Electronic energy transport in substitutionally disordered molecular crystals

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In this paper we present a theoretical study of incoherent electronic energy transfer (EET) in an impurity band of substitutionally disordered, mixed, molecular crystals. Dispersive diffusion of the electronic excitation was treated by an Average Dyson Equation Approximation (ADEA) to the master equation for EET. The ADEA rests on expressing the Green's function (GF) for the probability of site-excitations in a single fixed spatial configuration in terms of a Dyson equation with a normalized vertex function and subsequently performing the configurational average of the GF, invoking a decoupling approximation which omits many-site contributions. Explicit expressions were derived for the initial site occupation probability, $P_o(t)$, the mean square displacement, $\Sigma^2(t)$, and the time dependent diffusion coefficient $D(t)$. We have explored the relation between the ADEA and the stochastic continuous time random walk (CTRW) model applied by us for EET. We have demonstrated that the ADEA and the CTRW results for $\Sigma^2(t)$ and for $D(t)$ are identical, while $P_o(t)$ has a similar structure in both schemes. The ADEA/CTRW scheme was utilized to derive analytical results for $P_o(t)$, $\Sigma^2(t)$ and $D(t)$ in an impurity band where the pair-probability of EET is determined by multipolar interactions. From the analysis of asymptotic expansions for $D(t)$ in such cases we conclude that the short time diffusion coefficient has the time dependence $D(t) \propto t^{(5-n)/n}$ while the long time diffusion coefficient is independent of t, corresponding to an average superlattice of impurities. Numerical calculations based on the ADEA/CTRW scheme were performed to elucidate the quantitative features of the crossover from dispersive transport to pure diffusive behavior and how it is affected by the impurity concentration and by the range of the multipolar interactions. For short range high order multipolar interactions the effects of dispersive energy transport are expected to prevail over a broad concentration and time domain, being more pronounced than in the conventional case of dipole–dipole coupling.

I. INTRODUCTION

Some of the most interesting features of exciton states in pure molecular crystals involve the dynamic manifestations of electronic energy migration.[1,2] There have been quite extensive studies on the dynamics of singlet and triplet Frenkel type excitons in organic crystals,[1] as well as of Wannier (or intermediate) type excitons in solid rare gases.[3] These studies were interpreted in terms of a strong exciton–phonon mechanism, resulting in incoherent exciton transport, and led to reliable estimates of the exciton diffusion coefficient in pure molecular crystals. The effects of disorder on electronic energy transfer (EET) are of considerable interest. Two basic types of disorder should be considered in this context, involving structural disorder and substitutional disorder, both of which may, of course, prevail simultaneously.

A relevant example for EET in structurally disordered systems pertains to triplet energy migration in some pure and mixed organic liquids,[4] while effects of substitutional disorder prevail for EET in mixed molecular crystals.[5–11] There has been considerable activity in studies of EET between guest molecules in solids and liquids in relation to fluorescence depolarization, sensitized luminescence, organic photochemistry, and energy transport in biological systems. Most of these studies rest on the Förster–Dexter mechanism[12,13] focusing attention on EET from a single donor to randomly distributed acceptors.[14–18] At higher impurity concentrations in a substitutionally disordered solid or in solution, one has to surpass the pair interaction picture and to consider the migration of electronic excitation between randomly distributed molecules.

There has been considerable recent experimental and theoretical activity in the field of EET in impurity bands of substitutionally disordered molecular and ionic crystals. From the theoretical point of view, this problem is of interest because of two reasons:

(1) The possibility arises of observing Anderson localization[19] of an electronic excitation in an impurity band at low temperatures. Above the critical impurity concentration for the Anderson transition, the electronic states are expected to be extended, while below the critical concentration the states are localized. The possibility of observing localization for EET in an impurity band makes mixed molecular crystals attractive model systems for the study of electronic structure of disordered materials.

(2) At higher temperatures, the Anderson localized states in the impurity band will be "liberated" due to phonon-induced thermal hopping effects. An incoherent, strong-scattering EET process will now prevail. The interesting feature of the problem of incoherent EET in an impurity band is that energy transport cannot be described in terms of a conventional diffusion process.

