The Journal of Chemical Physics

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Citation: J. Chem. Phys. **72**, 849 (1980); doi: 10.1063/1.439237 View online: http://dx.doi.org/10.1063/1.439237 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v72/i2 Published by the American Institute of Physics.

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Trapping in dilute quasi-one-dimensional systems

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A model is developed for calculating the asymptotic trapping rate, by a sink, of an excitation migrating in a quasi-one-dimensional dilute system. The asymptotic behavior for the dilute limit differs considerably from that corresponding to a concentrated system. The migration is assumed to be incoherent and is described within the continuous time random walk approach. The competing roles of short range exchange coupling and of long range dipole-dipole coupling is also discussed using time scaling arguments.

I. INTRODUCTION

There has been growing interest in the problem of the quenching of excitation migrating in condensed media by a low lying trap or supertrap.¹⁻⁵ This problem overlaps strongly with the wide field of dynamical recombination controlled by random migration of the initially prepared species.⁸

Most of the works on excitation's trapping studied trapping rates of electronic excitation by x traps,¹ dimers,² or guest supertraps,³ trapping of vibrational energy which relaxes to a dimer,⁴ and also quenching of migrating spins by rapidly relaxing centers.⁵ The studies on electronic excitation transfer and trapping have been devoted either to the problem of localization at the low concentration limit⁷ or to incoherent migration at the high concentration limit.¹ In the cases of vibrational energy and spin relaxation a constant diffusion coefficient has been proposed^{8,9} in the usual diffusion controlled framework or using the "hopping" model.^{10,11}

In previous work, ¹² we have formulated the problem of excitation transfer in disordered crystals in the incoherent limit (strong scattering regime). We studied the long time behavior of the mean square displacement of the excitation and the long time evolution of the probability that the excitation remains at its origin. However, in many real systems the long time behavior may be dominated by migration to a sink, thereby masking the predicted¹² long time spectral and spatial diffusion.

In this article we develop a simple model for trapping of an electronic excitation which migrates incoherently in one dimension in the dilute limit. The model is easily extended to higher dimensionalities and is of course applicable to migrating species other than electronic excitations. In some sense our note describes the electronic excitation analogy of the recent theory by Theodorou and Cohen (TC) for random one-dimensional magnetic systems.¹³

The model is based on the first passage time version of the continuous time random walk (CTRW) by Montroll and Weiss¹⁴ (MW). The assumptions of the model presented here are as follows:

(a) Migration takes place on a *lattice* of impurities having a probability distribution labelled $\rho(\omega)$ of nearest neighbor hopping rates, ω , at each site.

(b) The concentration of sinks, C_s , is much smaller than the concentration of impurities, C, over which the excitation migrates $(C_s/C \ll 1)$.

(c) The energy level of the sinks is much below the impurities' excitation energy, and hence no detrapping is possible.

(d) We restrict the model to a strictly one-dimensional case.

(e) Only the asymptotic long time trapping rate is considered here.

Assumptions (b)-(d) are based on experimentally studied molecular crystals systems, especially concerning the EET problem.¹⁻³ Both 1, 4-dibromonaphthalene (DBN) and 1, 2, 4, 5-tetrachlorobenzen (TCB) may be considered as one dimensional^{1,2} and C_s , at least in the case of the supertrap, is adjustable and usually very small.³ The "depth" of sink is defined relative to the temperature needed for detrapping.^{2,3}

II. TRAPPING RATE

We are interested in the asymptotic trapping rate of an electronic excitation under the "diffusion" controlled assumption: random walk of the excitation towards the sink, which differs from the "hopping" or homogeneous quenching approach.¹¹ In what follows we adopt the MW¹⁴ first passage time problem in the framework of the CTRW.

We assume a lattice of impurities, where the excitation on each site has a distribution of hopping times $\Psi(t)$ [which will later be connected with the distribution of hopping rates $\rho(\omega)$]. $\Psi(t)$ contains the information about disorder in the system. The sinks, having very low concentration, ¹⁻³ C_s , where $C_s/C \approx 10^{-3}$, are assumed to be randomly distributed over the lattice – each lattice site is occupied with a sink with equal probability C_s .

