One-dimensional quantum transport in the presence of traps

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A study is made of the survival probability $P(t)$ for a quantum particle moving coherently on an ordered one-dimensional chain containing randomly placed irreversible traps in concentration q. We consider two separate models of the trapping process, focusing on the long-time limit of each. In the first model, intended to describe substitutional traps, the trapping impurities act as disruptive absorbing barriers which prevent further motion along the chain. For this model it is shown that $-\ln[P(t)]\sim t^{1/4}$. The second model is intended to describe interstitial trapping impurities which do not disrupt the transport. It is argued for this case that Anderson localization of the quasiparticle wave functions will occur in the otherwise ordered chain as a result of the disorder introduced by the trapping impurities. In addition, it is suggested that the asymptotic decay of $P(t)$ will be dominated by slowly decaying long-wavelength modes associated with asymptotically large segments of the chain which are free of traps. Our analysis predicts that the asymptotic decay will be of the same form as that which obtains in the substitutional model. Numerical results that we have performed support this prediction.

I. INTRODUCTION

A great deal of recent theoretical work has focused on understanding essential features of a basic trapping model,[1–16] wherein a single particle moves in a d-dimensional medium containing randomly placed irreversible traps in fixed concentration. Of particular interest, due to its relationship to experimental observables, has been the asymptotic decay of the survival probability $P(t)$, defined as the configuration-averaged probability for a particle placed in the medium at $t=0$ to survive until time t without being trapped. Much is known regarding this quantity in various classical limits.[1–13] For example, when transport is diffusive it has been rigorously shown[3] that at very long times

$$P(t)\sim \exp(-At^{d/(2+d)}) ,$$

where A depends on the diffusion constant and the trap concentration. This stretched exponential form has been shown to arise from the anomalously slow decay associated with large rarely occurring regions of the medium which are free of traps.[1–9] Such regions lead to asymptotic tails (sometimes referred to as Lifshitz tails[1,9,10]) in the distribution of decay times for the eigenmodes of the random system. However, numerical simulations[10] and exact enumeration techniques[11] performed over many orders of magnitude in $P(t)$ have shown that this predicted asymptotic behavior is achieved in experimentally accessible times only in one dimension. Thus, while the one-dimensional (1D) result

$$P(t)\sim \exp(-At^{1/3})$$

has apparently been inferred from fluorescence[17] and conductivity measurements,[18] it remains generally true that theoretical treatments which are valid over much shorter times[14–16]—although unable to reproduce the exact asymptotic behavior—are often more experimentally useful. Indeed, the development of a unified theoretical approach which correctly reproduces both limits and which would allow a study of the crossover behavior remains one of the central outstanding problems in this area.

However, while a great deal is known about the decay when particle motion is diffusive, there has been some concern that at low temperatures quantum effects may become important and that deviations from the diffusive result may occur.[16,19–24] Consider, for example, that at very low temperatures the mean free path for phonon scattering can exceed the average distance between trapping impurities. In this limit the standard trapping model (which assumes the motion to be diffusive over length scales much smaller than this) no longer applies. To understand trapping experiments at very low temperatures, therefore, one is led to consider the more difficult problem of a particle undergoing a strictly quantum-mechanical evolution in the presence of random impurities which can dephase, scatter, localize, as well as irreversibly trap the wavelike motion. In one of the earliest analyses to consider this coherent limit in any analytical detail, Pearlstein and co-workers[19] obtained a number of exact results for the trapping rate in one-dimensional chains containing a small number of traps (typically one or two). Subsequent work by Kenkre[20] and by Huber[21] considered the trapping of coherent Bloch-type excitations in the presence of a finite concentration of traps. In that work a variety of approaches (e.g., the relaxation-time approximation, Born approximation, average-t-matrix approximation, coherent-potential approximation) were investigated as a means of treating the difficulties associated with the multitrap problem. Later, the use of generalized master equations by Kenkre and co-workers[16] led to an approach to the coherent trapping problem similar to those that had been used for the case of

diffusive motion. Unfortunately, the nature of these earlier approaches restricted their domain of utility to relatively short times; rendering them insensitive to the asymptotic behavior of the survival probability and, in particular, to any Lifshitz-tail effects which might arise in the coherent case.

Such effects were recently investigated by the present author[22] for a quantum particle moving at zero temperature on a one-dimensional chain containing a finite fraction $q=1-p$ of randomly placed substitutional traps. As anticipated on the basis of the diffusion problem, the asymptotic decay of $P(t)$ in the coherent case is also dominated by large, rarely occuring trap-free regions of the solid. The purpose of the present paper is to provide a more complete description of our earlier work and to extend those results to more general (e.g., interstitial) trapping models. Specifically, for the substitutional model considered earlier we develop equations of motion for the reduced single-particle density matrix and solve them to recover our earlier exact result; namely, that at asymptotically long times the survival probability has a stretched exponential decay of the form

$$P(t)\sim \exp(-At^{1/4}) .$$

The decay is therefore asymptotically *slower* than that associated with diffusion, reinforcing the observation made earlier by Pearlstein *et al.*[19] that the trapping rate can actually be smaller for coherent particles than for diffusive ones. We also develop equations of motion to describe interstitial traps which do not disrupt motion along the chain, and give an approximate analysis which suggests that due to Anderson localization by the trapping impurities themselves the asymptotic decay should be of the same form as in the substitutional model, although with a different functional dependence of the constant in the exponent on the parameters of the system. We support this prediction by presenting the results of numerical diagonalizations of large but finite one-dimensional chains, focusing attention on the tails of the distribution of decay times for the eigenstates of the chain in the presence of random trapping impurities.