From the experimental point of view, recent informa-

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tion concerning the migration of electronic excitation in an impurity band emerged from the following sources: (a) Luminescence quenching of the emission from the impurity band occurs. EET in an impurity band of an isotopic or a chemical substituent was monitored by interrogating the emission yield for an energy acceptor, such as a chemical supertrap or an impurity dimer.[5-9] (b) Spectral diffusion studies probe time-resolved fluorescence-line-narrowing experiments. A small fraction of the impurities within the inhomogeneously broadened absorption line shape was excited by a narrow laser pulse, resulting in EET from the initially excited states to other impurities which are located at different microscopic host environments.[10,11] (c) Spatial diffusion studies, which monitor the range of the spread of the electronic excitation energy in an impurity band, were conducted by the picosecond transient grating method.[20]

The recent spectral and spatial diffusion studies were interpreted in terms of thermally induced incoherent hopping, while it is still an open question whether some of the low-temperature luminescence quenching experiments should be interpreted in terms of a kinetic model involving phonon-induced hopping of the electronic excitation or, alternatively, whether an Anderson localization of a triplet exciton is exhibited in these low-temperature systems.

In this paper, we shall address ourselves to the problem of the incoherent, strong-scattering EET process, where the excited impurity molecules have lost all memory regarding previous energy migration events. This state of affairs can be specified in terms of a master equation for energy hopping in the impurity band, which is characterized in terms of probabilities of EET between randomly distributed pairs or impurities. It was demonstrated recently by Sakun[21] and by Haan and Zwanzig[22] that this strong scattering EET process in an impurity band cannot be described in terms of an ordinary diffusion process, but rather is characterized by a dispersive (i.e., time-dependent) diffusion coefficient. Explicit analytical expressions for the time-dependent diffusion coefficient for incoherent EET were derived[21-23] within the pair approximation, i.e., for short times and/or low impurity concentrations. The long-time, high-concentration characteristics of the dispersive EET process constitute a challenging problem. Haan and Zwanzig have conjectured that for long times an ordinary diffusion process is exhibited for EET in an impurity band.

Very recent theoretical progress in this interesting field was accomplished originating from two independent modes of attack. The first approach[24,25] utilizes the kinetic master equation to describe the time evolution of the excitation probability. Haan[24] and Gouchanour, Andersen, and Fayer[25] have derived explicit formal Green's function solutions for the master equation. Gouchanour, Andersen, and Fayer[25] were able to advance a self-consistent approximate relation for the self-energy, resulting in a dispersive diffusion coefficient, which is time dependent at short times and constant at long times. The second approach rests on the use of the continuous time random walk (CTRW) method applied by us[26] for the study of dispersive diffusion of an electronic excitation in an impurity band. We were able to derive closed analytical expressions for the frequency dependence of the diffusion coefficient which spans the entire time regime, demonstrating that the long-time diffusion coefficient in the impurity band is constant, corresponding to an effective superlattice. Both the Godzik–Jortner (GJ)[26] and the Gouchanour–Andersen–Fayer (GAF)[25] approaches provide a strong support to the Haan–Zwanzig conjecture.

In this paper, we report the results of a theoretical study of dispersive diffusion of electronic energy in impurity bands, utilizing a novel approach to this problem which is based on an averaged Dyson equation approximation (ADEA) to the solution of the master equation. We shall demonstrate the close relationship between the ADEA solution and the stochastic CTRW method. From the point of view of general methodology, this interrelationship between the ADEA and the CTRW is of considerable interest in relation to the general problem of dispersive transport in amorphous semiconductors.[27,28] We would like to emphasize that the dispersive behavior of the diffusion coefficient for energy transport bears a close analogy to the problem of dispersive electron mobility in disordered materials,[28] whereupon the general features of both energy and electron hopping can be explored from a unified point of view. From the practical point of view, two new results were obtained. First, we have derived an explicit analytical expression for the time-dependent initial site excitation probability $P_0(t)$ in terms of the configurationally averaged density of excitation $P(\mathbf{r}, t)$. Second, we derived an analytic expression for the mean-square displacement $\Sigma^2(t)$ of the electronic excitation for dispersive diffusion, which is defined as the second spatial moment of the average density of excitation

$$\Sigma^2(t)=\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_0)^2 P(\mathbf{r}, t) \; . \tag{1.1}$$

$P_0(t)$ and $\Sigma^2(t)$ constitute the two basic observables in the description of dispersive diffusion. The third pertinent observable we shall discuss in this paper is the time dependent diffusion coefficient $D(t)$, which is closely related to the mean square displacement by the definition

$$D(t)=\tfrac{1}{6}[\partial\Sigma^2(t)/\partial t]=\frac{1}{6}\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_0)^2\frac{\partial}{\partial t}P(\mathbf{r}, t) \; . \tag{1.2}$$

These results are of considerable value for the interpretation of EET experiments, such as luminescence quenching, spectral diffusion, and spatial diffusion of electronic excitation, and can be confronted with experiment.

