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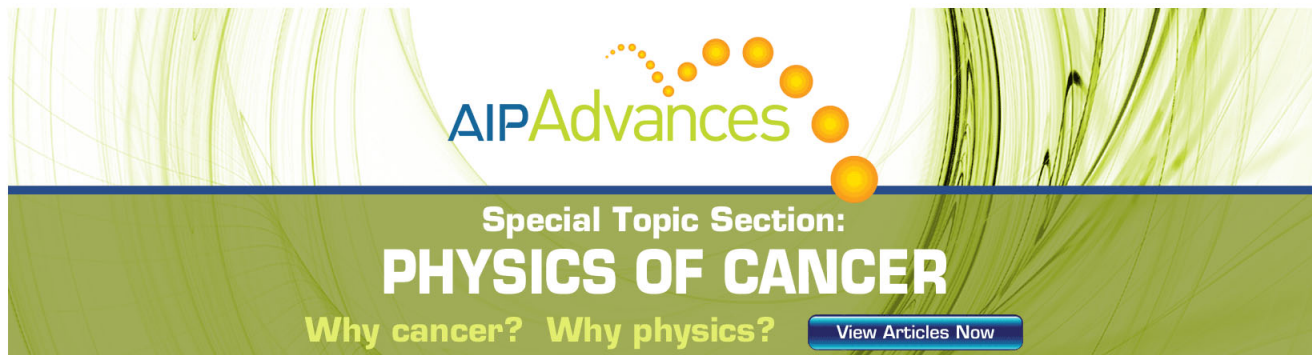
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A comment on the dynamics of excitation trapping in molecular crystals^{a)}

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In this paper we consider the long-time trapping rate, by a deep sink, of an excitation which migrates incoherently in a one-dimensional molecular crystal. The approaches based on the first passage time version of the continuous time random walk and on the master equation formalism are compared and put in a unified framework. Time domains are predicted for the different behaviors of the trapping rates for both one- and two-dimensional systems.

I. INTRODUCTION

Several theories have recently been proposed to describe time dependent energy transfer among impurity molecules in condensed media.¹⁻⁸ The motivation for this growing interest has been the valuable insight provided by the time dependent studies in understanding the mechanisms of the migration of excitation among impurity molecules (donors). Although most works refer to electronic excitations, the conclusions account well also for vibrational energy migration⁹ and for spin migration.¹⁰ In all these problems, at high temperatures, it is generally agreed that phonon assisted hopping processes dominate, and that the limit of incoherent migration prevails. It is assumed that the incoherent migration is described by a master equation

$$\frac{d}{dt} P_n(t) = \sum_{m \neq n} [W_{mn} P_m(t) - W_{nm} P_n(t)], \quad (1)$$

where $P_n(t)$ is the probability of finding the excitation on the n th impurity donor and W_{mn} are the transition rates which, in the case of randomly distributed impurities, depend on the configuration. For the high temperature limit, mentioned above, $W_{mn} = W_{nm}$.

In many systems, however, the migration of an excitation is quenched due to the presence of low lying sinks (acceptors): Electronic excitations in various molecular crystals are trapped by x traps,^{11,12} dimers,¹³ or guest supertraps¹⁴; vibrational energy was found to be trapped by dimers⁹ and migrating spins by rapidly relaxing centers.¹⁰ The quenching of migrating excitations by sinks has often been used to monitor the efficiency of energy transfer (electronic, vibrational) among impurity molecules,^{13,14} provided that the sink concentration is very low so that the dynamics of energy transfer among the impurities is not modified drastically by their presence. The experiments mentioned above¹¹⁻¹³ on trapping of electronic excitations in molecular crystals have been conducted on both ordered crystals^{11,12} and disordered crystals.^{13,14}

A model which accounts reasonably well for the basic features of the experimental systems assumes the following^{15,16}:

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(a) The excitation migrates on a *lattice* of impurities (donors). Each site *may be* characterized by a distribution of hopping rates.¹⁶

(b) The concentration of sinks c_s is much smaller than the impurity concentration, over which the excitation migrates.

(c) Deep sinks (acceptors) are assumed, and hence no detrapping is possible. The "depth" of the sink is defined relative to the temperature needed for detrapping.

