Spectral diffusion in a one-dimensional percolation model

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Spectral diffusion on a one-dimensional chain with a random distribution of interruptions is considered. An exact solution for the time decay of the initial excitation is computed. The solution exhibits an exponential behavior initially, diffusion ($t^{-1/2}$) behavior at intermediate times, and a long time decay $\sim \exp[-(\lambda t)^{1/3}]$. The relationship of this problem to the vibrating chain with some infinite masses, and to a related band-structure problem, is discussed. The possibility of observing the predicted behavior in fluorescent-line-narrowing experiments is also discussed, and some limits on the relevant parameters are given.

I. INTRODUCTION

There has been considerable interest recently in one-dimensional diffusion problems in disordered systems.[1-3] In part, this reflects the intensive experimental work on quasi-one-dimensional systems to which these studies are directly applicable. From a theoretical point of view, one hopes that the simpler one-dimensional situation will produce some insight into the more complicated situations of higher dimensionality. Our purpose here is to investigate spectral diffusion in a one-dimensional percolation model. Most of the questions one usually asks in studying percolation do of course become trivial in one dimension. It is obvious, for example, that all states are localized, and there is no spatial diffusion to infinity. We shall show, however, that one can obtain interesting and in a way surprising results by studying *spectral* diffusion in such a model. Also, the results are probably relevant to fluorescent-line-narrowing (FLN) experiments in suitable systems.[4]

To motivate the quantity we want to calculate, we first discuss the physical model briefly. Consider excitations, which, in a perfect system, would form an exciton band. In physical systems the individual site energies are not all equal but rather spread out over an energy range referred to as the inhomogeneous broadening. It is usually a good approximation to regard these shifts as uncorrelated in spatial position. If the inhomogeneous broadening is small compared to the near-neighbor transfer integral, the elementary excitations are exciton-like, with the site energy randomness acting only as a small scattering perturbation. If the reverse is true (i.e., if random vacancies were present) coherent propagation would not occur. The chain would be broken into segments, the length of each segment being a random variable. This is the model we shall deal with shortly.

Consider now a FLN experiment.[4] These experiments involve exciting the system with a pulse of narrow-band (e.g., laser) light considerably narrower than the excitation spectrum of the system (e.g., the inhomogeneous broadening). Thus, only states whose excitation energy coincides with the pulse frequency are initially excited. After the initial pulse the profile of the emission spectrum is monitored as a function of time. Initially it coincides with the excitation profile. As a result of the transfer of excitations to other states whose energy[5] is different, the profile will gradually decay towards the equilibrium density of states associated with the full system. This transfer of excitations to other energies is termed spectral diffusion. Spatial transfer is clearly involved, but the distance traveled is not directly relevant.

When the transfer Hamiltonian is weak, compared to the inhomogeneous broadening, excitations are localized. A single-state representation is useful, and transfer from one site to another proceeds by means of (incoherent) phonon-assisted energy transfer.[5] This essentially classical transfer obeys a classical diffusion equation for the case of those transfer processes where the transfer rate is independent of energy mismatch between initial and final sites. Reference 5 displays one such process.[6] These conditions lead to our model, which we hope, therefore, may be relevant to physical systems.

Our model consists of a linear chain of sites with random energies with nearest-neighbor transfer rates ($W_{n,n+1} = W_{n+1,n}$) distributed independently according to

$$\rho(W) = p\delta(W) + (1-p)\delta(W - W_0) . \quad (1)$$

We thus neglect any dependence of the transfer rates on energy mismatch as discussed above. We also note that one obtains a completely equivalent model if the disconnections ($W = 0$) are due to the presence of impurities on the chain. We define an excitable site as a site whose energy is in the initially excited (FLN) range. The density of such sites is designated by q. The probability that the

site is actually excited is designated by c. We calculate the density of excitations on the FLN sites as a function of time $[\bar{P}(t)]$. We are able to calculate this quantity exactly. The interesting results relate to the long-time behavior ($W_0 t \gg 1$). We obtain