The outline of this paper is as follows: In Sec. II, the microscopic time dependent probability of excitation $\bar{p}(t)$ is derived from the master equation. In Sec. III, we introduce the average density of excitation $P(\mathbf{r}, t)$ which constitutes the fundamental quantity for the macroscopic coarse-grained description of the EET process. In Secs. IV and V, we obtain explicit expressions for the pertinent experimental observables $P_0(t)$, $\Sigma^2(t)$, and $D(t)$ within the framework of the ADEA and the

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CTRW establishing the correspondence between these two schemes. Section VI is devoted to the dispersive diffusion in an impurity band where the transfer probabilities are determined by isotropic multipolar interactions while numerical results are presented in Sec. VII.

II. MICROSCOPIC MODEL

We consider a substitutionally disordered two component system, which consists of N molecules of an inert, optically transparent host and N_1 impurity molecules, which are randomly distributed at the lattice sites. Confining ourselves to flash excitation of the impurity, the initial conditions at time $t=0$ imply that the probability $\bar{p}_j(\mathbf{R}, t=0)$ of finding the molecule j located at r_j in the excited state will be independent of the configurations of the other (N_1-1) molecules

$$\bar{p}_j(\mathbf{R}, t=0)=F(r_j) , \quad \mathbf{R}=(r_1, r_2, \ldots, r_{N_1}) . \tag{2.1}$$

This also implies the simplifying assumption that each exciton is strictly localized at a particular lattice site, generally known as single site approximation, omitting any kind of interactions between clusters of sites. As a consequence, the density matrix will be diagonal in the site representation and we can reduce the problem to the study of the time evolution of populations. In addition, we will assume in what follows that the total impurity number density $C=N_1/N$ is large relative to the density C^* of optically excited molecules

$$C^* \ll C \tag{2.2}$$

so that the probability of exciton–exciton interaction processes is negligible.

The microscopic time evolution of the excitation probability $\bar{p}_j(t)$ of an individual impurity molecule j at time t will be described by a master equation of the gain–loss type:

$$\frac{d}{dt}p_j(t)=-\sum_n w_{jn}p_j(t)+\sum_n w_{nj}p_n(t) , \tag{2.3}$$

where

$$p_j(t)=\bar{p}_j(t)\exp(t/\tau)$$

and τ is the lifetime of the excitation. The sum over n is taken over all the impurities and w_{jk} are the rates for EET between the molecules k and j, and we assert that $w_{nj}=0$ when $n=j$. The way we are choosing the rates w_{jk} will fix the kind of randomness we are considering here. Since we will concentrate in this work on multipolar resonance interaction, we are omitting any randomness in site energies (diagonal disorder) and keep only the randomness which is due to the distribution of hopping rates in a spatially disordered medium.

The master equation (2.3), which reflects the dynamics of a particular configuration of our system, can easily be rewritten in matrix form:

$$\frac{d}{dt}\mathrm{p}(t)=\mathbf{W}\mathrm{p}(t) , \tag{2.4}$$

with

$$W_{jn}=-\delta_{jn}\sum_l w_{jl}+w_{jn} . \tag{2.5}$$

This transfer matrix $\mathbf{W}$ is real, symmetric, and singular. The latter feature means that summation with respect to row—or column index—gives zero:

$$\sum_j W_{jn}=\sum_n W_{jn}=0 , \tag{2.6}$$

which is just the mathematical expression for the conservation of the number of excited impurities. The formal solution of this first-order differential equation (2.4) is given by

$$\mathrm{p}(\mathbf{R}, t)=\exp(\mathbf{W}t)\cdot\mathrm{p}(\mathbf{R}, 0) . \tag{2.7}$$