II. BASIC MODELS

We begin with the basic models, which are intended to be simple quantum-mechanical versions of those developed to study diffusion-limited trapping. The Hamiltonian

$$H=-J\sum_n |n\rangle\langle n+1|+|n+1\rangle\langle n| \tag{1}$$

describes transport in a 1D tight-binding solid in the absence of trapping centers, with $|n\rangle$ representing a quasiparticle state centered at the nth lattice site, and J representing the transfer matrix element which connects nearest-neighbor sites along the chain. When trap molecules are introduced they bring with them associated states which have energies that are lower than those in the band by an amount Δ assumed to be much greater than $2J$. For *substitutional* trapping impurities these states are associated with sites located in the chain itself

FIG. 1. One-dimensional solid with nearest-neighbor transfer matrix element J and randomly placed substitutional traps of depth Δ. After elimination of bath variables at zero temperature, the chain is divided into isolated segments with a decay amplitude γ for each of the host sites neighboring a trap site.

(Fig. 1). Particles at sites next to a substitutional trap can then "fall into" the trap by emitting a phonon of the appropriate energy. For *interstitial* traps, on the other hand, the trapped states do not replace specific sites in the chain. Nonetheless, there will be host states along the chain which are closest to a given trapping impurity and we expect that trapping will occur by a similar process primarily from these sites (Fig. 2). In either case, once trapping has occurred we expect that at zero temperature the reverse process (detrapping) will not occur due to the lack of thermal phonons around to assist the transition. Thus, coupling to the phonons is absolutely essential to account for the irreversibility of the trapping process. In this paper we will not go into detail regarding the exact form of the coupling to the phonons responsible for trapping. Rather, our aim is to present simplified equations of motion which contain the essential features of quantum transport in the presence of these kinds of irreversible trapping processes. We do note, however, that there are several well-established ways to model this coupling, e.g., by making the matrix elements connecting the impurity and its neighboring host sites proportional to an appropriate bath operator.[19,24,25]

Thus, in the interstitial model, if we denote by n_i that site along the chain which is closest to the ith interstitial trap then we can add to the Hamiltonian a term of the form $-\Delta|i\rangle\langle i|$ to describe the trapped state itself, and a term

$$V(|i\rangle\langle n_i|+|n_i\rangle\langle i|)$$

to describe transitions between the trapped state and the host site in the chain to which it is coupled. To provide

FIG. 2. One-dimensional solid with randomly placed interstitial traps of depth Δ. After elimination of bath variables at zero temperature, a decay amplitude γ is associated with each host site along the chain which is located next to a trap. Motion along the chain is not disrupted as it is in the substitutional model.

for irreversibility of the transition we choose V to be a bath operator, e.g., of the form $V=\sum_b g_q(b_q^\dagger+b_{-q})$, where b_q and $b_q^\dagger$ are destruction and creation operators for the qth vibrational mode of the phonon bath and g_q is the coupling constant of the quasiparticle system to that mode. At zero temperature, coupling of this form will allow a particle to make transitions into the trap by emitting a phonon of energy $E\simeq\Delta$. With no thermal phonons around for the particle to absorb the required energy, however, it will be unable to move back onto the chain. Nonetheless, because interstitial impurities do not disrupt the chain (i.e., the bare matrix element J coupling the host site n_i to its neighbors is relatively unaffected by the trap molecules in the interstice), it is possible for a particle to pass through site n_i without being trapped. The probability of doing so will evidently depend upon the relative strengths of J and V.

On the other hand, if n_i is a site in the chain occupied by a substitutional trap, then we should modify the original Hamiltonian by including a term of the form $-\Delta|n_i\rangle\langle n_i|$ to lower the energy at this site, and describe transitions between site n_i and its neighbors by a term of a similar form, viz.,

$$V(|n_i\rangle\langle n_i\pm1|+|n_i\pm1\rangle\langle n_i|)$$

with V as before. Thus, a particle moving along some segment of the chain located between two substitutional trapping impurities can become trapped by emitting a phonon while at one of the sites located next to the traps. Once trapped it will, as in the interstitial model, be unable to make transitions out of the trapped site at zero temperature. Since a particle cannot leave a given segment without passing through a trap site, and since it cannot get out of the trap site once it has been trapped, motion along the chain is disrupted. As in the classical problem,[6,12] therefore, substitutional traps effectively divide the chain into isolated clusters of random length.

III. SUBSTITUTIONAL TRAPS

We now consider, in more detail, the dynamical behavior of particles governed by the simpler substitutional trapping model previously described. In as much as we are only interested in the dynamics of the transport particle, and not that of the bath with which it is interacting, we can describe the evolution of a single particle on the chain by a reduced density matrix ρ, obtained by tracing the full system density matrix over the phonon variables.[24,25] For substitutional traps at zero temperature, we can expect that the primary effect of such a reduction is to give a lifetime τ (or a decay amplitude $\gamma=\frac{1}{2}\tau^{-1}$) to the two end sites in each cluster that are coupled to a trap. (There will also be energy shifts which develop, but they do not substantially affect the asymptotic dynamics and will therefore be ignored.) Also, because a particle will never visit any other cluster than the one in which it was initially created, we can restrict our attention to a single cluster, and then find the total density matrix by statistically averaging over the different clusters in which a particle can be created (see Fig. 1). Thus, our first task is to describe the dynamical behavior of a particle created in a given cluster. As in the earlier work of Pearlstein *et al.*[19] we argue that the following Liouville–von Neumann equation of motion for the reduced density matrix provides a reasonable description of the zero-temperature dynamics of a particle initially located in a segment of N host sites (which we label by $m=1,2,\ldots,N$) bounded at $m=0$ and $m=N+1$ by substitutional traps

$$d\rho/dt=-i[H_N,\rho]-\mathcal{K}\rho\ , \tag{2}$$

where the Hamiltonian H_N describes transport within the cluster, i.e.,

$$H_N=-J\sum_{m=1}^{N-1}|m\rangle\langle m+1|+|m+1\rangle\langle m|\ , \tag{3}$$

while the relaxation operator, defined through its action on ρ

$$[\mathcal{K}\rho]_{m,n}=-\gamma\rho_{m,n}(\delta_{m,1}+\delta_{n,1}+\delta_{m,N}+\delta_{n,N}) \tag{4}$$

