Diffusion with critically correlated traps and the slow relaxation of the longest-wavelength mode

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We study diffusion on a substrate with permanent traps distributed with critical positional correlation, modeled by their placement on the perimeters of a critical percolation cluster. We perform a numerical analysis of the vibrational density of states and the largest eigenvalue of the equivalent scalar elasticity problem using the method of Arnoldi and Saad [Y. Saad, Linear Algebra Appl. **34**, 269 (1980)]. We show that the critical trap correlation increases the exponent appearing in the stretched exponential behavior of the low frequency density of states by approximately a factor of two as compared to the case of no correlations. A finite-size scaling hypothesis of the largest eigenvalue is proposed and its relation to the density of states is given. The numerical analysis of this scaling postulate leads to the estimation of the stretch exponent in good agreement with the result for the density of states.

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I. INTRODUCTION

Understanding the behavior of a particle diffusing in the presence of traps is important, as it captures the essence of many physical processes, including diffusion controlled reactions where one of the reactants is immobile, trapping of excitons, etc. Mapping of the diffusion problem with traps to the scalar elasticity problem also affords insight into lattice vibration of systems such as binary alloys with contrasting elastic constants. From a theoretical point of view, this problem is analogous to the ideal chain in inhomogeneous media. The ideal chain problem is interesting, since it is the Gaussian limit of the self-avoiding walks and yet possesses a universality class of its own in inhomogeneous media, that is distinct from the usual random walk.

These considerations have resulted in many analytical and numerical attempts to gain an understanding of the problem [1,2]. Typical quantities used to characterize diffusion in the presence of traps include $P_0(t)$, the probability that the diffusing particle will return to the starting point after time t. $P_0(t)$ is related to the number of distinct sites visited by the diffusing particle and is the Laplace transform of the vibrational density of states of the corresponding scalar elasticity problem, which can often be measured experimentally by methods such as Raman and neutron scattering [3].

For the case of diffusion in the presence of traps distributed randomly with no correlations, it has been proven rigorously by Donsker and Varadhan [4] that the decay of $P_0(t)$ with time is slower than exponential. Essentially the same behavior also results when the traps have only short-range correlations such as the hard core repulsion [1]. This fact indicates that, in the long time limit, the properties of the diffusing particle are domi-nated by the presence of large trap-free regions that have a finite (though small) probability of occurrence. This is because if the traps were uniformly distributed, the diffusing particle would be trapped at a constant rate, which would result in an exponential decay of $P_0(t)$. It also means that the *quenched* disorder average must be carried out, since an annealed averaging would smear out the trap positions.

In this paper we ask the question of whether and how this interesting behavior of the diffusing particle with traps is modified when we introduce long-range, *critical* correlations into their positions, with their associated critical fluctuations [5]. In the equivalent scalar elasticity problem, the correlated traps map to the clamping of sites with a correlated distribution. In this sense, the present problem extends the so-called *fractino* problem [7] where a fractal boundary of an otherwise nonfractal object is clamped to the case where the bulk of the substrate is itself a fractal. It is also an extension of the *fracton* problem [6] as the traps (or clamped boundaries) are introduced into the scalar elasticity of fractals.

Calculational difficulties have prevented this problem from receiving its share of attention even though, often in real physical situations, the positions of traps are correlated at least within limited length scales. For the case of uncorrelated trap distribution, a Poisson distribution is usually assumed, which simplifies the theoretical calculation [8]; however, this assumption fails for correlated traps. As for computational calculations, techniques based on exact enumeration are highly computer time and memory intensive because of the high sensitivity of the behavior of the diffusing particle to the actual positions of the traps in the sample, leading to large fluctuations in the measured quantity from sample to sample. This translates to requiring an ensemble average to be taken over a large number of disorder configurations for meaningful results. Moreover, the onset of the asymp-

totic regime is very slow in this type of problem, which adds to the computational difficulties [9].