III. MACROSCOPIC MODEL

The quantities we are interested in, e.g., mean square displacement, diffusion coefficient, or the time evolution of the initial site-excitation probability, are not determined by a particular configuration of the system. The experimental data provide only information about the properties of the system sampled over all possible configurations. The quantity we are therefore interested in is the average density of excitation. Until recently, only approximate solutions for these observables have been obtained, valid for short times or low densities.[21-23] In what follows, we will give a treatment which provides a solution over the complete time and concentration range and compare it with the recent independent self-consistent treatment of GAF.[25] The average density of excitation $P(\mathbf{r}, t)$ is defined as

$$P(\mathbf{r}, t)=\left\langle\sum_j \delta(\mathbf{r}_j-\mathbf{r})p_j(\mathbf{R}, t)\right\rangle , \tag{3.1}$$

where

$$\langle\cdots\rangle=V^{-N_1}\int_V d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_{N_1}\cdots \tag{3.2}$$

denotes the usual configurational average under the assumption of an independent and homogeneous distribution of impurity sites (continuum approximation). Here, V is the volume of the system.

Since the probability $p_j(\mathrm{R}, 0)$ is taken to be independent of the configuration of the other (N_1-1) molecules, the initial condition for the $P(\mathbf{r}, t)$ is, according to Eq. (3.1),

$$P(\mathbf{r}, t=0)=\rho F(\mathbf{r}) , \tag{3.3}$$

where $\rho=N_1/V$ is the impurity number density. Since the physical observables we are interested in are expressed in terms of the moments of $P(\mathbf{r}, t)$, it turns out to be convenient to introduce the Green's function representation for the solution of Eq. (3.1):

$$P(\mathbf{r}, t)=\int d^3r' G(\mathbf{r}, \mathbf{r}'; t)P(\mathbf{r}', 0) , \tag{3.4}$$

where the configurationally averaged Green's function is defined as

$$G(\mathbf{r}, \mathbf{r}'; t)=\rho^{-1}\sum_j\sum_k\langle\delta(\mathbf{r}_j-\mathbf{r})A_{jk}\delta(\mathbf{r}_k-\mathbf{r}')\rangle , \tag{3.5}$$

with

$$A_{jk}=[\exp(t\mathbf{W})]_{jk} . \tag{3.6}$$

It is apparent that $G(\mathbf{r}, \mathbf{r}'; t)$ is just a function of the distance $|\mathbf{r}-\mathbf{r}'|$ and has the simple interpretation that it

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represents the average density of excitation in the case of a δ-like initial distribution.

In the following, we are going to derive a representation for the averaged Green's function which is amenable to a perturbation treatment.

Performing now the Laplace transform (LT) of Eqs. (3.5) and (3.6), i.e.,

$$\tilde{A}(\mathbf{r}, s)=\int_0^\infty dt\, e^{-st}A(\mathbf{r}, t) , \tag{3.7}$$

we obtain

$$\tilde{G}(\mathbf{r}, \mathbf{r}'; s)=\rho^{-1}\sum_j\sum_k\langle\delta(\mathbf{r}_j-\mathbf{r})g_{jk}\delta(\mathbf{r}_k-\mathbf{r}')\rangle , \tag{3.8}$$

where g_{jk} is the Green's function for the probability of excitation for a single fixed configuration

$$g_{jk}=[(s-\mathbf{W})^{-1}]_{jk} . \tag{3.9}$$

In the evaluation of the Green's function (3.8), it is convenient and useful to separate the diagonal and the nondiagonal contributions according to

$$\begin{aligned}\tilde{G}(\mathbf{r}, \mathbf{r}'; s)&=\rho^{-1}\delta(\mathbf{r}-\mathbf{r}')\sum_j\langle\delta(\mathbf{r}_j-\mathbf{r})g_{jj}(s)\rangle\\ &\quad+\rho^{-1}\sum_{j\neq k}\langle\delta(\mathbf{r}_j-\mathbf{r})g_{jk}(s)\delta(\mathbf{r}_k-\mathbf{r}')\rangle\\ &=\rho^{-1}\delta(r-r')(N-1)\langle\delta(\mathbf{r}_1-r)g_{11}(s)\rangle\\ &\quad+\rho^{-1}(N-1)(N-2)\langle\delta(\mathbf{r}_1-\mathbf{r})g_{12}(s)\delta(\mathbf{r}_2-\mathbf{r}')\rangle ,\end{aligned} \tag{3.10}$$

where in the second equality we have used the fact that the configurational averages are independent of the special labeling of the variables.