$$\bar{P}(t) = cq[q + p(1-q)] + cq(1-q)\,\frac{1}{(4\pi W_0 t)^{1/2}} \times [1 + (\lambda t)^{1/3}]\exp[-\tfrac{3}{2}(\lambda t)^{1/3}], \quad (2)$$

where $\lambda = \frac{1}{2}\pi^2\alpha^2 W_0$ and $\alpha = -\ln(1-p)$. This result has curious consequences. For small p (nearly all bonds connected) there is a time regime where the amplitude falls as expected for the diffusion equation

$$\bar{P}(t) - \bar{P}(\infty) \propto \frac{1}{(4\pi W_0 t)^{1/2}}, \quad 1 \ll 2W_0 t \ll 4/\pi^2\alpha^2. \quad (3)$$

For longer times the decay is again exponential

$$\bar{P}(t) - \bar{P}(\infty) \propto \exp[-\tfrac{3}{2}(\lambda t)^{1/3}]. \quad (4)$$

This latter regime reflects a situation where (rare) large clusters dominate the time dependence of the correlation function. We note that for large p ($p \gtrsim 0.2$) the diffusion regime ($t^{-1/2}$) disappears.

A second feature of importance is that, from the nature of the model, all excitations are spatially trapped. This enhances the constant term in Eq. (2) over the simple average which one might expect for the full system.

We present the model and calculations in Sec. II. We discuss the significance of the results and their possible generalization in Sec. III. We also briefly discuss some other problems to which these results are applicable.

II. CALCULATION OF $\bar{P}(t)$

We consider a linear chain with nearest-neighbor transfer rates distributed according to (1). The site occupation probabilities obey the linear rate equations

$$\frac{dP_n}{dt} = W_{n,n+1}(P_{n+1} - P_n) + W_{n-1,n}(P_{n-1} - P_n), \quad (5)$$

for any initial distribution and degree of excitation.[7] We denote the set of excitable sites by $\{n\}$. We want to calculate the probability that excitations which were initially on $\{n\}$ are still on this set at time t,

$$\bar{P}(t) = \sum_{n\in\{n\}} \sum_{n'\in\{n\}} P_n(t) P_{n'}(0), \quad (6)$$

where the averaging is over all (equally probably) configurations of initially excited sites and is normalized to give the (average) probability per site in the chain. Now, because of the distribution of bonds (1), the chain is actually separated into segments of different lengths. The probability of finding a segment of length N is[8]

$$R(N) = p(1-p)^{N-1}, \quad (7)$$

and we can write

$$\bar{P}(t) = \sum_{N=1}^{\infty} R(N) N \bar{P}_N(t) \Big/ \sum_{N=1}^{\infty} R(N) N, \quad (8)$$

where $\bar{P}_N(t)$ is defined as in Eq. (6), but for a finite segment of length N:

$$\bar{P}_N(t) = \sum_{M,L} Q_{NM} C_{ML} P_{NML}(t), \quad (9)$$

where

$$Q_{NM} = \binom{N}{M} q^M (1-q)^{N-M} \quad (10)$$

is the probability of having M excitable sites on the chain segment and

$$C_{ML} = \binom{M}{L} c^L (1-c)^{M-L} \quad (11)$$

is the probability of having L excitations on these M sites. $P_{NML}(t)$ is the probability that excitations are on excitable sites for segments of length N with M excitable sites and L initial excitations, averaged over all configurations of the (M) sites and L initial excitations on the segment.