(d) Only long-time trapping rates are considered here. Assumptions (b) and (c) are justified by experimental studies on molecular crystal systems.¹¹⁻¹⁴ We restrict the model to a strictly one-dimensional case, which was also studied experimentally on some molecular crystals: 1,4-dibromonaphthalene (DBN) and 1,2,4,5-tetrachlorobenzene (TCB) may be considered as one dimensional.¹¹⁻¹³

Two different approaches have recently been used to study the above model: (A) Ghosh and Huber (GH) [Ref. 15(a) and see also Appendix A of Ref. 15(b)] suggested a modification of Eq. (1) to include also a sink at $n=0$:

$$\frac{d}{dt} P_n = \sum_{m \neq n} [W_{nm} P_m(t) - (X_{0n} + W_{mn}) P_n(t)]. \quad (2)$$

X_{0n} is the transfer rate from the impurity (donor) at site n to sink (acceptor) at site $n=0$. Only nearest neighbor transfer is assumed between the impurities and from the impurities to the sink, and only an *ordered* lattice of impurities was considered. GH used an averaged t -matrix approximation in order to solve Eq. (2). (B) We developed a model¹⁶ based on the first passage time version of the continuous time random walk proposed by Montroll and Weiss.¹⁷ This approach can be easily extended from ordered arrays to the case of disordered systems described by a distribution of hopping rates (or times). This approach will be referred to as the first passage time approach (FPT).

Both (A) and (B) were interested in the long-time behavior of the trapping process, but they differ considerably in their results. GH¹⁵ studied the time evolution of $f(t)$, where $f(t) = \sum_n P_n(t)$; we focused our study¹⁶ on $k(t)$, the time dependent trapping rate, which GH did not define in their work [see the conclusion of Ref. 15(a)].

In what follows we briefly review the FPT approach to the trapping rate $k(t)$, and then we try to unify the various approaches and to define the time scales for the existence of each of the behaviors predicted according to the GH solution and according to the FPT. We extend our conclusions to two-dimensional systems, and relate the FPT trapping rates to experimental data.

We should remark that Kenkre¹⁷ and Wong and Kenkre¹⁷ have looked at the time dependence of the trapping in the k space representation, i. e., when bandlike transport is important.

II. TRAPPING RATE IN THE FPT APPROACH

We assume that the origin $n=0$ on a lattice of donors is occupied by an acceptor and that at time $t=0$ all the sites n ($n \neq 0$) have the same probability of being populated. Following Montroll and Weiss,¹⁸ we define $\bar{F}(n, t)$ as the probability density of an excitation starting at site n to reach site $n=0$ for the first time. The trapping rate is then defined as

$$k(t) = c_s \sum_{n \neq 0} \bar{F}(n, t). \tag{3}$$

$\bar{k}(u)$, the Laplace transform of $k(t)$, can be expressed¹⁸ in terms of the random walk generating function $R(n, z)$ ¹⁷ and the function $\bar{\psi}(u)$, which is the Laplace transform of the distribution function for hopping time $\psi(t)$ ¹⁷:

$$\bar{k}(u) = c_s \left\{ \frac{1}{[1 - \bar{\psi}(u)] R(n=0, \bar{\psi}(u))} - 1 \right\}. \tag{4}$$

$\bar{k}(u)$ in Eq. (4) depends on the dimensionality via the generating function $R(n=0, \bar{\psi}(u))$ and on $\bar{\psi}(u)$, which reflects the nature of migration among the donors. We now express $\bar{k}(u)$ in terms of $\bar{P}_0(u)$, which is defined as

$$\bar{P}_0(u) = \int_0^\infty e^{-ut} P_0(t) dt. \tag{5}$$

$P_0(t)$ is the probability of the excitation staying at its initial site at time t , where no acceptor is present. It was shown elsewhere⁵ that

$$\bar{P}_0(u) = \frac{1 - \bar{\psi}(u)}{u} R(n=0, \bar{\psi}(u)) \tag{6}$$

so that from Eqs. (4) and (6) we have

$$\bar{k}(u) = c_s \left[\frac{1}{u \bar{P}_0(u)} - 1 \right]. \tag{7}$$

In the case of a one-dimensional ordered array of donors,⁵

$$P_0(t) \sim W^{-1/2} t^{-1/2}, \quad t \rightarrow \infty. \tag{8}$$

W is the average nearest neighbor transition rate. The Laplace transform of Eq. (8) is

$$\bar{P}_0(u) \sim W^{-1/2} u^{-1/2}. \tag{9}$$

From Eqs. (7) and (9) it follows that

$$k(t) = c_s W^{1/2} t^{-1/2}, \quad t \rightarrow \infty. \tag{10}$$

This result holds also for the general case where $\bar{\psi}(t)$ represents a disordered system, but still has a first moment. When disorder results in a more complicated

behavior of $\bar{\psi}(u)$, and of $\bar{P}_0(u)$, namely,¹⁸

$$P_0(t) \sim t^{-(1-\alpha)/2}, \tag{11}$$

then

$$k(t) \sim t^{-(1+\alpha)/2}. \tag{12}$$

Equation (10) has also been derived in other ways (see Ref. 1 and references cited therein). The time dependent population of the donor system $f(t)$ is given by the rate equation

$$\dot{f}(t) = -k(t)f(t), \tag{13}$$

where $k(t)$ is the trapping rate calculated above.