From this point on, one can proceed along two different lines to obtain a Dyson type equation for g_{jk} and also for the averaged Green's function $\tilde{G}(\mathbf{r}, \mathbf{r}', s)$. The first approach rests on expressing Eq. (3.9) in a form which results in a Dyson equation with a renormalized vertex function and then perform the configurational average upon this quantity. We shall demonstrate that this approach is intimately connected to a stochastic, semi-Markovian description of the process within a generalized random walk model. This method was introduced by us[26] and will be explored in the present work. The second approach rests on a self-consistent diagrammatic method (SCDM) of GAF.[25] We shall briefly comment on that method in Appendix A, while in Sec. VII we provide some comparison between the results of our semi-Markovian method and the results of the diagrammatic approach.

IV. THE AVERAGED DYSON EQUATION APPROACH

In the following, we shall exploit a special property of the transfer matrix $\mathbf{W}$. According to Eq. (2.5), $\mathbf{W}$ can be segregated into diagonal and nondiagonal contributions

$$\begin{aligned}&\mathbf{W}=\mathbf{W}_d+\mathbf{W}_{nd} ,\\ &(\mathbf{W}_d)_{jj}=-\sum_l W_{jl} ,\\ &(W_{nd})_{jn}=W_{jn} , \quad j\neq n .\end{aligned} \tag{4.1}$$

Defining now the bare diagonal Green's function or vertex function $\mathbf{g}_0$ as

$$\mathbf{g}_0=[s-\mathbf{W}_d]^{-1} , \tag{4.2}$$

the following Dyson equation is obtained for the microscopic Green's function $\mathbf{g}$ [Eq. (3.9)]:

$$\mathbf{g}=\mathbf{g}_0+\mathbf{g}_0\mathbf{W}_{nd}\mathbf{g} \tag{4.3}$$

or equivalently

$$\mathbf{g}=\mathbf{g}_0+\mathbf{g}\,\mathbf{W}_{nd}\,\mathbf{g}_0 . \tag{4.4}$$

Iteration of this equation by means of the operator identity

$$\frac{1}{s-A}=\frac{1}{s}+\frac{A}{s}\frac{1}{s-A} \tag{4.5}$$

results in the expansion

$$\mathbf{g}=\mathbf{g}_0+\mathbf{g}_0\mathbf{W}_{nd}\mathbf{g}_0+\mathbf{g}_0\mathbf{W}_{nd}\mathbf{g}_0\mathbf{W}_{nd}\mathbf{g}_0+\cdots , \tag{4.6}$$

which due to the relations

$$\begin{aligned}&(g_0)_{ij}=g_j^0\delta_{ij} ,\\ &g_j^0=[s-(\mathbf{W}_d)_{jj}]^{-1}\end{aligned} \tag{4.7}$$

can easily be recast in the form

$$g_{jk}=\delta_{jk}g_j^0+g_j^0w_{jk}g_k^0+\sum_n g_j^0w_{jn}g_n^0w_{nk}g_k^0+\cdots . \tag{4.8}$$

This expansion is formally similar to the "locator" expansion in the theory of amorphous systems.[27] The main difference is that in our case the locator is a nonlocal quantity, so that the configurational average becomes quite involved if not impossible after a few iterations.

The Dyson equation (4.4) is an algebraic matrix equation and hence can be segregated into its diagonal and nondiagonal parts

$$\mathbf{g}_{ii}=(\mathbf{g}_0)_{ii}+(\mathbf{g}_0\mathbf{W}_{nd}\mathbf{g}_0)_{ii} , \tag{4.9}$$

$$\mathbf{g}_{ij}=(\mathbf{g}\mathbf{W}_{nd}\mathbf{g}_0)_{ij} , \tag{4.10}$$

respectively, or explicitly in terms of the individual matrix elements

$$g_{11}=g_1^0+\sum_m{}' g_{1m}^0w_{m1}g_1^0=g_1^0+(N-1)g_{12}w_{21}g_1^0 , \tag{4.11}$$

$$\begin{aligned}g_{12}&=g_{11}w_{12}g_2^0+\sum_m{}' g_{1m}w_{m2}g_2^0\\ &=g_{11}w_{12}g_2^0+(N-2)g_{13}w_{32}g_2^0 ,\end{aligned} \tag{4.12}$$

where we have assumed that there is translational invariance with respect to the starting point.