describes the decay of amplitude from sites $m=1$ and $m=N$ due to the traps at $m=0$ and $m=N+1$. These equations describe a particle which moves coherently in the region between the two traps, while undergoing scattering, dephasing, and absorption at the end sites of the cluster due to the traps to which they are coupled. To proceed, we observe that Eq. (2) can be formally written

$$d\rho/dt=-i\mathcal{L}_N\rho=-i[\mathcal{H}_N,\rho]\ , \tag{5}$$

where for mathematical convenience we have introduced an effective (but non-Hermitian) "Hamiltonian" $\mathcal{H}_N$, which is identical to (3) except that it includes an "imaginary site energy" of magnitude γ at each end of the segment, i.e.,

$$\mathcal{H}_N=-i\gamma(|1\rangle\langle1|+|N\rangle\langle N|)-J\sum_{n=1}^{N-1}|n\rangle\langle n+1|+|n+1\rangle\langle n|\ . \tag{6}$$

The capture strength γ determines the rate of decay for particles located at the end sites. In the simple model of phonon coupling discussed earlier, γ will depend on the square of the coupling constant and the density of phonon states at frequency Δ.

We are interested in obtaining the probability for a particle to remain in the cluster in which it was initially created. From Eq. (2) it is a straightforward exercise to derive the formal relation[19,22]

$$dP_N(t)/dt\equiv\sum_{m=1}^{N}d\rho_{mm}/dt=-2\gamma(\rho_{11}+\rho_{NN}) \tag{7}$$

for the decay in a segment of length N. Equation (7) shows that the decay rate is simply related to the probability that the particle is actually located in one of the states from which it can decay to the trap. In addition, we note that because of the form of Eq. (5) it is possible to determine the complete dynamical behavior of a particle in the cluster by finding the eigenvectors and complex eigenvalues of the effective Hamiltonian $\mathcal{H}_N$. For example, if we let $|k\rangle$ represent the kth eigenvector of $\mathcal{H}_N$ (corre-

sponding to eigenvalue $E_k=\epsilon_k-i\Gamma_k$) then the survival probability can be written in terms of the matrix elements of ρ in this basis as

$$P_N(t)=\sum_k \rho_{kk}(0)\exp(-2\Gamma_k t) . \tag{8}$$

The quantity Γ_k represents the rate at which the kth eigenvector decays to the trap state due to the coupling at each end of the cluster. Moreover, the *asymptotic* decay of $P_N(t)$ will be determined by those eigenvectors with eigenvalues having the smallest imaginary component. As we will see, these turn out to be the states at the edges of the band, so the argument holds in the presence of other processes (that we have neglected for clarity) which would cause the particle to equilibrate to the lowest-energy states. To demonstrate this we need to obtain the eigenstates $|k\rangle$ of $\mathcal{H}_N$. Based on what occurs in ordered lattices we expect these to be "complex" standing waves of the form

$$|k\rangle=\sum_n [A_k\cos(kn)+B_k\sin(kn)]|n\rangle , \tag{9}$$

for appropriate constants A_k, B_k, and complex wave vector k. By applying $\mathcal{H}_N$ to the eigenstate $|k\rangle$ and then multiplying on the left by a state $\langle n|$ corresponding to one of the interior sites we find that

$$\langle n|\mathcal{H}_N|k\rangle=-2J\langle n|k\rangle\cos(k), \quad N>n>1 , \tag{10}$$

which allows us to identify the eigenvalue associated with eigenvector $|k\rangle$ as $E_k=-2J\cos(k)$. We now enforce this same eigenvalue condition on the end sites. Introducing the dimensionless trapping strength $\xi=\gamma/J$, we obtain, after some manipulation, two equations: from site $|1\rangle$ we obtain one which fixes the coefficients

$$A_k/B_k=i\xi\sin(k)/[1-i\xi\cos(k)] , \tag{11}$$

while from site $|N\rangle$ we obtain an equation which reduces under (11) to

$$\tan(kN)=(1+\xi^2)\sin(k)/[2i\xi-(1-\xi^2)\cos(k)] . \tag{12}$$

Equation (12) can be solved to find the allowed wave vectors. Anticipating that the asymptotic decay will be dominated by increasingly larger cluster lengths it suffices to obtain solutions which are asymptotic in N. It is readily verified by substitution into (12) that the mth allowed wave vector from the bottom of the band for $N\gg m$, is given to $O(N^{-2})$ by

$$k_m=(m\pi/N)(1-f_1/N)-i\pi m f_2/N^2\equiv q_m-i\lambda_m , \tag{13}$$

where $f_1=(1-\xi^2)/(1+\xi^2)$ and $f_2=2\xi/(1+\xi^2)$. We should add that while this result is asymptotic in N it is valid for all ξ. The real and imaginary parts of the eigenvalues for these wave vectors are then readily obtained

$$\epsilon_m=-\mathrm{Re}[2J\cos(k_m)]$$
$$=-2J\cos(q_m)\cosh(\lambda_m)\sim-2J\cos(m\pi/N) , \tag{14a}$$

and

$$\Gamma_m=\mathrm{Im}[2J\cos(k_m)]$$
$$=2J\sin(q_m)\sinh(\lambda_m)\sim 4\gamma\pi^2m^2/[N^3(1+\xi^2)] . \tag{14b}$$