III. THE MASTER EQUATION APPROACH

In this section, we solve the master equation for a highly simplified model, obtaining an exact result which recovers the asymptotic GH result and the FPT result. Assume a one-dimensional cyclic array with M donor molecules and with acceptor molecules situated above every N th donor. Thus, the donors form a translationally invariant array with repeat distance unity, and the traps form a translationally invariant array with repeat distance N . The concentration of acceptors c_s equals $1/N$. The equations of motion for the donor probabilities p_n and the acceptor probabilities $P_{\nu N}$, $n=0, 1, 2, \dots, M-1$, $\nu=0, 1, 2, \dots, (M/N)-1$ are

$$\dot{p}_n = -2Wp_n - X \sum_{\nu} \delta_{n,\nu N} p_n + W(p_{n+1} + p_{n-1}), \tag{14}$$

$$\dot{P}_{\nu N} = Xp_{\nu N}, \tag{15}$$

where we have assumed nearest neighbor transition probabilities only. The total probability of finding the excitation on the donors is given by

$$f(t) = \sum_{n=1}^M p_n. \tag{16}$$

By conservation of probability,

$$\dot{f}(t) = - \sum_{\nu=1}^{(M/N)} \dot{P}_{\nu N}(t) = -X \sum_{\nu=1}^{M/N} p_{\nu N}(t) \tag{17}$$

so that the Laplace transform of $f(t)$ is

$$\bar{f}(u) = \frac{1}{u} - \frac{X}{u} \sum_{\nu=1}^{M/N} \bar{p}_{\nu N}(u). \tag{18}$$

Thus, to know the behavior of $f(u)$ it is sufficient to know the probabilities at the donor sites next to the acceptors. In order to solve Eq. (14) for these quantities, we note that we can write this equation as a matrix equation

$$\dot{\mathbf{p}} = \mathbf{W}\mathbf{M}_0\mathbf{p} - X\delta\mathbf{M}\mathbf{p}, \tag{19}$$

where

$$\begin{aligned} (\mathbf{M}_0)_{nm} &= -2\delta_{nm} + \delta_{n,m+1} + \delta_{n,m-1}, \\ (\delta\mathbf{M})_{nm} &= \delta_{n,m} \sum_{\nu=0}^{M/N} \delta_{n,\nu N}. \end{aligned} \tag{20}$$

Thus,

$$\begin{aligned} p_{\nu N}(t) &= p_{\nu N}^{(0)}(t) \\ &- X \sum_{\nu'=0}^{M/N-1} \int_0^t d\tau \langle \nu N | e^{\mathbf{W}\mathbf{M}_0\tau} | \nu' N \rangle p_{\nu' N}(t-\tau) \end{aligned} \tag{21}$$

or, by Laplace transformation,

$$\tilde{p}_{\nu N}(u) = \tilde{p}_{\nu N}^{(0)}(u) - X \sum_{\nu'=0}^{M/N-1} \langle \nu N | (u - W\mathbf{M}_0)^{-1} | \nu' N \rangle \tilde{p}_{\nu' N}(u), \quad (22)$$

$$\begin{aligned} \langle \nu N | e^{W\mathbf{M}_0\tau} | \nu' N \rangle &= \frac{1}{M} \sum_{k=0}^{M-1} \exp \left[i \frac{2\pi k}{M} N(\nu - \nu') \right] e^{-2Wt} \exp[2Wt \cos(k2\pi/M)] \\ &= \frac{1}{M} + \frac{1}{M} \sum_{k=1}^{M-1} \exp \left[i \frac{2\pi k}{M} N(\nu - \nu') \right] \exp[-2Wt(1 - \cos(2\pi k/M))] = \frac{1}{M} + F_{\nu-\nu'}(\tau). \end{aligned} \quad (23)$$