In this paper, we establish that $P_0(t)$ has a stretched exponential form *qualitatively* similar to the case of the Poissonian trap distribution but with a substantially different stretch exponent. We show this behavior from the analysis of the density of eigenvalues of the transition probability matrix **W**, which describes the diffusion process. We also study the finite-size scaling of the largest eigenvalue of **W**, which serves as an extremely powerful tool with which to extract the stretch exponent characterizing the long time behavior of $P_0(t)$. A preliminary account of this work was presented at the Hayashibara Forum (1995) and appears in its proceedings. [10]

II. IDEAL CHAIN IN CRITICALLY CORRELATED DISORDER

We choose percolation cluster [11] formed at critical probability of occupation p_c as the substrate for diffusion. The sites on the external perimeter (hull) [12] as well as on the internal perimeter of the percolation cluster are made absorbing and once the diffusing particle reaches the perimeter sites it is trapped permanently. The hull sites and the sites constituting the internal perimeter form fractals at p_c [13]. Thus, placing the traps along the perimeters induces spatial correlations among the traps because of the long-range correlations among the sites of a fractal. While we do not pursue the distinction of external versus internal perimeters in this work, there *are* interesting effects when different boundary conditions are applied to them, at least in two dimensions [14].

The time evolution of the probability $P_i(t)$ that the diffusing particle is at site i at time t is Markovian and the process can be described in the continuous time limit by the following master equation:

$$(\partial/\partial t)P_i(t) = \sum_j w_{ij}P_j(t) - P_i(t), \qquad (1)$$

where w_{ij} is the hopping rate from site j to i. In this problem we consider only nearest neighbor hopping and so w_{ij} is nonzero only for the nearest neighbor pairs i, j. We have chosen w_{ij} to be $1/z$ for all occupied nearest neighbors j, where z is the full coordination number of the underlying lattice; otherwise w_{ij} is set equal to zero. What this amounts to is that once the particle hops to a trap site there is no further time evolution of that particular random walk and only those walks that have escaped getting trapped in the perimeter sites evolve further. Thus the traps act as permanent particle absorbers.

Processes in which time evolution is governed by Eq. (1) can be cast into an eigenvalue problem of the transition probability matrix **W**. The matrix elements w_{ij} of **W** control the dynamics of the random walk, and the locations of the nonzero elements of **W** have the information about the structure of the underlying fractal substrate responsible for the correlations among the trap sites on its perimeters.

The density of normal modes of **W** is related to the return to the starting point probability of the diffusing particle by the Laplace transform [15]. The probability distribution of the number of walks $C_0(t)$ that return to their starting point after time t, denoted as $P(C_0(t); t)$, was studied in [16] and found to be a truncated lognormal distribution. Thus

$$P(C_0(t); t) \approx \frac{1}{C_0(t)\sqrt{2\pi\sigma_t^2}}\exp\left(\frac{-(\ln C_0(t) - \lambda_t)^2}{2\sigma_t^2}\right).$$
$$(2)$$

In [16] it was further found from the first moment of this distribution that

$$\ln P_0(t) \sim -t^{2(1-\chi_0)} \qquad (3)$$

in the asymptotic long time limit, where $P_0(t)$ is obtained as $\overline{C_0(t)/z^t}$, the bar above the quantity indicating the quenched disorder average. The exponent χ_0 is the same one as that which appears in the long time behavior of the width of the log-normal distribution, σ_t^2,

$$\sigma_t^2 \sim \beta t^{2\chi_0}. \qquad (4)$$

Since $P_0(t)$ has a stretched exponential behavior according to Eq. (3), we expect the density of normal modes ρ [which is the inverse Laplace transform of $P_0(t)$] to also have a stretched exponential form [16],

$$\ln \rho(\epsilon) \sim -\epsilon^{-d_0/2} \qquad (5)$$

in the limit of small $\epsilon \equiv |\ln \lambda|$, where λ denotes the eigenvalues of **W**, and the exponents χ_0 and d_0 are related to each other by $d_0 = 4(1 - \chi_0)/(2\chi_0 - 1)$. The results from [16] give support for the presence of such a behavior, although their numerical estimates of d_0 need to be improved as they did not take into account the proper normalization of ρ as well as the substantial nonasymptotic effects [17].

We can also relate the behavior of $\rho(\epsilon)$ to the finite size effects of the edge of the spectrum. First, note that for any finite substrate, however large, the largest eigenvalue of **W**, which we denote by λ_1, must be less than one. This is because the eigenvalue of one would indicate the existence of a stationary state, whereas there are always particles that are trapped, leading to a *leakage* of probability for the diffusing particle, in contrast to the diffusion *without* traps. The value of $|\ln \lambda_1|^{-1}$ then corresponds to the slowest time scale of the problem, and there is always a gap between λ_1 and one, the latter being what the maximum eigenvalue would be for diffusion without traps. The interesting question is whether this gap is bounded from below by a nonzero constant or it approaches zero as the substrate size increases.