A direct computation using the eigenfunctions of Eq. (5) for a finite segment gives

$$P_{NML}(t) = \frac{LM}{N^2} + \frac{L(N-M)}{N^2(N-1)} \times \sum_{l=1}^{N-1} \exp\left[2W_0 t\left(\cos\frac{\pi l}{N} - 1\right)\right]. \quad (12)$$

Substitution of (12) into (9) and carrying out the sum on M and L gives

$$\bar{P}_N(t) = \frac{1}{N} cq \left\{1 + q(N-1) + (1-q) \times \sum_{l=1}^{N-1} \exp\left[2W_0 t\left(\cos\frac{\pi l}{N} - 1\right)\right]\right\}. \quad (13)$$

Finally, substitution into (8) yields

$$\bar{P}(t) = cq\{q + p(1-q)[1 + I(t)]\}, \quad (14)$$

where

$$I(t) = \sum_{N=2}^{\infty} R(N) \sum_{l=1}^{N-1} \exp\left[2W_0 t\left(\cos\frac{\pi l}{N} - 1\right)\right]. \quad (15)$$

It will be convenient to rewrite (15) as a Laplace transform

$$I(t) = (p)^{-1} \int_0^\infty d\epsilon \rho(\epsilon) \exp(-\epsilon W_0 t), \tag{16}$$

where $\rho(\epsilon)$ is the density of states of the eigenvalues of (5) (except for the delta function which we have removed at $\epsilon = 0$). Domb *et al.*[9] have discussed the analogous problem of lattice vibrations, and Rice and Bernasconi[10] the electronic density of states for interrupted chains. Both problems are mathematically equivalent to our problem. Rice and Bernasconi find an expression for the density of states,[10]

$$\rho(\epsilon) = \frac{1}{2\pi\sqrt{\epsilon}} \times \frac{(\pi\alpha/2\sqrt{\epsilon})^2}{[\exp(\pi\alpha/2\sqrt{\epsilon}) - 1][1 - \exp(-\pi\alpha/2\sqrt{\epsilon})]}. \tag{17}$$

The quantity exhibited in (17) is "smoothed"; Ref. 9 shows that the true density of states is highly irregular. We require only integrals of $\rho(\epsilon)$ so that use of a smoothed density of states is justified.

The expression (17) inserted into (16) is very complicated, though it can be examined in the long-time limit. We prefer to use an integral approximation for the sum in (15) which will enable us to pass continuously between two limiting behaviors in the long-time limit (see below). The more correct result, Eq. (17), is too complicated to allow a similar calculation, though we shall use it for comparison.

We are interested in the long-time behavior of $I(t)$, where $W_0 t \gg 1$. Thus, the lowest eigenvalues in (15) will dominate. These correspond to small $q = \pi l / N$, so that one can expand the exponent in (15). The dominant effect for the density of states is the fact that a finite cluster has a finite lowest eigenvalue (at $q = \pi/N$). If one describes this by a cutoff in an otherwise continuous cluster density of states (proportional to $1/\sqrt{\epsilon}$), one finds,

$$\rho(\epsilon) = \frac{\alpha^2}{2\pi\sqrt{\epsilon}} \int_{\pi/2\sqrt{\epsilon}}^\infty N dN e^{-\alpha N}, \tag{18}$$

for sufficiently small $\epsilon (\epsilon \ll \frac{1}{4}\pi^2)$. Integrating (18) yields

$$\rho(\epsilon) = (1/2\pi\sqrt{\epsilon})[1 + (\pi\alpha/2\sqrt{\epsilon})] \exp(-\pi\alpha/2\sqrt{\epsilon}). \tag{19}$$

Substituting (19) into (16), and evaluating the integral by the method of saddle points, gives

$$pI(t) = \frac{1}{(3\pi W_0 t)^{1/2}} [1 + (\lambda t)^{1/3}] \exp[-\tfrac{3}{2}(\lambda t)^{1/3}], \tag{20}$$

where $\lambda = \frac{1}{2}\pi^2\alpha^2 W_0$.