In the above we have separated the time independent $k=0$ term explicitly. By summing Eq. (22) over ν we find

$$\sum_{\nu=0}^{M/N} \tilde{p}_{\nu N}(u) = -X \sum_{\nu=0}^{M/N} \sum_{\nu'=0}^{M/N} \left[\frac{1}{Mu} + \tilde{F}_{\nu-\nu'}(u) \right] \tilde{p}_{\nu' N}(u)$$

or

$$\sum_{\nu=0}^{M/N} \tilde{p}_{\nu N}(u) = (Nu)^{-1} \left[1 + X(Nu)^{-1} + X \sum_{n=0}^{M/2N} \tilde{F}_n(u)(1 + \delta_{n0}) \right]^{-1}. \quad (25)$$

Substituting into Eq. (18), we find

$$\begin{aligned} \tilde{f}(u) &= \frac{1}{u} - \frac{X}{S} (Nu)^{-1} \left[1 + X(Nu)^{-1} + X \sum_{n=0}^{M/2N} \tilde{F}_n(u)(1 + \delta_{n0}) \right]^{-1} \\ &= [u + c_s \tilde{T}(u)]^{-1}, \end{aligned} \quad (26)$$

or

$$\begin{aligned} \tilde{f}(u) &= \left\{ u + \frac{X}{N} \left[1 + X \sum_{n=0}^{M/2N} \tilde{F}_n(u)(1 + \delta_{n0}) \right] \right\}^{-1} \\ &= [u + c_s \tilde{T}(u)]^{-1}, \end{aligned} \quad (27)$$

where

$$\tilde{T}(u) = X \left[1 + X \sum_{n=0}^{M/2N} (1 + \delta_{n0}) \tilde{F}_n(u) \right]^{-1}. \quad (28)$$

This is similar to that derived by GH.¹⁵ We now evaluate $F_n(t)$ by noting that, using Eq. (23), we can take the limit $M \rightarrow \infty$, to find

$$\begin{aligned} \tilde{F}_n(t) &= \frac{e^{-2Wt}}{M} \sum_{k=1}^{M-1} \exp[2\pi k N n / M] \exp[2Wt \cos(2k\pi/M)] \\ &= e^{-2Wt} I_{nN}(2Wt), \end{aligned} \quad (29)$$

where $I_m(z)$ is the modified Bessel function of order m . We can now evaluate $f(t)$ for long times. We must take care however in specifying our time regions carefully. By noting the asymptotic form of $I_{nN}(2Wt)$, we see that for $1 \ll 2Wt \ll N^2 (= 1/c_s^2)$, $I_0(2Wt) \sim e^{-2Wt} (2Wt)^{-1/2}$ while $I_{nN}(2Wt) \sim (2Wt)^{nN} / (nN)! \ll 1$ for all other n . Therefore, in this region ($u \sim 0$ but $u \gg 2Wc_s^2$)

$$\tilde{T}(u) \sim (2Wu)^{1/2} \quad (30)$$

and

$$\tilde{f}(u) \sim [u + c_s(2Wu)^{1/2}] \quad (31)$$

where $p_n^{(0)}(t)$ is the probability of finding the excitation at site n in the absence of trapping. We will assume that initially all donor sites were equally occupied, then $p_n^{(0)}(t) = 1/M$ for all time, so $\tilde{p}_n^{(0)}(u) = 1/Mu$. The eigenvalues and eigenfunctions of M_0 are well known so that

so that

$$f(t) \sim e^{2c_s^2 Wt} \operatorname{erfc}[(2Wc_s^2)^{1/2} t^{1/2}]. \quad (32)$$

However, in this time regime $2c_s^2 Wt \ll 1$, so

$$f(t) \sim 1 - \frac{2}{\sqrt{\pi}} (2Wc_s^2)^{1/2} t^{1/2} \sim \exp\left[-\left(\frac{8}{\pi} Wt c_s^2\right)^{1/2} t^{1/2}\right] \quad (33)$$

and

$$k(t) = \dot{f}(t)/f(t) \sim 1/t^{1/2}, \quad (34)$$

agreeing with the FPT result.

At later times, such that $N^2 \ll 2Wt \ll 4N^2$, both the terms $I_0(2Wt)$ and $I_N(2Wt)$ contribute to $\tilde{T}(u)$, and in this case $(2c_s^2 W/u)^{1/2}$ will not necessarily be small compared to 1, so Eq. (32) holds, but for this case $(2Wc_s^2)t \gg 1$, so that

$$f(t) \sim (2Wc_s^2 t)^{-1/2} \quad (35)$$

and

$$k(t) = -\dot{f}(t)/f(t) \sim 1/t, \quad (36)$$

in agreement with GH.

