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One-Dimensional Trapping Kinetics at Zero Temperature

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The asymptotic decay of the survival probability is calculated for a quantum particle moving at zero temperature on a one-dimensional tight-binding chain possessing randomly placed irreversible traps of strength γ. The survival probability exhibits a decay, $P(t) \sim \exp(-At^{1/4})$, which is slower than that associated with a diffusing particle.

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A common means for probing the transport properties of neutral excitations such as excitons, vibrons, spin excitations, etc., is to monitor their interaction with other species such as impurity atoms which have been doped into the solid to irreversibly trap or quench the excitation. Consequently, a great deal of recent theoretical work has focused on understanding essential features of a basic trapping model[1-4] 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. A great deal has been learned about this quantity in various classical limits.[1-4] For example, when transport is diffusive[3] it has been shown that the probability $P(t) \sim \exp(-At^{d/(2+d)})$, where A depends on the diffusion constant and the trap concentration. This asymptotic behavior has actually been observed in some one-dimensional physical systems[5] and in numerical simulations[2] where it has been shown that in higher dimensions the asymptotic regime can occur at exceedingly long times.

At any rate, these results become less useful for quantum-mechanical systems at low temperatures when the mean free path for phonon scattering becomes large and eventually exceeds 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 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 and scatter (and perhaps localize), as well as irreversibly trap, the wavelike motion. Some initial work has been done in this direction,[6,7] but exact results are rare. In this Letter we calculate the asymptotic survival probability for a particle moving at zero temperature on a one-dimensional (1D) tight-binding chain containing a fraction $q=1-p$ of randomly placed impurities which can irreversibly trap the excitation, and show that it has a stretched exponential decay of the form $P(t) \sim \exp(-At^{1/4})$.

We begin with the basic model, which is intended to be a simple quantum-mechanical version of the classical one. The Hamiltonian

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

describes transport in a 1D tight-binding solid in the absence of the trapping centers, with $|n\rangle$ representing a quasiparticle state centered at the nth lattice site, and with all energies, frequencies, etc., measured in units of the transfer matrix elements which connect nearest-neighbors along the chain. When trap molecules are introduced they occupy lattice sites substitutionally and lower the energy associated with a particle being at those sites by an amount $\Delta \gg 1$. To account for the irreversibility of the trapping process we need to specify a mechanism whereby the particle can give up energy to the phonon bath as it moves onto the impurity site. Perhaps the simplest kind of particle-phonon coupling which produces this effect is one in which the matrix elements connecting the impurity site and its neighboring host sites are proportional to an appropriate bath operator.[7,8] For example, if site n_i is a trap, then we can add to the Hamiltonian 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 the form

$$V(|n_i\rangle\langle n_i \pm 1| + |n_i \pm 1\rangle\langle n_i|)\,,$$

where, e.g., the operator $V = \sum_q g_q (b_q^\dagger + b_{-q})$. Here, b_q and $b_q^\dagger$ are, respectively, destruction and creation operators for the qth vibrational mode of the 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 move irreversibly from sites $n_i \pm 1$ onto the trap at site n_i by emitting a phonon of energy $E \simeq \Delta$. With no thermal phonons around to absorb the required energy, however, it will be unable to move back onto a host site once it has been trapped. Thus, as in the classical problem, we expect the traps to divide the chain into isolated clusters of random length (see Fig. 1), and we neglect any processes that allow the particle to tunnel

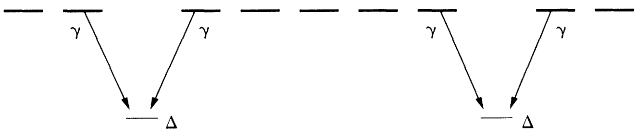

FIG. 1. One-dimensional solid with unit nearest-neighbor transfer matrix and randomly placed traps of depth Δ. After elimination of bath variables at zero temperature, the chain is divided into isolated segments with a decay amplitude γ for each of the host sites neighboring a trap.

between clusters.

