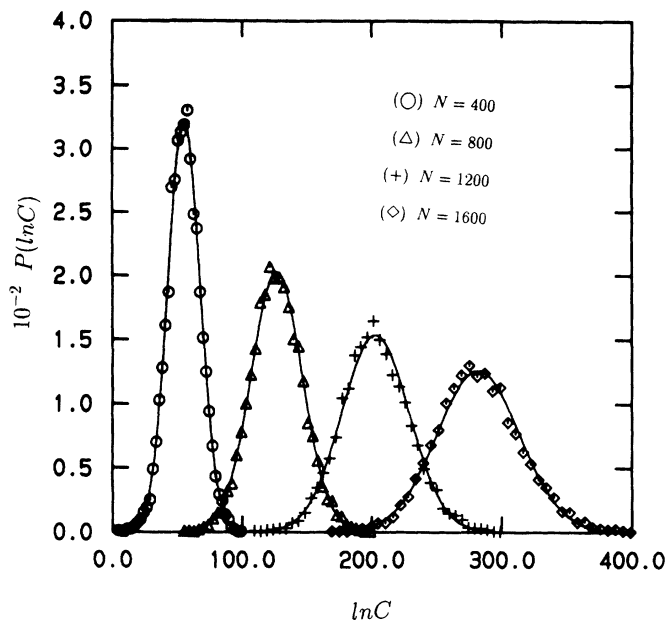

FIG. 5. Calculated distribution $P(\ln C)$. The solid lines are the best-fit results derived from Eq. (3). The points shown are raw data without any smoothing procedure, and with a normalization factor of 2.8^N for C.

to-end distance [see Eq. (1)] and comparing them with the prediction coming from Eq. (2) and the assumed form of the universal function F.

Results of almost the same quality have been obtained in $d=3$ where we found $\delta=1.61\pm0.05$ and $g=-0.33\pm0.07$. The value of δ obtained from the relation $(1-v)^{-1}$ would be $\delta=2.00\pm0.12$, which again is not compatible with the above numerical values.

From Eq. (2) the quenched average of the return probability behaves asymptotically as $\overline{P(\mathbf{x}_0,N)} \underset{N\gg 1}{\sim} N^{-\tilde{d}/2}$. Here $\tilde{d}$ is given by $\tilde{d}/2=(d_F+g)v$, which generalizes the Alexander-Orbach relation [12], and reduces to it when $g=0$. A linear fit to the data shown in Fig. 4 gives $\tilde{d}/2=0.94\pm0.06$. This is in perfect accord with the value $(d_F+g)v=0.93\pm0.02$ obtained by using the values of v and g previously calculated.

The values shown are derived from an average over eight different sets with 1000 configurations each. In $d=3$ we also find a value $\tilde{d}/2=1.02\pm0.07$ from the best fit, while $(d_F+g)v=1.08\pm0.04$, which is again compatible.

The exponent g is a measure of how favorable the conditions are for the walk to return to the origin. Unlike the SAW on a Euclidean lattice where $g=(\gamma-1)/v>0$ [13] and unlike the case of kinetically weighted paths on any (disordered or not) structure where $g=0$ [12], the IC has $g<0$, i.e., it is quite probable to the return to the starting point [14].

To better understand the role of large statistical fluctuations [15], we evaluated numerically the probability density $P(C,N)$ for the distribution of C_N over different realizations of disorder [analogous results have been obtained for the number N of step returning walks $C_{\mathbf{x}_0,\mathbf{x}_0}(N)$]. Figure 5 shows the function $P(\ln C)$ $\equiv CP(C,N)$ for $N=400$, 800, 1200, and 1600 for the case

$d=2$ where $C \equiv C_N$. They are very well fitted by a logarithmic-normal distribution (solid line) of the form

$$P(C,N) = \frac{1}{C\sqrt{2\pi\sigma_N^2}} \exp\left[\frac{-(\ln C - \lambda_N)^2}{2\sigma_N^2}\right], \qquad (3)$$

where the mean λ_N, as well as the variance σ_N^2, depend on N. In terms of the scaled variables $(\ln C - \lambda_N)/\sqrt{2\sigma_N^2}$, the values of $\sqrt{2\pi\sigma_N^2}P(C,N)$ nicely collapse onto a single universal curve (not shown) [16].

It is easy to relate this result to the moments of the distribution. Indeed from Eq. (3), the logarithmic moment is $Z_0(N) \equiv \ln C_N = \lambda_N$.