Thus, the minimum decay rate for each cluster occurs for those states nearest the bottom of the band. [Note from (11) that $k=0$ is not a solution since it has zero amplitude at each site.] The important point to observe[19,22] is that the decay rate for these states scales as N^{-3}. This fact (which ultimately determines the asymptotic decay) can also be obtained from the following physical argument: As we have shown in Eq. (7), the decay rate for a given mode depends upon the probability for a particle in that mode to be at one of the end sites (i.e., to be at one of the sites from which it can actually decay), therefore, those states with the smallest amplitudes at the end sites decay most slowly. But the boundary conditions for this problem require that the wave function for untrapped particles *vanish* at the trap sites. For modes which are slowly varying in space, i.e., for small wave vectors $k_m\sim m\pi/N$ in which a small number of half wavelengths $\lambda=2\pi/k$ fit into the segment, this condition forces the wave function in the vicinity of the traps to be very small. Thus, C_1 and C_N, the normalized amplitudes to be at the end sites will go (approximately) as

$$N^{-1/2}\sin(k_m)\sim m\pi N^{-3/2} ,$$

and the probabilities ρ_{11} and ρ_{NN} as $m^2\pi^2N^{-3}$. Hence, for these slowly varying modes the decay rate will have the form $\Gamma\sim 2\gamma m^2\pi^2N^{-3}$. The additional factor of $2/[1+\xi^2]$ appearing in (14b) comes from the fact that the amplitude is decreased even more at the end sites due to the change in dispersion associated with the imaginary site energy. Thus, for very large values of $\xi=\gamma/J$ it is difficult for the particle to move onto the end sites due to the large (imaginary) difference in site energies between those sites and the rest of the sites in the cluster.

Provided a finite fraction of the amplitude ends up near the band edge, Eq. (14) shows that the asymptotic decay of the survival probability for particles created in a cluster of size N will take the form

$$P_N(t)\sim A_N\exp[-8\pi^2\gamma t/N^3(1+\xi^2)] . \tag{15}$$

If the excitation is created at the bottom of the band, or if there are equilibration processes which take the particle there on time scales short compared to trapping, then A_N will equal one at long times. Otherwise, A_N will equal the probability that the particle was in one of the states at the band edge at $t=0$. (If the particle is initially localized on one site, or if it is completely delocalized within the cluster, then A_N will be of order $1/N$, since it requires a linear combination of all k states in a cluster to produce a site state.) In either case, we can (as in the diffusion problem[6,12]) average over the cluster distribution to obtain

$$P(t)\sim\sum_N f(N)p^N\exp[-8\pi^2\gamma t/N^3(1+\xi^2)] , \tag{16}$$

where $f(N)=q^2NA_N/p$ depends algebraically on the

cluster size and so is slowly varying in comparison to the exponential factors in the summand. For $p<1$, the factor p^N decays sharply with increasing N; it will therefore compete with the sharply rising term

$$\exp\{-8\pi^2\gamma t/[N^3(1+\xi^2)]\},$$

to make the summand strongly peaked about some maximal cluster size $N_m(t)$. At large times, $N_m(t)\gg 1$, and the value of the sum in (16) will approach

$$P(t)\sim\int_0^\infty f(N)\exp-(\alpha N+\beta t/N^3)dN\ , \tag{17a}$$

which after changing variables to $y=\mathrm{N}t^{-1/4}$ becomes

$$P(t)\sim\int_0^\infty \tau f(y\tau)\exp[-\tau(\alpha y+\beta y^{-3})]dy\ , \tag{17b}$$

where $\alpha=\ln(1/p)\simeq q$ for $q\ll 1$, $\beta=8\gamma\pi^2/[(1+\xi^2)]$, and $\tau=t^{1/4}$. The asymptotic properties of Eq. (17b) are readily determined.[26] Expanding the exponent about its maximum value, $y_m(t)=(3\beta/\alpha)^{1/4}$, and performing a Gaussian integration we obtain

$$P(t)\sim C(q,t)\exp(-At^{1/4})\ , \tag{18}$$

where the constant in the exponent is $A=4(\beta\alpha^3/27)^{1/4}$, and the prefactor

$$C(q,t)=(\pi/2)^{1/2}(3\beta t/\alpha^5)^{1/8}f(y_m t^{1/4})\ ,$$

is an algebraic function of time which may depend on the initial conditions.

The 1D decay is therefore slower than that associated with a diffusing particle,[6] for which

$$P(t)\sim\exp(-At^{1/3})\ ,$$

but faster than that predicted for classical particles interacting via hard core potentials, where an $\exp(-At^{1/5})$ decay law obtains.[13] In the latter case the anomalously slow decay can be traced to slower-than-diffusive 1D motion of the individual particles in the regions between traps; an effect which arises from the interactions. In the present circumstance, motion between the traps is faster than diffusive and the slowness of the decay arises from wavelike reflection at trap sites due to the sudden change in dispersion which occurs at those points. As in the classical problem, however, the decay law continues to be asymptotically governed by large but rarely occurring trap-free regions.

It is often assumed that trapping becomes more efficient as quasiparticle motion becomes more coherent; this expectation is based upon the idea that it is easier for a particle to get to a trap if it is not being continually scattered by phonons. It is certainly true, for example, that $P(t)$ decays more rapidly for a diffusing particle as its diffusion constant increases. Indeed, heuristic arguments can be found in the literature which suggest that in the coherent limit, due to very fast motion and relatively slow trapping at the ends of each segment, the population should quickly become uniform in the region between the traps. Trapping from a segment would then occur with a rate proportional to $1/N$, giving an $\exp(-At^{1/2})$ law, faster than that associated with diffusion. However, as observed earlier,[19,22] the zero-temperature decay is ultimately slower than the diffusion result. Clearly, the naive argument breaks down because it ignores the coherence of the wave function, i.e., the phase relationships associated with the incident and reflected parts of a wave which produce the long-lived standing waves. Analysis reveals that a localized absorbing site is more efficient at scattering a particle than it is at capturing it, no matter how large the capture strength γ becomes. This can be seen most easily by decomposing the standing wave solutions into traveling waves: From (11) one can easily show that a traveling wave of unit magnitude incident upon an absorbing site is reflected with a reflection probability