The evolution of a particle in a given cluster will then be determined by a reduced density matrix ρ, obtained by tracing the full system density matrix over the bath variables.[7,8] At zero temperature the primary effect of such a reduction is simply to give a lifetime $\tau=(2\gamma)^{-1}$ to the two end sites in each cluster that are coupled to a trap. (There are also energy shifts which develop, but they do not substantially affect the dynamics and will be ignored.) Thus, rather than deal with the full density-matrix equations, we can use a standard phenomenological procedure which gives the same dynamical results; i.e., we can modify the Hamiltonian for each isolated cluster by including a "complex potential" consisting of an imaginary site energy at each end. For a cluster of N host sites, this leads to the effective cluster Hamiltonian

$$H_N=-i\gamma(|1\rangle\langle 1|+|N\rangle\langle N|)-\sum_{n=1}^{N-1}|n\rangle\langle n+1|+|n+1\rangle\langle n|\,, \quad (2)$$

in which the capture strength γ depends on the square of the coupling constant and the density of phonon states at frequency Δ. A particle on a single host state isolated by such impurities will decay to a trapped state with a rate of 4γ. In general, however, the evolution of the system will depend upon the eigenvectors and complex eigenvalues of the effective Hamiltonian for each cluster. If, for example, the particle is in a cluster of size N at $t=0$, then the survival probability will be

$$P_N(t)=\sum_k C_k^*(0)C_k(0)\exp(-2\Gamma_k t)\,, \quad (3)$$

where $E_k=\epsilon_k-i\Gamma_k$ is the complex eigenvalue of the kth eigenvector of H_N, and $C_k(0)$ is the initial amplitude to be in state $|k\rangle$. 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.

The asymptotic decay of $P_N(t)$ will be determined by those eigenvectors with the smallest imaginary component of the energy. These turn out to be the states at the edges of the band, so the argument holds in the presence of other processes which cause the particle to equilibrate to the lowest-energy states. To show this we obtain the eigenstates $|k\rangle$ of H_N. These will be "complex" standing waves of the form $\langle n|k\rangle=A_k\cos kn+B_k\sin kn$, for appropriate constants A_k and B_k, and complex wave vector k. For an interior site $|n\rangle$ one finds that $-\langle n|H|k\rangle=2\langle n|k\rangle\cos k$, giving the eigenvalue associated with eigenvector $|k\rangle$ as $E_k=-2\cos k$. Enforcing this same eigenvalue condition on the end sites we obtain from site $|1\rangle$ an equation determining the coefficients

$$A_k/B_k=i\gamma\sin k/(1-i\gamma\cos k)\,, \quad (4)$$

while from site $|N\rangle$ we obtain a condition which reduces under (4) to

$$\tan kN=(1+\gamma^2)\sin k/[2i\gamma-(1-\gamma^2)\cos k]\,, \quad (5)$$

thereby providing a means to determine the allowed wave vectors. It is readily verified by substitution into (5) that the mth allowed wave vector from the bottom of the band for $N\gg m$, is given to $O(N^{-2})$ by

$$k_m=(m\pi/N)[1-f_1/N]-i\pi m f_2/N^2\equiv q_m-i\lambda_m\,, \quad (6)$$

where $f_1=(1-\gamma^2)/(1+\gamma^2)$ and $f_2=2/(\gamma+\gamma^{-1})$. We should add that the validity of (6) is independent of the magnitude of γ. The real and imaginary parts of the eigenvalues for these wave vectors are then

$$\epsilon_m=-\mathrm{Re}(2\cos k_m)=-2\cos q_m\cosh\lambda_m\sim-2\cos(m\pi/N) \quad (7a)$$

and

$$\Gamma_m=\mathrm{Im}(2\cos k_m)=2\sin q_m\sinh\lambda_m\sim 4\pi^2m^2/N^3(\gamma+\gamma^{-1})\,. \quad (7b)$$