Our argument for the behavior $\lambda_1 \to 1$ as the substrate size $S \to \infty$ follows the observation of [4] for the case of uncorrelated trap distribution. In that case, the return probability $P_0(t)$ was shown to be a stretched exponential, which is slower than a pure exponential (although not as slow as a power law, which would be the case in the absence of traps), and this behavior was attributed to the

dominance of the trap-free regions, although they occur relatively infrequently. In our case of critically correlated trap distribution, we also have a slow, stretched exponential for $P_0(t)$, which we interpret as a similar dominance of the nearly trap-free regions. Although there are more traps in the critically correlated case, there are also much greater fluctuations in their density. Thus, regions of relatively low concentrations of the traps are likely to be present, probably with a hierachical size distribution. Since the leakage of probability is *nearly* zero in a *nearly* trap-free region, we would expect λ_1 to approach one as the size of the largest trap-free region grows indefinitely.

Another argument is as follows: if there were indeed a nonzero lower bound for $\epsilon_1 \equiv |\ln \lambda_1|$, then it would also give a bound for the slowest relaxation rate. Thus, $P_0(t)$ would have to decay at least exponentially in time corresponding to this rate. Since $P_0(t)$ in fact decays as a stretched exponential with the stretch exponent less than one ([16] as well as this work), no such bound can exist for the rate; rather $\epsilon_1 \to 0$ as $S \to \infty$.

We further propose a scaling relation between ϵ_1 and S via

$$1/S \sim \int_0^{\epsilon_1} \rho(\epsilon)d(\epsilon), \qquad (6)$$

where a possible numerical prefactor has been neglected. This relation follows from the assumption that, say, the largest (λ_1) and second largest (λ_2) eigenvalues scale relative to the value one in the same way when $S \to \infty$. That is, if we assume

$$\int_0^{\epsilon_1} \rho(\epsilon)d(\epsilon) \sim C_1 f(S), \qquad (7)$$

$$\int_0^{\epsilon_2} \rho(\epsilon)d(\epsilon) \sim C_2 f(S), \qquad (8)$$

where $\epsilon_2 \equiv |\ln \lambda_2|$, then the difference must also scale in the same way,

$$\int_{\epsilon_1}^{\epsilon_2} \rho(\epsilon)d(\epsilon) \sim (C_2 - C_1)f(S), \qquad (9)$$

but this latter integral must scale as $1/S$ if the integral of the density of normal modes $\rho(\epsilon)$ is normalized to unity. This means $f(S) \sim 1/S$, thus Eq. (6) follows.

The assumption of the same asymptotic behavior for the two largest eigenvalues is plausible if we consider the difference between λ_1 (or λ_2) and one to be the reflection of the finite size of the largest (or the second largest) trap-free region (respectively). As long as the large trap-free regions are geometrically similar (as would be the case in a hierarchical distribution of such regions), and as long as their sizes all go to infinity as $S \to \infty$, it seems reasonable that the gaps between λ_i ($i = 1, 2$) and one behave in the same manner.

If we substitute a stretched exponential form of $\rho(\epsilon)$ in Eq. (6) we get an incomplete gamma function. On retaining only the leading term of the incomplete gamma function and taking the natural logarithm of both sides, we get

$$\ln S = a\epsilon_1^{-x} - (x + 1) \ln \epsilon_1 + b, \qquad (10)$$

where a general stretched exponential form of $\rho(\epsilon)$,

$$-\ln \rho(\epsilon) \sim a\epsilon^{-x} + c, \qquad (11)$$

has been assumed and $b = c + \ln(ax)$.