$$P_R=[1-2\xi\sin(k)+\xi^2]/[1+2\xi\sin(k)+\xi^2] \tag{19}$$

and is absorbed (i.e., decays to the trap) with probability

$$P_A=1-P_R\sim 4k/(\xi+\xi^{-1}),\quad (k\ll 1)\ . \tag{20}$$

Hence, for small wave vectors $[k\sim O(\pi/N)]$ the relative absorption probability actually decreases with increasing cluster size as $1/N$. It is also interesting to note that this form for the reflection and absorption probability is valid for arbitrary γ, so that for fixed N the absorption probability has a maximum when $\gamma=J$. For values of γ larger than this the change in dispersion at the end sites due to the coupling reduces the ability of the particle to move onto those sites, thereby decreasing the actual trapping efficiency. This is in marked contrast to the classical problem where it is always possible to arbitrarily increase the strength of the localized capture process so as to make the trap "perfectly absorbing." Whether it is possible to identify a coupling mechanism between the phonons and a *strictly localized* impurity state which is more efficient at capture than it is at scattering remains an open question.

IV. INTERSTITIAL TRAPS

We now turn to the interstitial model described in Sec. II in which the traps do not disrupt motion along the chain. The problem is intrinsically more difficult than that addressed in the last section, due to the fact that a particle located on a segment of the chain between two interstitial traps now has the possibility of passing by the traps without getting trapped. The problem does not, therefore, neatly divide up into isolated clusters as it did in the substitutional model. The analysis which we present below, therefore, is necessarily more qualitative than the one presented in Sec. III. Nonetheless, we can expect the results of the reduction over the phonon variables to lead to similar effects regarding the states which are coupled to the interstitial impurities. In particular, if we assume a short-range interaction to be responsible for trapping, then we can expect those sites in the chain which are located next to the interstitial impurities to develop a decay amplitude γ as before (see Fig. 2). Thus the reduced density matrix for the interstitial model can be taken to obey an equation similar to (2) except that it will now apply to the whole chain rather than to one isolated cluster. We write

$$d\rho/dt=-i[H,\rho]-\mathcal{K}\rho\ , \tag{21}$$

where now the Hamiltonian H describes uninterrupted motion along the chain and is therefore given by Eq. (1) without modification, while the relaxation operator now includes a sum over all host sites in the chain which are located next to the traps

$$[\mathcal{K}\rho]_{m,n} = -\gamma \sum_i \rho_{m,n}(\delta_{m,n_i} + \delta_{n,n_i}) \ . \tag{22}$$

In Eq. (22), n_i is the host site closest to the ith interstitial trap and the sum runs over all such sites. As in Sec. III we can rewrite Eq. (21) in a form involving an effective non-Hermitian Hamiltonian $\mathcal{H}$, i.e.,

$$d\rho/dt = -i\mathcal{L}\rho = -i[\mathcal{H},\rho] \ , \tag{23}$$

where

$$\mathcal{H} = H - i\gamma \sum_i |n_i\rangle\langle n_i| \ . \tag{24}$$

The imaginary site energies in the summation in Eq. (24) again lead to a decay of amplitude from those sites in the chain located next to the traps. The probability for a particle in the chain to survive until time t without being trapped can then be written in a form similar to Eq. (7), i.e.,

$$dP(t)/dt \equiv \sum_m d\rho_{mm}/dt = -2\gamma \sum_i \rho_{n_i n_i} \ . \tag{25}$$

Once again we are faced with the problem of finding the eigenstates and eigenvalues of an effective Hamiltonian; however, the eigenstates are now considerably more complicated than in the substitutional model. We begin by observing that the effective Hamiltonian $\mathcal{H}$ whose states we are attempting to determine is almost identical in form to that associated with a one-dimensional tight-binding binary alloy consisting of two types of sites with different site energies; the important difference, of course, is that in the present model the site energy associated with one species is strictly imaginary. Even so, based upon the large body of work that has been done on disordered systems (and on disordered one-dimensional systems in particular), it is natural to expect that the eigenstates of $\mathcal{H}$ will be localized as a result of the disorder associated with the random positions of traps along the chain. If we accept this, then the problem reduces to one of characterizing the localized states which have the smallest imaginary component of the "energy," and then to determining the distribution of eigenvalues associated with such states. It is clear from Eq. (25) that the required states are those which have the smallest fraction of their amplitude on the decaying sites n_i. Thus, we are naturally led to consider those states which are delocalized over large but rarely occuring trap-free regions of linear dimension L, surrounded by regions containing traps in a density more closely reflecting the average trap concentration q. Note that the trap-free region is locally ordered since all sites within it have the same site energy, while the surrounding regions are disordered due to the presence of both kinds of sites (decaying and nondecaying). This leads us to expect that wave functions which are delocalized inside the trap-free region will fall off exponentially as they pass into the disordered region, with a localization length ζ that will depend on the energy. In the limit in which $L \gg \zeta$, we obtain a picture of states which are delocalized over a large region of size L, vanishing with small (compared to L) tails of length ζ into the regions where trapping can occur.

We now observe that this picture is not too disimilar to that associated with the wavefunctions of the substitutional model, where L is identified with the length of the region between the substitutional traps, and where the length ζ associated with the region where trapping can occur is, in the substitutional model, effectively equal to one (all distances are measured in units for which the lattice spacing is equal to unity). The main difference between these two pictures is that the length ζ is given *a priori* in the substitutional model, while in the interstitial model it is determined by the change of effective dispersion between the ordered and disordered regions. Our experience with the substitutional model, therefore, leads us to expect that the most slowly decaying states for the interstitial model will be long-wavelength states which are slowly varying in space inside the trap-free region, and which fall off over comparatively short distances outside the region.