Thus, the minimum in both the band energy and the decay rate for each cluster occurs for those states nearest the bottom of the band [note from (4) that $k=0$ is not a solution since it has zero amplitude at each site]; the decay rate for these states scales as N^{-3}. This latter fact (which ultimately determines the asymptotic decay) can be understood physically as follows: 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 condition for this problem (which follows from the assumption of isolated clusters) requires 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 $k_m \sim m\pi/N$, this condition forces the wave function in the vicinity of the trap to be small, so that C_1, the normalized amplitude to be at the end site, goes as $N^{-1/2}\times\sin k_m\sim N^{-3/2}$. Hence for these modes $\Gamma_1\sim|C_1|^2\sim N^{-3}$.

Thus, provided a finite fraction of the amplitude ends up near the band edge, the asymptotic decay of the survival probability for particles created in a cluster of size

N will take the form

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

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 that are short compared to trapping, then A_N will equal 1 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, 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 any case, we can now average over the distribution of cluster lengths to obtain

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

where $f(N)=qA_N/p$ depends algebraically on the cluster size and so is slowly varying in comparison with 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 $\exp[-8\pi^2 t/N^3(\gamma+\gamma^{-1})]$, 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 (8) will approach

$$P(t) \sim \int_0^\infty f(N) \exp[-(\alpha N + \beta t/N^3)] dN$$
$$= \int_0^\infty \tau f(y\tau) \exp[-\tau(\alpha y + \beta y^{-3})] dy , \qquad (9)$$

where $\alpha = \ln(1/p) \simeq q$ for $q \ll 1$, $\beta = 8\pi^2/(\gamma+\gamma^{-1})$, and $\tau = t^{1/4}$. The asymptotic properties of the second integral in Eq. (9) are readily determined.[9] Expanding the exponent about its maximum value $y_m(t) = (3\beta/\alpha)^{1/4}$ and performing a Gaussian integration, we obtain

$$P(t) \sim C(q,t) \exp(-At^{1/4}) , \qquad (10)$$

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.

The 1D decay is therefore slower than that associated with a diffusing particle,[3] for which the probability $P(t) \sim \exp(-At^{1/3})$, but faster than that predicted for classical particles interacting via hard-core potentials, where an $\exp(-At^{1/5})$ decay law obtains.[4] 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 we have shown, 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. Indeed, a localized absorbing site is evidently 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 (4) one can easily show that a traveling wave of unit magnitude incident upon an absorbing site is reflected with a reflection probability

$$P_R = (1 - 2\gamma \sin k + \gamma^2)/(1 + 2\gamma \sin k + \gamma^2)$$

and is absorbed (i.e., decays to the trap) with probability $P_A = 1 - P_R \sim 4k/(\gamma+\gamma^{-1})$ for small k. Hence, for small wave vectors ($k_m \sim \pi/N$) the absorption probability actually decreases with increasing cluster size as $1/N$. It is also interesting to note that this form for the reflection probability is valid for arbitrary γ, so that for fixed N the absorption probability has a maximum when $\gamma=1$. 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.[6] 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 localized impurity state which is more efficient at capture than it is at scattering remains an open question.

The results we have obtained are strictly valid only at zero temperature. At finite but small temperatures the mean free path for phonon scattering will alter the asymptotic decay. For times large enough for the asymptotic behavior of Eq. (10) to have set in, but still small compared to the phonon scattering time, the asymptotic decay will behave as $\exp(-At^{1/4})$, as we have demonstrated. At very long times the maximal term in the sum appearing in Eq. (9) will be associated with a cluster size which is large compared to the mean free path for phonon scattering, and so the decay should cross over to the form $\exp(-At^{1/3})$ associated with trapping in a one-dimensional system with diffusive motion.[1] In principle, observations of the crossover point could provide a means for monitoring the phonon mean free path as a function of temperature in quasi-one-dimensional systems.

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