While the above gives a particular scaling prediction for the case of the critically correlated trap distribution, the argument leading to Eq. (6) applies more generally. For example, a similar procedure should apply to the uncorrelated trap distribution of [4]. Also, for the trapless case (or the *ants* case [15]), where the largest eigenvalue is actually one (because there *is* a stationary state), a similar argument should work with, say, the second (λ_2) and third (λ_3) largest eigenvalues. Of course, if there is no trap, a probability leakage per se does not occur. However, each mode with a large λ tends to be associated with a *blob* of high connectivity region to which the same kind of argument can be applied. Indeed, in the trapless case, Eq. (6), together with the power law density of states

$$\rho(\epsilon) \sim \epsilon^{d_s/2 - 1}, \qquad (12)$$

where d_s is the spectral dimension of the substrate, leads to a power law relation between S and ϵ_2,

$$\epsilon_2 \sim S^{-2/d_s}, \qquad (13)$$

which is identical to the relation proposed on the basis of the finite-size scaling of the largest nontrivial normal mode and numerically verified in [15]. Such finite-size scaling relations provide a very powerful technique with which to obtain the quantitative characterization of the density of states, since they reduce the computational effort drastically, requiring only the information on the highest (or second highest) mode.

III. RESULTS OF NORMAL MODE ANALYSIS

In this section we give numerical results for the exponent x for the stretched exponential decay of the density of states as discussed above. We extract this exponent directly from the density of states [cf. Eq. (11)] and also independently from the finite-size scaling of the largest eigenvalue of **W** [cf. Eq. (10)] in two and three dimensions (square and simple cubic lattice, respectively).

In order to reduce the computational time and memory requirements, we take advantage of the fact that we are interested only in the asymptotic long time relaxation of the system controlled by those normal modes with large eigenvalues λ. Thus we use the Arnoldi-Saad algorithm [18,15] to reduce the original **W** to a smaller matrix that contains the approximate information about the highest normal modes.

We analyze the density of states per site, $\rho(\epsilon)$. It is obtained from the eigenvalues of **W** by binning them linearly in the ϵ space. The number of eigenvalues in each bin is divided by the bin width, the size of the cluster and also by the number of clusters over which the quenched disorder average is performed. The number of indepen-
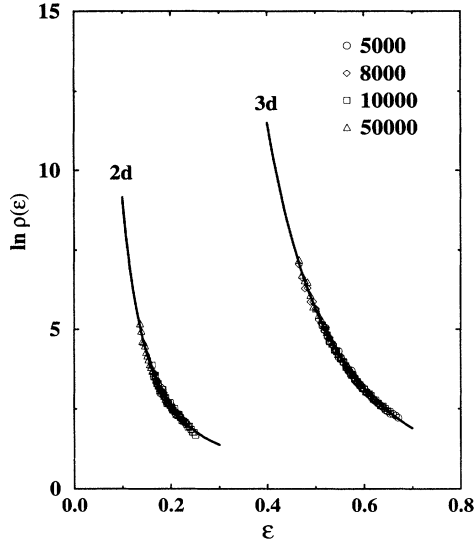
FIG. 1. Natural log of the density of eigenvalues $\rho(\epsilon)$ against ϵ in $d = 2$ and $d = 3$. The data collapse very well for different sizes of substrates.

FIG. 2. Natural log of the size of substrate $\ln S$ against ϵ_1 in $d = 2$ and $d = 3$.

dent cluster realizations over which the disorder average was taken is of the order 1000 for cluster sizes $S = 8000$, 10 000, and 50 000 and of the order 10 000 for $S = 5000$. To avoid partial binning, we retained in the final results only those bins that contained eigenvalues contributed from every substrate realization.

Since $\rho(\epsilon)$ has a stretched exponential decay, we have plotted in Fig. 1, $-\ln \rho(\epsilon)$ versus ϵ, which is expected to have the form $a\epsilon^{-x} + c$. There is an excellent data collapse for all the cluster sizes both in two and three dimensions. The solid curve drawn through the data is obtained by fitting the data to an expression of this form. The numerical estimates of x and the numerical values of a and c corresponding to the central values of x are tabulated in Table I. Note that the value of x cannot be accurately obtained simply from the slope of the double log plot of $\ln \rho(\epsilon)$ with respect to ϵ, since the value of the constant c might be appreciable.

The sizes of the symbols in Fig. 1 are larger than the cluster to cluster statistical fluctuations. The quoted error bars are obtained visually from changing the effective estimate of x for the nonlinear fit until it no longer fits the data points. The small scaling regime, which is typical for these kinds of problems (i.e., diffusion with traps) [9], makes the precise extraction of x difficult. This accounts

for the large error bars in our results as compared to the case, of diffusion in a percolation cluster without absorbing sites [15]. In the latter case, the density of states has a power law form and the scaling regime increases appreciably with the size of the cluster, which results in much smaller error bars for the extracted exponents even with the same numerical technique.