By means of this partitioning, we have obtained a set of coupled algebraic equations. In principle, one can perform the same procedure for any finite order of iteration of the Dyson equation. However, as it turns out, due to the nonlocal nature of the vertex function g_n^0, one has to stay in zeroth order, i.e., not to perform any iteration at all, since otherwise the configurational averaging becomes untractable. Taking the configurational average of Eqs. (4.11) and (4.12), we get

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$$\bar{g}_{11}=\bar{g}_1^0+(N-1)\langle\bar{g}_{12}\overline{w_{21}g_1^0}\rangle_{(2)}\ , \tag{4.13}$$

$$\bar{g}_{12}=\bar{g}_{11}\overline{w_{12}\,g_2^0}+(N-2)\langle\bar{g}_{13}\overline{w_{32}\,g_2^0}\rangle_{(3)}\ , \tag{4.14}$$

where the bar indicates averaging with respect to all variables except the ones which appear as indices of the quantity under the bar, while the indexed brackets $\langle\ \rangle_{(1)}$ mean averaging with respect to the variable (1) indicated by the index.

Equations (4.13) and (4.14) will be used to derive explicit and tractable approximate expressions for the pertinent physical quantities we have introduced in Sec. II. Let us first concentrate on the probability $P_0(t)$ to find an exciton at site 1 at time t if it started there at time $t=0$. This quantity is closely related to the diagonal part of the configurationally averaged Green's function.

To decouple the Eqs. (4.13) and (4.14), we omit many-site interactions, i.e., we neglect the second term on the rhs of Eq. (4.14). Substituting the approximate expression for $\bar{g}_{12}$ into Eq. (4.13), we get

$$\bar{g}_{11}=\bar{g}_1^0+\bar{g}_{11}(N-1)\langle\overline{w_{12}\,g_2^0}\,\overline{w_{21}\,g_1^0}\rangle_{(2)}\ . \tag{4.15}$$

Using Eqs. (3.4) and (3.5) for the diagonal part of the Green's function, we can recast the LT of $P_0(t)$ as

$$\tilde{P}_0(s)=\tilde{G}(\mathbf{r},\mathbf{r},s)\ , \tag{4.16}$$

which together with Eq. (4.15) results in

$$\tilde{P}_0(s)=\tilde{\Phi}(s)[1-\rho\tilde{F}(s)]^{-1}\ , \tag{4.17}$$

where we have defined the configurational average of g_1^0 [Eq. (4.7)] as

$$\tilde{\Phi}(s)=\bar{g}_1^0\ , \tag{4.18}$$

which is expressed in terms of the LT of a waiting function $\Phi(t)$:

$$\begin{aligned}&\Phi(t)=\langle Q(t)\rangle\ ,\\ &Q(t)=\exp\Bigl(-\sum_l w_{1l}t\Bigr)\ ,\end{aligned} \tag{4.19}$$

so that

$$\tilde{\Phi}(s)=\int_0^\infty \exp(-st)\Phi(t)dt\ . \tag{4.20}$$

The waiting function (4.19) has a simple physical interpretation. It is the probability that the exciton, which is at site 1 at time $t=0$, stays there till time t; this probability is averaged over all configurations of the remaining (N_1-1) sites.

The function $\tilde{F}(s)$ appearing in Eq. (4.17) is

$$\tilde{F}(s)=\langle\overline{w_{12}\,g_2^0}\ \overline{w_{21}\,g_1^0}\rangle_{(2)}\ , \tag{4.21}$$

which can be explicitly rewritten as

$$\begin{aligned}\tilde{F}(s)&=\int_0^\infty dt\,e^{-st}\int_0^t d\tau\,\Phi(\tau)\Phi(t-\tau)\\ &\quad\times\int_V d\mathbf{r}_2\,w_{12}\exp(-w_{21}\tau)w_{21}\exp[-w_{12}(t-\tau)]\\ &=\int_0^\infty e^{-st}\Phi(t)*\Phi(t)\cdot f(t)dt\ ,\end{aligned} \tag{4.22}$$

where we have defined the convolution integral

$$\Phi(t)*\phi(t)=\int_0^t d\tau\,\Phi(\tau)\Phi(t-\tau) \tag{4.23}$$

and where

$$f(t)=\int_V d\mathbf{r}_2\,w_{12}^2\exp(-w_{12}t)\ . \tag{4.24}$$

We have also used here the fact that the microscopic interactions we take into consideration will depend only on the distance between two sites. Equation (4.17) constitutes our final result for $P_0(t)$.