We see that there are two asymptotic time regimes in this trapping problem: (i) for $1 \ll 2Wt \ll c_s^{-2}$, $k(t) \sim 1/t^{1/2}$, in agreement with the FPT result, and (ii) for $c_s^{-2} \ll 2Wt$, $k(t) \sim 1/t$, in agreement with GH. Thus, the first passage time result is not incorrect as stated by GH, but belongs to a different time regime. Note that the rate found for (ii) is typical for all $f(t) \sim t^{-\alpha}$. As a side comment, we note that GH invert Eq. (27) to get

$$\dot{f}(t) = -c_s \int_0^t T(t-\tau) f(\tau) d\tau, \quad (37)$$

which they claim is the correct form of the rate equation rather than Eq. (13):

$$\dot{f}(t) = -k(t)f(t).$$

However, it can easily be seen that these are formally identical by defining $\Phi(u) = [u + c_s \tilde{T}(u)]^{-1}$. Then

$$f(t) = \Phi(t) f(t) \quad (38)$$

and

$$\dot{f}(t) = -k(t)f(t),$$

with

$$k(t) = -\dot{\Phi}(t)/\Phi(t) \quad (39)$$

Finally, we note that we can solve our model in two and three dimensions also, with appropriate functions $\tilde{T}(u)$ and the results are similar to the one-dimensional case. We can see this in the work of GH also by noting that in two dimensions they find (note that if N is the lattice constant of the two-dimensional array of traps, $c_s = 1/N^2$)

$$\tilde{f}(u) \sim \left[u - \frac{4c_s W}{\ln(u/2W)} \right]^{-1} \quad (40)$$

For $4c_s W/u \ll 1$ and $W/u \gg 1$ [i. e., $1/4c_s \gg Wt \gg 1$],

$$\tilde{f}(u) \sim \frac{1}{u} + \frac{4Wc_s}{u^2 \ln(u/2W)} \quad (41)$$

$$f(t) \sim 1 - \frac{4c_s Wt}{\ln(2Wt)} \quad (42)$$

$$k(t) \sim 4c_s W / \ln(2Wt) \quad (43)$$

agreeing with the FPT results in two dimensions. For $Wt \gg 1/4c_s$, on the other hand, $f(t) \sim 1/t$ and $k(t) \sim 1/t$ as in GH.

IV. DISCUSSION

We have established the relationship between the first passage time approach to the trapping rate and the master equation formalism which includes a trapping term. We demonstrated the correctness of the FPT result and defined two time scales: (I) moderately long times where $1/c_s^2 \gg Wt \gg 1$ for one dimension and $1/c_s \gg Wt \gg 1$ for two dimensions, with Eqs. (34) and (43), respectively; (II) long times $Wt \gg 1/c_s^2$, where $f(t) \sim t^{-1/2}$ in one dimension ($Wt \gg 1/4c_s$) and $f(t) \sim 1/t$ in two dimensions¹⁵ and $k(t) \sim t^{-1}$. In this time regime the FPT results coincide with the master equation results. Due to the lack of sufficient experimental data, we can only determine the range (I) in a rough way. For triplet excitations in TCB,¹¹ $c_s \sim 10^{-5}$ and $W \sim 10^{11} \text{ sec}^{-1}$. The FPT result for $k(t)$ is then obeyed for time between 10^{-9} and 10^{-2} s (the order of the excitation lifetime). For smaller W , corresponding to larger average hopping times, t is pushed to even longer times. For singlet excitations in naphthalene, which may be considered two dimensional, $W \sim 10^{11} - 10^{12} \text{ sec}^{-1}$ and $c_s \sim 10^{-5}$. In this case the FPT $k(t)$ is valid for $10^{-8} \cong t \geq 10^{-11}$ s.

The above predicted time domains are amenable to further experimental justification by conducting trapping studies at various sink concentration c_s and at various impurity concentrations, which determine the donor-donor excitation transfer rate W . In the case of singlet

excitation, where one expects higher values of W to dominate the excitation transfer process, the FPT result should have a smaller range of validity and the GH results should be more accessible (depending of course on c_s). Generally, the FPT is expected to be a good approximation in low concentration systems where multipolar interactions dominate and W is well defined.⁵ Just before this paper was submitted, we received a preprint from Dr. Harvey Scher which gives the solution of Eq. (14) for any dimension in terms of a continuous time random walk model.

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