We follow MW^{14} closely and define $\overline{F}(s, t)$ as the probability density of an excitation starting from s = 0 to reach site s at time t for the first time. We then assume that the trapping rate is given by

$$k(t) \sim \sum_{s \neq 0} \overline{F}(s, t) \quad , \tag{1}$$

which in the terminology of the regular diffusion theory means that the effective, or reaction, radius is an interimpurity distance. Defining the set $\{\Psi_n(t)\}$ by

$$\Psi_0(t) = \delta(t) \quad , \tag{2a}$$

$$\Psi_n(t) = \int_0^t \Psi(\tau) \Psi_{n-1}(t-\tau) d\tau; \quad n \ge 1 \quad , \tag{2b}$$

where $\Psi_n(t)$ is the probability density for the occurrence the *n* step at time *t*, it can be shown¹⁴ that $\{\Psi_n(t)\}$ have the property

$$\int_0^\infty e^{-ut} \Psi_n(t) dt = [\tilde{\Psi}(u)]^n \quad , \tag{3}$$

where

$$\tilde{\Psi}(u) = \int_0^\infty dt \, e^{-ut} \Psi(t) \quad . \tag{4}$$

 $F_n(s)$ is defined as the probability that the excitation reaches site s for the *first* time at step n. The generating function of $F_n(s)$ is

$$F(s,z) = \sum_{n=0}^{\infty} F_n(s) z^n \quad . \tag{5}$$

In terms of $F_n(s)$ and of Eq. (5), $\overline{F}(s, t)$ is given by

$$\overline{F}(s,t) = \sum_{n=0}^{\infty} F_n(s)\Psi_n(t) \quad , \tag{6}$$

with the Laplace transform

$$\overline{F}(s,u) = \sum_{n=0}^{\infty} F_n(s) [\tilde{\Psi}(u)]^n$$

$$= F(s, \tilde{\Psi}(u)) \quad .$$
(7)

The Laplace transform of the trapping rate is then

$$\bar{k}(u) = \sum_{s\neq 0} F(s, \bar{\Psi}(u)) \quad . \tag{8}$$

The generating function F(s, z) is given in the terms of the random walk generating function R(s, z),¹⁴

$$F(s,z) = [R(s,z) - \delta s, 0]/R(0,z) \quad . \tag{9}$$

Using the relation¹⁴

$$\sum_{s} R(s,z) = (1-z)^{-1} \quad , \tag{10}$$

we obtain

$$\sum_{s\neq 0} F(s,z) = \frac{1}{(1-z)R(0,z)} - 1 \quad , \tag{11}$$

 \mathbf{or}

$$\tilde{k}(u) = \frac{1}{[1 - \tilde{\Psi}(u)]R(0, \tilde{\Psi}(u))} - 1 \quad , \tag{12}$$

and k(t) is its inverse Laplace transform. The trapping rate k(t) depends of course on $\tilde{\Psi}(u)$ [or $\tilde{\Psi}(t)$], which reflects the nature of migration over the impurity sites, and on $R(0, \tilde{\Psi}(u))$, which has a typical behavior depending on dimensionality. The known^{1,14} results for the long time dependence of the trapping rates in an ordered system with low sink concentration can be recovered.

In an ordered system^{1,15}

$$\Psi(t) = \lambda e^{-\lambda t} \quad , \tag{13}$$

$$\tilde{\Psi}(u) = \lambda/(\lambda + u)$$
(14)

and

$$\tilde{k}(u) = \frac{\lambda + u}{uR(0, \lambda/\lambda + u)} - 1 \quad . \tag{15}$$

For 1D,

$$R(0,z) = (1-z^2)^{1/2} , \qquad (16a)$$

and therefore

$$k(t) \sim \lambda^{1/2} t^{-1/2} \qquad t \to \infty \text{ or } t > \lambda^{-1}$$
 (16b)

For 2D,

$$R(0,z) = -\pi^{-1} lg(1-z) , \qquad (17a)$$

and

$$k(t) \sim 1/\lg \lambda t \quad t \to \infty \quad . \tag{17b}$$

For 3D,

$$R(0,z) \sim \text{const} \quad \text{as } z \to 1 \quad , \tag{18a}$$

and

$$k(t) \sim \lambda \qquad t \to \infty \quad . \tag{18b}$$

The above conclusions are not changed even when $\Psi(t)$ is different from Eq. (13), provided that it has at least first moment

$$\overline{t} = \int t \Psi(t) dt \quad . \tag{19}$$

 \overline{t} is the average hopping time (for instance multipolar interaction in all dimensions).

In the above framework we also understand the k(t) discussed by Wieting *et al.*^{1b} in the case of a concentrated TCB system, where $\Psi(t)$ is given by Eq. (13) (or at least has a first moment). The same approach should be used for electronic energy transfer in the highly concentrated naphthalene systems studied by Argyrakis *et al.*³ if the situation is that of incoherent migration.