The second physical quantity we want to calculate is the mean square displacement of the excitation

$$\Sigma^2(t)=\int d\mathbf{r}(r-r_0)^2P(\mathbf{r},t)\ , \tag{4.25}$$

which is the second spatial moment of the average density of excitation $P(r,t)$. Substituting the expression for the average density of excitation from Eq. (3.4) into (4.25) and taking the Laplace transform results in

$$\tilde{\Sigma}^2(s)=(N-1)\langle(\mathbf{r}_2-\mathbf{r}_1)^2\bar{g}_{12}(s)\rangle_{(2)}\ , \tag{4.26}$$

where $\bar{g}_{12}(s)$ is the conditionally averaged nondiagonal part of the Green's function, which is given by Eq. (4.14).

Again we have to perform an approximation on the set of coupled equations (4.13) and (4.14). Omitting the second term on the rhs of Eq. (4.13), i.e., we represent the averaged diagonal part of **g** by the waiting time distribution only, we formally decouple Eqs. (4.13) and (4.14) and obtain

$$\bar{g}_{12}=\overline{g_1^0}\ \overline{w_{12}\,g_2^0}+(N-2)\langle\bar{g}_{13}\ \overline{w_{32}\,g_2^0}\rangle_{(3)}\ . \tag{4.27}$$

The zeroth and second moment is then easily calculated and we get

$$\langle\bar{g}_{12}\rangle_{(2)}=\bar{g}_1^0\langle\overline{w_{12}\,g_2^0}\rangle_{(2)}+(N-2)\langle\bar{g}_{13}\rangle_{(3)}\langle\overline{w_{32}\,g_2^0}\rangle_{(2)} \tag{4.28}$$

and

$$\begin{aligned}\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}&=\overline{g_1^0}\langle r_{21}^2\ \overline{w_{12}\,g_2^0}\rangle_{(2)}\\ &\quad+(N-2)\langle r_{21}^2\bar{g}_{13}\ \overline{w_{32}\,g_2^0}\rangle\ ,\end{aligned} \tag{4.29}$$

with $r_{21}=r_2-r_1$. Equation (4.28) is now recast in its final form by bearing in mind that the moments appearing in Eq. (4.26) do not any longer depend on the site variables used as indices. The second term of Eq. (4.29) can be separated into three parts with the aid of the identity

$$r_{21}^2=r_{23}^2+2r_{23}r_{31}+r_{31}^2\ . \tag{4.30}$$

Renumbering the moments and omitting the "mixed" term in Eq. (4.30), which is supposed to vanish due to symmetry considerations, we finally get a set of coupled equations

$$\langle\bar{g}_{12}\rangle_{(2)}=\overline{g_1^0}\langle\overline{w_{12}\,g_2^0}\rangle_{(2)}+(N-2)\langle\bar{g}_{12}\rangle_{(2)}\langle\overline{w_{12}\,g_2^0}\rangle_{(2)} \tag{4.31}$$

and

$$\begin{aligned}\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}&=\overline{g_1^0}\langle r_{21}^2\ \overline{w_{12}\,g_2^0}\rangle_{(2)}+(N-2)(\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}\langle\overline{w_{12}\,g_2^0}\rangle_{(2)}\\ &\quad+\langle g_{12}\rangle_{(2)}\langle r_{21}^2\ \overline{w_{12}\,g_2^0}\rangle_{(2)})\ ,\end{aligned} \tag{4.32}$$

or alternatively

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$$\langle\bar{g}_{12}\rangle_{(2)}=\overline{g_1^0}\langle\overline{w_{12}g_2^0}\rangle_{(2)}[1-(N-2)\langle\overline{w_{12}g_2^0}\rangle_{(2)}]^{-1} \tag{4.33}$$

and

$$\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}=[\overline{g_1^0}\langle r_{21}^2\,\overline{w_{12}g_2^0}\rangle_{(2)}+(N-2)\langle\bar{g}_{12}\rangle_{(2)}\langle r_{21}^2\,\overline{w_{12}g_2^0}\rangle_{(2)}]\times[1-(N-2)\langle\overline{w_{12}g_2^0}\rangle_{(2)}]^{-1} \, . \tag{4.34}$$

Substituting Eq. (4.33) into (4.34), we obtain

$$\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}=\overline{g_1^0}\langle r_{21}^2\,\overline{w_{12}g_2^0}\rangle_{(2)}\times[1-(N-2)\langle\overline{w_{12}g_2^0}\rangle_{(2)}]^{-2} \, . \tag{4.35}$$