A. Approximate analytical treatment

The physical picture expressed above has led us to develop a simple phenomenological model for quantitatively analyzing the important features of those states important to the asymptotic decay, i.e., the slowly decaying states centered in large trap-free segments. In our model, depicted schematically in Fig. 3, that part of the solid which surrounds a trap-free segment of length L is treated as a uniform region having a constant site potential equal to its average value $\langle \mathcal{H}_{nn} \rangle = -iq\gamma$. This is equivalent to treating the surrounding part of the crystal in terms of the so-called virtual-crystal approximation (VCA). We should emphasize that this would probably *not* be a good approximation if we were interested in states away from the band edge, but since we are interested in states of asymptotically long wavelength ($\lambda/2 \sim L$, with $L \to \infty$) it should be more than adequate for qualitatively determining the asymptotic behavior. In addition, for large L and long wavelengths (corresponding to the states of interest), the lattice structure becomes unimportant and we can treat the system as being effectively continuous. Thus, we write an effective Hamiltonian

$$H = Jk^2 + V(x) = -Jd^2/dx^2 + V(x) \ , \tag{26}$$

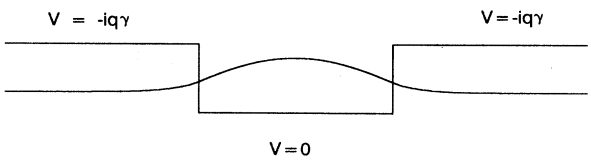

FIG. 3. Schematic "square-well" model used to analyze the slowly decaying states in a trap-free region of length L surrounded by region of more typical trap density. Curve indicates state of interest having smallest decay amplitude.

where the "potential" function takes the form

$$V(x)=-iq\gamma\Theta(|x|-L/2)\ , \tag{27}$$

in which $\Theta(x)$ is the Heaviside step function. For convenience we have centered the trap-free region at $x=0$ and shifted the Hamiltonian of Eq. (1) by a constant amount equal to $2J$. Thus, the problem closely resembles one treated in most introductory textbooks on quantum mechanics,[27] involving a particle of effective mass $m=(2J)^{-1}$ moving in a square-well potential (which in this problem is of imaginary depth). Let $\mathcal{E}$ denote the eigenvalue of the lowest mode of Eq. (26), and define the dimensionless quantity $E=\mathcal{E}/J$. By proceeding in analogy to standard treatments[27] we find that the eigenfunction of Eq. (26) corresponding to this lowest mode will be an even function having the form $\psi(x)=A\cos(kx)$ for $|x|<L/2$, and the form $\psi(x)=B\exp[i\kappa|x|]$ for $|x|>L/2$. In these expressions $k^2=E$ and $\kappa^2=E+iq\xi$. By the usual procedure of requiring continuity of ψ and its derivative at $x=\pm L/2$ we obtain two equations, the ratio of which is equivalent to

$$k^2\sec^2(kL/2)+iq\xi=0\ . \tag{28}$$

Equation (28) allows us to determine the complex wave vector k. We now search for solutions to (28) of the form $k^2=\epsilon+\alpha$, where $\epsilon\equiv\pi^2/L^2$ is assumed to be much less than 1, and where the magnitude of α is assumed to be much less than ϵ. This corresponds to choosing a wave vector k such that the interior solution vanishes a short distance (compared to L) outside the boundary. A straightforward calculation then yields

$$\alpha\sim-\frac{(1+i)4\pi^2}{(2q\xi)^{1/2}L^3}\quad(L\gg1)\ , \tag{29}$$

so that the eigenfunction corresponding to this solution decays to the traps with an amplitude

$$\Gamma_L=\mathrm{Im}(\mathcal{E})\sim\frac{4J\pi^2}{(2q\xi)^{1/2}L^3}\ . \tag{30}$$

The state associated with this decay amplitude will dominate the asymptotic decay for particles initially localized within this trap-free region. Note that the decay amplitude depends upon the length of the trap-free region to the inverse third power, as in the substitutional model. If we now average the asymptotic decay stemming from Eq. (30) over the size L of the trap-free region, we obtain an expression similar to Eq. (16) with L replacing N and with $\exp(-2\Gamma_L t)$ replacing the exponential in that equation. The asymptotic analysis for $P(t)$ then follows that of the substitutional model without change and leads to an asymptotic decay of the same form, namely,

$$P(t)\sim C(q,t)\exp(-At^{1/4})\ , \tag{31}$$

where, as before, $C(q,t)$ is algebraic in time and, in general, depends upon the initial conditions, while the constant in the exponent can be estimated using Eq. (30) as $A=4(\delta\alpha^3/27)^{1/4}$, with $\alpha=\ln(1/p)$ and $\delta=8J\pi^2(2q\xi)^{-1/2}$.

B. Comparison with numerical results

To evaluate the accuracy of the simple theory presented in the last section we have performed a large number of numerical diagonalizations of the Hamiltonian $\mathcal{H}$ for large but finite one-dimensional chains with random imaginary site energies. If, as we have argued, the states of the random chain are localized with a localization length which is small compared to the size of the chain, then the distribution of eigenvalues for the finite system should closely resemble the distribution of eigenvalues for the infinite one-dimensional chain. To test the theory, therefore, we can compare the distribution of decay amplitudes, $P(\Gamma)d\Gamma$, obtained from numerical diagonalizations, with the distribution that follows from the analysis presented above. Our basic assertion is that the asymptotic decay of the survival probability is determined by slowly decaying states centered in rare trap-free regions. From this it follows that the distribution $P(\Gamma)d\Gamma$ will be governed, for small Γ, by the functional dependence (on L) of Γ_L and by the statistical probability $P(L)dL$ for finding a trap-free region of length L. That is, we can invert Eq. (30) to find the size of the trap-free region corresponding to a given decay amplitude,