III. THE QUASI-ONE-DIMENSIONAL SYSTEM

We now turn to one-dimensional (1D) molecular crystals, which have been the subject of some recent studies.^{1,2,16} For the triplet excitations of these crystals, the intermolecular interactions are dominated by exchange or superexchange,¹⁷ and we have for the transfer rate

$$\omega(m) = \omega_0 e^{-K(m-1)} . \tag{20}$$

Taking the concentration of the impurities as C, two lengths can be defined in the problem,¹³

$$d = C^{-1}, \quad R = K^{-1} \quad , \tag{21}$$

The mean separation between impurities and the range of interaction, respectively. When d and R are both large, and this is the limit we are interested in, then mand therefore ω can be treated as continuous variables. The probability distribution of ω is then¹³

$$\rho(\omega) = \frac{\gamma}{\omega_0} \left(\frac{\omega_0}{\omega}\right)^{1-\gamma} \sim \omega^{-\alpha} \quad 0 < \omega < \omega_0 \quad , \tag{22}$$

 $\rho(\omega) = 0$ otherwise,

where

$$\alpha = 1 - \gamma \tag{23}$$

and

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(24)

 $\gamma \cong c/K$.

on the value of α :

In Ref. 12 we analyzed the properties of $\rho(\omega)$ depending

- (i) $\alpha > 0$ (low concentration limit);
- (ii) $\alpha = 0$ (crossover);
- (iii) $\alpha < 0$ (high concentration limit).

A transition from low concentration $\rho(\omega)$ ($\alpha > 0$), and therefore a corresponding transition in certain properties of the system, have been predicted by TC¹³ for dilute random magnets in one dimension. In studying the incoherent electronic energy transfer among the *monomer* impurities in TCB¹ or in DBN, ¹⁶ both quasi 1D, it will be reasonable to restrict the model to case (i), namely, the low concentration limit. At higher concentrations impurity clusters must be considered, and it is not clear if $\rho(\omega)$ in Eq. (22) has the same concentration dependence at these higher C values.

Restricting our discussion to $\alpha > 0$ we now apply our results in Ref. 12 to derive k(t) from Eq. (22):

$$\Psi(t) = \int_0^\infty \omega e^{-\omega t} \rho(\omega) d\omega \quad , \tag{25}$$

and

$$\tilde{\Psi}(u) = \int_0^\infty \frac{\omega \rho(\omega)}{\omega + u} \, d\omega \quad ; \tag{26}$$

the asymptotic limit of $\Psi(t)$ is found by taking the $u \rightarrow 0$ limit of $\tilde{\Psi}(u)$,

$$\tilde{\Psi}(u) \sim 1 - Au^{(1-\alpha)} , \qquad (27)$$

where A is independent of u. Using the formulas for k(t) with this form of $\tilde{\Psi}(u)$, we find

$$k(t) \sim t^{-(1+\alpha)/2} = t^{(-2+\gamma)/2}, \quad t \to \infty$$
 (28)

Equation (28) demonstrates the fast decay of the trapping rate in the low concentration limit, in comparison with the ordered or high concentration limit, Eq. (16b).

We shall now present the asymptotic form of k(t) for $\alpha = 0$ and $\alpha < 0$, although they are not directly related to the problem of electronic energy trapping in the dilute case¹⁸:

α = 0:

 $\Psi(u)$ according to Eq. (26) is given by

$$\Psi(u) \sim 1 + u \ln u, \ u \to 0 \tag{29}$$

and

$$\tilde{k}(u) \sim \frac{1}{u^{1/2} \ln^{1/2}(1/u)}$$
, (30)

$$k(t) \sim 1/[t \ln t]^{1/2}$$
, $t \to \infty$. (31)

This interesting behavior is closer to the "ordered" k(t) and is defined¹³ as a crossover between the highly disordered limit (low concentration) and the ordered behavior (high concentration).

 $\alpha < 0$:

In this case

$$\tilde{\Psi}(u) \sim 1 - \omega_{\text{off}}^{-1} u \quad , \quad u \to 0 \tag{32}$$

$$\omega_{\text{eff}}^{-1} = \langle 1/\omega \rangle \quad , \tag{33}$$

so that the trapping rate is

$$k(t) \sim t^{-1/2} \omega_{\text{eff}}^{1/2} , t \to \infty$$
 (34)

Equation (34) represents the asymptotic trapping rate for all $\rho(\omega)$ having a ω_{eff}^{-1} .

The form of $\rho(\omega)$, Eq. (22), is derived for purely exchange (or superexchange) interactions in the dilute limit; however, the exchange interaction falls off quickly with distance, and if there is any small component of dipole-dipole interaction in the matrix element governing transfer, then there will be a distance beyond which the intermolecular interaction (and the migration) will be dominated by the dipolar (or multipolar in the general case) interaction.¹³ Assume that the distance at which this crossover occurs is equivalent to an intermolecular interaction ω_d , then the correct distribution of interactions is given by

$$\rho(\omega) = \begin{cases} \omega^{-\alpha} & \omega_d < \omega \le \omega_m \\ \omega^{-4/3} \exp(-D/\omega^{1/3}) & \omega < \omega_d \end{cases},$$
(35)

where D is a constant independent of ω . Using this $\rho(\omega)$, we can see the effect of this crossover by the following argument. For $t < \omega_d^{-1}$, the system will behave as if the ω 's smaller than ω_d are unimportant; hence the trapping rate will be given by Eq. (28),

$$k(t) \sim t^{-(1+\alpha)/2}, \quad t < \omega_d^{-1}$$
 (36)