In Fig. 2, we plot $\ln S$ with respect to ϵ_1 in two and three dimensions, where S is the size of the substrate. The solid curves are obtained by fitting the data to an expression $a\epsilon_1^{-x} - (x + 1)\ln \epsilon_1 + b$, which is what we expect from the finite-size scaling analysis of the largest eigenvalue. The sizes of the symbols are larger than the cluster to cluster fluctuations. The number of clusters over which the disorder average was performed is of the order 1000 for the larger clusters, the same as for the density of states, and for smaller clusters of size 100, 400, 1000, and 5000 the average was taken over 10 000 clusters. The estimates of x and the values of a and b corresponding to the central values of x, which we obtain from the nonlinear fit, are tabulated in Table II. The error bar for the value of x is obtained in a similar way to that for the density of states.

We note that the estimates of x and a obtained from the density of states and from the finite-size scaling of the

TABLE I. Estimates of the exponent x and the constants a and c from $\rho(\epsilon)$ for the square lattice in two dimensions and simple cubic lattice in three dimensions. The data for $-\ln \rho(\epsilon)$ have been fitted to the form $a\epsilon^{-x} + c$.

d	x	a	c
2	2 ± 0.5	0.084	0.42
3	$3.24^{+0.3}_{-0.7}$	0.64	-0.077

TABLE II. Estimates of the exponent x and the constants a and $b = \ln(ax) + c$ from the finite size scaling of ϵ_1, for the square lattice in two dimensions and simple cubic lattice in three dimensions. The data have been fitted to the form $a\epsilon^{-x} - (x + 1)\ln \epsilon + b$.

d	x	a	b
2	$2.23^{+0.3}_{-0.7}$	0.072	-1.06
3	$3.26^{+0.3}_{-0.7}$	0.5	0.72

largest eigenvalue, given in Tables I and II, respectively, are in good agreement with each other. The values of d_0 thus obtained, however, turn out to be about a factor of two larger than the corresponding stretch exponents for the uncorrelated distribution of traps [4]. The estimates of x also differ from those of $d_0/2$ as given by [16] due, we believe, primarily to the failure of [16] to take properly into account ϵ being not quite in the asymptotic region (thus proper normalization and prefactors becoming important) (cf. [17]). However, the exponent χ_0 [Eq. (4)] is relatively insensitive to x $(= d_0/2)$ and the analysis of $P_0(t)$ in [16] is not affected by these problems. We also believe that their main conclusions remain valid.

IV. SUMMARY

In summary, we have studied the problem of diffusion on a substrate with permanent traps that are distributed with critical correlation in their positions. The critical correlation has been modeled by placing the traps on the perimeters of critical percolation clusters, which are obtained by Monte Carlo simulation. The statistical behavior of the diffusing particle in the time domain is then mapped to the scalar elasticity problem with fixed, fractal boundaries, and a numerical analysis of the vibrational density of states of the latter problem is carried out using an approximate diagonalization algorithm of Arnoldi and Saad [18]. This problem may be considered a generalization both of the *fracton* problem of Alexander and Orbach [6], where there are no traps but the substrate is fractal, and of the *fractino* problem of Sapoval, Gobron, and Margolina [7], where a fractal boundary is clamped (equivalent to traps) but the substrate itself is not fractal.

We have shown that introducing critical spatial correlations among the traps does not change the *qualitative* behavior of the density of states as compared to the case of uncorrelated traps, but that there are substantial effects of correlations *quantitatively*. This strongly suggests that the diffusion process is dictated by the presence of nearly trapless regions similarly to the case of uncorrelated traps, but the long-range correlations among the trap positions lead to a decrease in the number and size of these regions nearly free of traps, which induces a faster decay in the density of states and consequently a smaller probability of return to the starting point after time t. This is reflected in a much larger exponent in the stretched exponential form of density of states than the case of uncorrelated traps.

On the other hand, as compared to the case of the same *fractal* substrate but with *no* traps, the density of states is *qualitatively* different, since the latter problem produces a power law density of states in the low energy limit known as *fractons*, accumulating to an infinite density toward the maximum eigenvalue of one [15]. In contrast, with the perimeters acting as traps, the density of states becomes a stretched exponential, rapidly falling to zero toward the maximum eigenvalue.

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