The advantage of this procedure is that it exhibits the crossover from a diffusive ($t^{-1/2}$) regime to the exponential ($\exp[-(\lambda t)^{1/3}]$) long-time behavior in closed form. Unfortunately, the combination of approximating the sum in (15) by an integral, and the approximation contained in the saddle-point method, does induce some errors into our final result [Eq. (20)]. For the diffusive regime, $\lambda t < 1$, one should have

$$pI(t) = (4\pi W_0 t)^{1/2}. \tag{21}$$

This differs from (20) by the numerical coefficient $(\frac{3}{4})^{1/2}$. Note that one would obtain the correct result, (21), if one puts $\alpha = 0$ in (19) directly, and then evaluates the integral. In the exponential regime, another error enters, also in the prefactor. For $\epsilon \ll \alpha^2$, (19) becomes

$$\rho(\epsilon) \approx (\alpha/4\epsilon) \exp(-\pi\alpha/2\sqrt{\epsilon}), \tag{22}$$

while the more exact expression (17) reduces to

$$\rho(\epsilon) = (\pi\alpha^2/8\epsilon^{3/2}) \exp(-\pi\alpha/2\sqrt{\epsilon}). \tag{23}$$

This has the effect of changing the exponent of the coefficient of the exponential in (20) from $t^{-1/6}$ to $t^{1/6}$. This has no significant impact on the time dependence because of the dominance of the exponential in (20).

III. DISCUSSIONS

The percolation model discussed in this paper is formally equivalent to that discussed by Domb *et al.*[9] and by Rice and Bernasconi.[10] The essential difference is the measurable quantities one computes and, therefore, the physical system to which the model relates. For example, the effects we predict may be observable in suitable FLN experiments.

Summarizing our own results, we find three time regimes for $I(t)$. An initial exponential decay [$\sim\exp(-W_0 t)$] for $2W_0 t \lesssim 1$. In the vicinity of $2W_0 t \sim 1$, this crosses over into a diffusion regime [$(W_0 t)^{-1/2}$] for the interval

$$4/\pi^2\alpha^2 \gg 2W_0 t \gg 1. \tag{24}$$

Finally, at long times, we predict the time dependence of Eq. (20).

The diffusion regime can only be observed if p (i.e., α) is sufficiently small so that the time interval for which it is valid becomes reasonably long. To obtain a decade in the requirement (24) results in a subsidiary condition,

$$\alpha \approx p \lesssim 0.2, \tag{25}$$

i.e., an average segment size of at least five connected bonds. For these values, the crossover to

the exponential regime occurs when

$$t_{\text{c.o.}} \sim 10/W_0, \tag{26}$$

appropriate to which the crossover amplitude is reasonably large

$$[\bar{P}(t_{\text{c.o.}}) - \bar{P}(\infty)]/\bar{P}(0) \sim 0.1. \tag{27}$$

To evaluate the feasibility of an experiment, $t_{\text{c.o.}}$ should be compared with the radiative lifetime τ_{rad} and with the spatial trapping time of an excitation in a segment (τ_{trap}), which is finite in any physical system though infinite in our model. One requires

$$\tau_{\text{rad}} W_0,\ \tau_{\text{trap}} W_0 \gtrsim 100, \tag{28}$$

to observe the two regimes. This should be feasible. The continuum approximation we have used assumes large $N(\approx p^{-1})$ and may still be rather poor at the crossover for values of p as high as 0.2. This would tend to make the conditions (28) somewhat more stringent.

For less idealized linear-chain systems, with a general (continuous) distribution $\rho(W)$ of nearest-neighbor transfer rates, the long-time behavior can become much more complex and will be discussed in a future publication.[11] We can expect, however, that the most prominent features of our present result will remain. The long-time exponential decay (20) to an enhanced constant term $\bar{P}(\infty)$ will govern the long-time behavior of systems with a large fraction of very small transfer rates. If no real interruptions are present, the enhanced constant term will, of course, eventually also decay. Depending on the form of $\rho(W)$ for $W \to 0$, this final decay can be much slower than ordinary diffusion ($t^{-1/2}$).[11]

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