On the other hand, for $t > \omega_d^{-1}$, the system will behave as if all the ω 's are important. Since ω_{eff}^{-1} exists for the $\rho(\omega)$ given by Eq. (35), we have for a one-dimensional system

$$k(t) \sim t^{-1/2}, \quad t > \omega_d^{-1}$$
 (37)

This argument can be made more carefully by introducing a cutoff ω_1 in the $\rho(\omega)$ near $\omega \sim 0$. We may then calculate ω_{off} for the cutoff distribution and use the scaling argument that $t \sim \omega_1^{-1}$ to find the temporal behavior of k(t). When one introduces the cutoff in the exchange dominated $\rho(\omega)$, it is easily shown¹² that ω_{off}^{-1} $= \langle \omega_1^{-1} \rangle = \omega_1^{-\alpha}$. Using Eq. (32), we get in the cutoff distribution for $\omega_1 > \omega_d$,¹²

$$\tilde{\Psi}(u) \sim 1 - \omega_1^{-\alpha} u = 1 - \omega_{\text{eff}}^{-1} u$$
, (38)

so that

$$k(t) \sim \omega_{\text{eff}}^{1/2} t^{-1/2} = \omega_1^{\alpha/2} t^{-1/2} = t^{-(1+\alpha)/2}$$
(39)

as in Eq. (36). Since this result is valid for $\omega_1 > \omega_d$, then $t < \omega_d^{-1}$, making it identical to Eq. (36).

For $\omega_1 < \omega_d$, ω_{eff} can be calculated approximately and we find

$$\omega_{\text{eff}}^{-1} \simeq \omega_{d}^{-\alpha} + \int_{\omega_{d}^{-1/3}}^{\omega_{d}^{-1/3}} x^{3} e^{-kx} dx \quad , \tag{40}$$

so that, for $\omega_1 < \omega_d$, or $t > \omega_d^{-1}$, $k(t) \sim \omega_d^{\alpha/2} t^{-1/2}$ for a strictly one-dimensional system.

Finally, it should be noted that since the dipolar interaction is less "directional" than the exchange or superchange interactions in the quasi-one-dimensional sys-

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tems (e.g., DBN or TCB), it is possible that at the crossover point $t \sim \omega_d^{-1}$ the system becomes two, or three dimensional in character. The k(t) would be given for Eq. (17b) or (18b) for $t > \omega_d^{-1}$. The long time trapping rate is characterized by two regimes—a disordered regime, where k(t) depends on t through Eq. (28), and an "ordered" regime, where k(t) is independent of t, having the usual ordered case form.¹

The rate at which the initial number of excited impurities decays to sinks is given by

$$\int_0^t k(\tau) d\tau \quad . \tag{41}$$

In one-dimensional systems we find, using Eqs. (28) and (37), the interesting relation

$$\int_{0}^{t} k(\tau) d\tau \sim \xi^{2} > \frac{1}{2} , \qquad (42)$$

where $\langle \xi^2 \rangle$ is the excitation's mean square displacement.¹² Due to the one dimensional relation¹² between $\langle \xi^2 \rangle^{1/2}$ and $\langle p_0(t) \rangle$, the excitation probability to remain in the origin, we find that

$$\int_0^t k(\tau) d\tau = \langle p_0(t) \rangle^{-1} , \qquad (43)$$

which may be related to the system density of states $D(\epsilon)$ at low energies via

$$\langle p_0(t) \rangle = \int_0^\infty e^{-\epsilon t} D(\epsilon) d\epsilon$$
 (44)

IV. SUMMARY

In the present note, we have formulated a theory of the trapping rate of excitations by sinks in the first passage time and continuous time random walk models. This has allowed a discussion of trapping (in the long time limit) for a variety of models of intermolecular interactions. In particular, the theory, when applied to quasi-one-dimensional systems like TCB or DBN predicts that a change in the rate of trapping (as a function of time) occurs at time $t \sim \omega_a^{-1}$, where ω_d is the value of the transition rate at which the exchange interaction becomes smaller than the dipolar (or multipolar) interaction. A scaling argument is used which allows a smooth transition from the exchange dominated behavior to the dipolar dominated behavior.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this work. It was also partially supported by the NSF.

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- ¹⁸In cases where α is temperature dependent the transition from $\alpha > 0$ to $\alpha < 0$ may provide a mechanism for a transition from a disordered regime to an ordered regime induced by activation.