The direct numerical computation of the logarithmic moment gives, for $N\gg1$,

$$Z_0(N) = N\ln\mu - \alpha N^\psi, \qquad (4)$$

with $\mu=3.76\pm0.02$, $\psi=0.80\pm0.01$, and $\alpha=0.52\pm0.01$, in $d=2$ [17]. These values were determined by fitting the tail of the quantity $\ln[Z_0(N+\Delta N)/Z_0(N)]$ on data obtained by averaging over eight different sets of 1000 different configurations each. Almost identical values are found by making the linearization transformation $\Delta N/N \rightarrow (\Delta N/N)^{1-\psi}$, which gives a straight line when $\psi=0.8$. These values can be checked against the N dependence obtained for λ_N assuming the logarithmic-normal distribution of Eq. (3). The values obtained for the above parameters are $\mu=3.76\pm0.01$, $\alpha=0.52\pm0.01$, and $\psi=0.79\pm0.01$, which is in very good agreement with the previous estimates.

In the three dimensions we found $\psi=0.85\pm0.01$ directly and $\psi=0.85\pm0.03$ from the fit of λ_N [17]. The other parameters were also compatible.

The variance σ_N^2 is directly related to the free-energy fluctuations, since $\sigma_N^2 = (\ln C_N)^2 - (\ln C_N)^2 \sim N^{2\chi}$ where χ

is a new exponent. From the fit of the logarithmic-normal distribution in $d=2$ we obtain $\chi=0.66\pm0.01$, which we checked against a direct computation of the logarithmic moments, giving $\chi=0.68\pm0.01$. In $d=3$ we found $\chi=0.72\pm0.01$ directly and $\chi=0.70\pm0.01$ from the logarithmic-normal distribution. Consistent values are obtained from extrapolation methods and from the Padé analysis. Note that the exact inequality $(1-\chi)/\nu\leq d/2$ [18] is always satisfied.

The fact that the values for the variance and the mean are such that $\sigma_N^2\gg\lambda_N$, for $N\gg1$, is not surprising, since there is no equivalent to the central limit theorem for random multiplicative processes [19]. We shall refer to the condition $\sigma_N^q\gg\lambda_N$ $(q>1)$, but with $\sigma_N\ll\lambda_N$ as *weak non-self-averaging behavior*. The averages are dominated by rare events with large values and therefore do not well represent the asymptotic behavior of the system [20]. In this respect, a direct evaluation of the probability distribution is essential in order to understand the overall asymptotic behavior [15].

In the evaluation of the nonlogarithmic moments like $\overline{C_N^q}$, using Eq. (3), it is necessary to specify the upper limit of integration, i.e., $C_N\leq z^N$ (the lower limit is of course $C_N\geq1$). This stems from the fact that the tail of the distribution does not decay fast enough and thus violates Carleman's criterion [21].

It is easily shown that the upper and lower cutoffs have no effect on the results for the moments of $\ln C_N$ whose distribution is a sharply peaked Gaussian for $N\gg1$. A straightforward calculation in the large-N limit gives

$$Z_q(N)\equiv\overline{C_N^q}^{1/q}=z^N\exp[-AN^\phi]\,,\tag{5}$$

where $A=1/2q[\ln(z/\mu)]^2$ and $\phi=2(1-\chi)$, leading to a survival probability $P_S(N)=C_N/z^N\sim\exp[-AN^\phi]$ $(N\gg1)$.

Were the average unrestricted, i.e., taken over all clusters (finite and infinite), then a rigorous result for the asymptotic behavior of the survival probability in a disor-

dered d-dimensional lattice in which perfect absorbing traps are present (with probability $1-p$) [22,23] would give an exponent $\phi=d/(d+2)$. Some attempts to identify when this asymptotic limit sets in have been unsuccessful [24] due to the large fluctuations present, presumably of the same kind as those reported here.

No rigorous results are known for the present case. However, a straightforward extension of the heuristic argument previously applied to the case of unrestricted averages [23] would lead to $\phi=d_F\nu/(d_F\nu+1)$ and $\chi=(d_F\nu+2)/(2d_F\nu+2)$. With our values for ν this would yield $\chi=0.74\pm0.02$ in $d=2$ and $\chi=0.72\pm0.01$ in $d=3$, which is satisfactory only in $d=3$.

In conclusion, we presented a detailed investigation of the properties for the statistic of equally weighted random paths on a percolating cluster both in two (square lattice) and three (simple cubic) dimensions. Besides describing diffusion occurring only on the incipient infinite cluster when the rest of the environment acts as a perfect trap, this model corresponds to the usual self-avoiding walk on the same structure, with the self-avoidance turned off. The coupling between disorder and self-avoidance seems indeed responsible for the lack of a definite plausible scenario for the intriguing problem of the SAW on percolating clusters [7]. The main aim of the present work was to clarify the effect of the fluctuations and is expressed in Eqs. (3)–(5). We also computed the quenched averaged end-to-end distances and return probability in two and three dimensions. A generalization of the relation between spectral dimension and the fractal dimension of the lattice was proposed. A proper methodology to deal with anomalies in the logarithmic-normal distributions, which might be useful in other fields, was also described.

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