$$L(\Gamma)=[4J\pi/(2q\xi)^{1/2}\Gamma]^{1/3}\ , \tag{32}$$

and then use this along with the probability of finding a trap-free region of length L

$$P(L)\sim\exp(-\alpha L)\ , \tag{33}$$

to obtain the probability density for Γ. This leads to the asymptotic prediction for small Γ that $P(\Gamma)$ will be proportional to the function

$$\exp[-b(J/\Gamma)^{1/3}]\ ,$$

with

$$b=\alpha(4\pi^2)^{1/3}/(2q\xi)^{1/6}\ .$$

It is convenient to express this result in terms of a dimensionless decay time $s\equiv(J/\Gamma)^{1/3}$. The probability density for finding a given value of s should (up to algebraic prefactors) then be exponential

$$P(s)\sim\exp(-bs)\quad(s\gg1) \tag{34}$$

with the exponent given in terms of the parameters of the system through the expression

$$b=-\ln(1-q)(4\pi^2)^{1/3}/(2q\xi)^{1/6}\ . \tag{35}$$

In Figs. 4 and 5 we show the results obtained from the numerical diagonalization of the effective Hamiltonian for a large number of random chains containing $M=50$ and 100 sites, for two different trap concentrations, $q=0.1$ and 0.2. In all these figures we have taken the dimensionless trapping parameter $\xi=\gamma/J=1$. For each chain, a random configuration of traps was chosen. This was done by assigning to each site a random number uniformly drawn from the interval [0,1] and occupying the site with a trap whenever the associated random number was less than the trap concentration q. The matrix corresponding to the effective Hamiltonian for the given trap

configuration was then constructed and numerically diagonalized. From the complex eigenvalues E_i ($i=1,\ldots,M$) obtained in the diagonalization, the imaginary parts Γ_i were extracted and used to calculate the dimensionless quantities $s_i=(J/\Gamma_i)^{1/3}$. These values were then "binned" to find the number $n(s)$ of values of s_i which fall within the range s to $s+1$. To obtain adequate statistics, this was repeated for 1600 different random matrices for $q=0.2$, and 2400 different random matrices for $q=0.1$. For each concentration the results were then averaged to obtain $N(s)\equiv\langle n(s)\rangle$, the average number of s values falling in the given intervals, and $\sigma_m(s)$, the standard deviation of the mean for each average calculated over the total number of runs. If our arguments are correct, then we expect $N(s)$ to be proportional to $P(s)$, as given by Eq. (34), at least for values of s corresponding to trap-free regions approaching the length of the chain. Thus, a logarithmic plot of $N(s)$ versus s should follow a straight line with a slope given by Eq. (35) for sufficiently large s.

The results for trap concentration $q=0.1$ are presented in Fig. 4(a) for chains of length $M=50$ and in Fig. 4(b) for chains of length $M=100$. The upper and lower histogram in each figure corresponds to $N(s)\pm\sigma_m(s)$. The straight lines correspond to fits to the data of the form $N(s)=N_i\exp(-bs)$, as suggested by Eq. (34) with the value of the constant $b=0.47$ calculated from our theoretical expression, Eq. (35); only the value of the prefactor N_f was varied to adjust the vertical position of the line on the logarithmic plot. In Fig. 4(a) the value $N_f=14$, and in Fig. 4(b) $N_f=30$. Thus, the histogram for $M=100$ is approximately twice the magnitude as that for $M=50$, because there are twice as many eigenvalues in a 100-site chain as there are in a 50-site chain. In spite of the statistical fluctuation, the histograms do appear to have the expected functional form, with the results for the exponent being insensitive to the chain length. This is, of course, as we had hoped based upon the localization argument. Indeed, given the nature of the arguments and approximations leading to Eqs. (34) and (35) the agreement with the numerical results, particularly regarding the slope of the line, is surprisingly good.

In Figs. 5(a) and 5(b) we present similar results calculated with a trap concentration $q=0.2$. At this higher concentration it was found that a smaller number of diagonalizations, 1600, were sufficient to give acceptable statistics. As before, the straight line corresponds to a fit to the numerical data of the form $N(s)=N_f\exp(-bs)$, with the slope $b=0.88$ calculated from Eq. (35). We find $N_f=58$ for $M=50$, and $N_f=116$ for $M=100$. Thus, again the number of eigenvalues in a given bin scales with the number of states in the chain. The agreement between the numerical results and the theoretical analysis of Sec. IV A appears to be even better at this higher trap

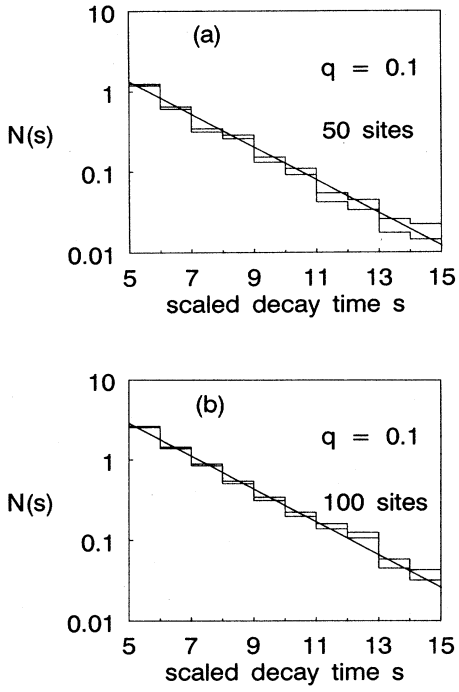

FIG. 4. Average distribution of (dimensionless) decay times $s=(J/\Gamma)^{1/3}$ for one-dimensional chains containing randomly placed interstitial traps of strength $\gamma/J=1$, in concentration $q=0.1$. Histograms are averages over 2400 matrices of $N(s)\pm\sigma_m$, and the straight line is the theoretical prediction. (See discussion in the text.)

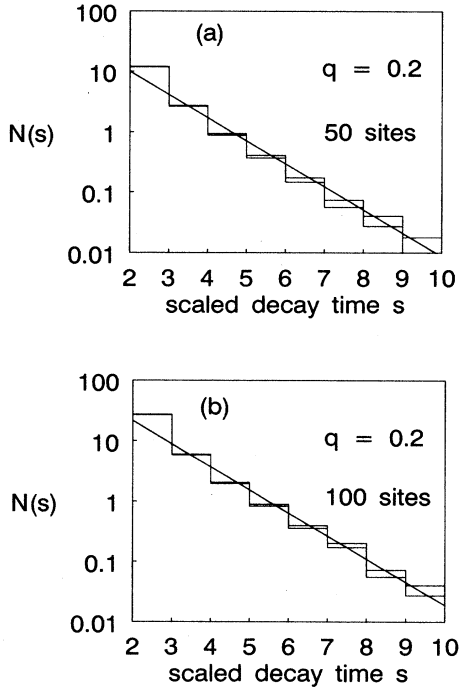

FIG. 5. Average distribution of (dimensionless) decay times $s=(J/\Gamma)^{1/3}$ for one-dimensional chains containing randomly placed interstitial traps of strength $\gamma/J=1$, in concentration $q=0.2$. Histograms are averages over 1600 matrices of $N(s)\pm\sigma_m$, and the straight line is the theoretical prediction. (See discussion in the text.)

concentration.

The numerical work, therefore, tends to support the analysis given in Sec. IV A and, in particular, lends further credibility to the asymptotic form for the survival probability predicted by Eqs. (34) and (35). Whether the agreement we have obtained between the theory and numerical work continues for significantly lower concentrations and for significantly different values of ξ remains an open question. As the product $q\xi$ gets smaller the chain length necessary for the numerical work increases and this puts greater demands on computer memory and time. We are currently working on extending the numerical results to smaller concentrations so that the theory can be tested for a wider range of parameters.

V. DISCUSSION AND SUMMARY

Our analysis indicates that in one-dimensional systems the zero-temperature asymptotic decay of excitations due to irreversible trapping has a characteristic stretched-exponential behavior

$$P(t)\sim \exp(-At^{1/4}) ,$$

with details on the form of the exponential constant depending upon the nature of the trap (i.e., interstitial or substitutional). The results we have obtained may be useful for understanding low-temperature measurements of charge carrier and excitation transport in quasi-one-dimensional organic solids,[28] such as 1,2,4,5-tetrachlorobenzene, or inorganic[29] ones such as $CsNiF_3$. For this reason, it is important to consider some of the general conditions under which the asymptotic behavior we have obtained might be observed.

Clearly, the most important precondition for the applicability of our analysis is that the temperature be sufficiently low that phonon scattering be minimal over the time period of the decay. Since the asymptotic decay arises from long-lived states with energies near the edge of the band, this also means that the temperature should be small compared to the bandwidth of the excitation. Provided that these general requirements regarding the temperature can be satisfied, there remains the question of determining the time frame associated with the asymptotic behavior. One might first ask when the stretched-exponential form [e.g., Eq. (18)] accurately describes the integral, Eq. (16), or sum, Eq. (17), from which it has been obtained. Numerical evaluations that we have done suggest that this will occur rather rapidly for reasonable trap concentrations and trapping strengths. We should emphasize, however, that even when this is not the case it is still possible to use the full expressions in the analysis of experimental data.

A more difficult question is that of the time frame over which Eqs. (16) and (17) provide accurate descriptions of the survival probability. Recall that these expressions include only the most slowly decaying states in each cluster, and so the relevant question is at what time is it safe to ignore the contributions from other (more rapidly decaying) eigenmodes. Unfortunately, the answer to this question depends rather strongly on the initial conditions of the experiment. With optically created excitonic states there is a small wave vector ($k\simeq 0$) selection rule which could result in the states in each cluster located nearest the band edge being preferentially excited. For this situation (provided that the other relevant conditions are met), the asymptotic behavior could set in quite early because there would be no masking contribution from states close to the center of the band. On the other hand, if the excitations were created at individual sites, say, with equal probability (equivalent to a uniform initial population over the k states) then the results of our analysis could be masked by contributions from the rest of the eigenmodes. If equilibration to the bottom of the band occurs rapidly then this need not be a limitation, however such a condition might bring with it an unacceptably high rate for phonon scattering. At any rate, since the density of states in a one-dimensional system is heavily weighted near the band edge one might hope that the irrelevant portion of the decay for such an initial condition would be a small component of the total. It is worth noting that similar initial conditions in the corresponding diffusion problem lead to an asymptotic regime which occurs early enough [$P(t)\sim\frac{1}{100}$] so as to be easily observed[10] in numerical simulations.

In summary, we have investigated the properties of quantum particles which move coherently in one-dimensional systems containing randomly placed irreversible traps. We have shown for a substitutional model that the survival probability decays asymptotically as a stretched exponential of the form

$$P(t)\sim \exp(-At^{1/4}) .$$

We have also presented an analysis for interstitial traps which suggests that due to Anderson localization of the particle wave function by the traps, the asymptotic decay will be of the same functional form as in the substitutional model. We have provided estimates of the constants in the exponent for the interstitial model which reproduce the essential features found in the distribution of decay amplitudes for large one-dimensional chains that have been diagonalized numerically, and we have discussed the conditions under which the asymptotic behavior obtained in our analysis might be seen in experimental measurements. As in the corresponding diffusion problem, a unified theoretical approach which handles both the long-time behavior investigated in the present paper, as well as the short-to-intermediate time frame investigated in earlier treatments[19–21] remains an important theoretical task. In a future publication[23] we extend these results to higher dimensional systems, using an analysis similar to that developed in Sec. IV A.

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