At this stage, we can utilize the local continuity relation, i.e., that the change of the population at a site 1 is equal to the flux out of this site

$$\frac{\partial}{\partial t}Q(t)=-\sum_m{}' \, w_{m1}Q(t) \, , \tag{4.36}$$

where $Q(t)$ is defined by Eq. (4.19). We obtain by taking the LT of Eq. (4.36) and formally averaging over all configurations

$$s\,\overline{g_1^0}=1-(N-1)\langle\overline{w_{21}g_1^0}\rangle_{(2)} \, . \tag{4.37}$$

In the thermodynamic limit, Eq. (4.35) takes the form

$$\langle r_{21}^2\bar{g}_{12}\rangle_{(2)}=s^{-2}\langle r_{21}^2\,\overline{w_{12}g_2^0}\rangle_{(2)}/\overline{g_2^0} \, . \tag{4.38}$$

Substituting Eq. (4.38) into (4.26), we finally obtain the desired expression for the Laplace transform of the mean square displacement

$$\tilde{\Sigma}^2(s)=s^{-2}(N-1)\langle r_{21}^2\,\overline{w_{12}g_2^0}\rangle_{(2)}\cdot\overline{g_2^0}^{\,-1} \, , \tag{4.39}$$

which reads explicitly

$$\tilde{\Sigma}^2(s)=\int_0^\infty dt\,e^{-st}\Phi(t)\chi(t)/s^2\tilde{\Phi}(s) \, , \tag{4.40}$$

with $\Phi(t)$ being the waiting function (4.19) and

$$\chi(t)=4\pi\rho\int_0^\infty dr\,r^4 w(r)\exp[-w(r)t] \, . \tag{4.41}$$

Equation (4.39) constitutes the second final result of the ADEA.

V. STOCHASTIC APPROACH: CONTINUOUS TIME RANDOM WALK (CTRW)

This approach offers a very nice and physically transparent picture of the hopping migration process in disordered systems, at least as far as the basic understanding is concerned. We shall demonstrate that the final result for the mean square displacement agrees exactly with the ADEA result (4.39).

The CTRW constitutes a description of a stochastic process which incorporates the essential physical features of hopping EET among a random spatial distribution of impurity sites.[28-33] This approach simulates the hopping process among randomly located sites by a CTRW on a discrete lattice which is characterized by a distribution of hopping times. The basic underlying assumption for the applicability of the CTRW is that the spread in the impurity spacings is mild relative to the large dispersion in the hopping times. In view of the strong dependence of the transition probability for a single hop on the interimpurity spacing, this assumption is reasonable.

We shall now outline the basic results of the CTRW.[30-33] The average density of excitation can be expressed in the form

$$P(\mathbf{r},t)=\int_0^t d\tau\,R(r,\tau)\Phi(t-\tau) \, , \tag{5.1}$$

where $R(\mathbf{r},t)$ is the probability per unit time to reach the site $\mathbf{r}$ at time t in an arbitrary number of steps while $\Phi(t)$ is the waiting time function [Eq. (4.19)] which corresponds to the probability for the excitation to remain fixed in the time interval $[0,t]$. Both functions appearing in the integral in Eq. (5.1) can be expressed by means of the joint distribution function $\psi(\mathbf{r},t)$ of a (random) hopping event, which represents the probability per unit time for a single hopping event to occur in the time interval $[t,t+\Delta t]$ over a distance $\mathbf{r}$. In order to establish a recurrence relation for the probability to arrive at time t at a certain site $\mathbf{r}$ in n steps, one has to make the following considerations: In the usual random walk on a lattice,[29] it is assumed that the time interval between two consecutive hops is constant. The process is essentially Markovian. For a random distribution of impurities on a lattice, this assumption is no more valid due to the distribution of transition probabilities. If we consider instead the time intervals between consecutive steps as independent random variables, which are characterized by a common distribution, for an ensemble of identical systems, then the process is semi-Markovian[34] in the sense that the future of the migrating species is not only determined by the probability of occupation of a site $\mathbf{r}$, but also by the time distribution to arrive at the next site. The recurrence relation can then be set up according to

$$R_0(\mathbf{r},t)=\delta_{\mathbf{r},\mathbf{r}_0}\delta(t-0) \, , \tag{5.2}$$

$$R_1(\mathbf{r},t)=\sum_{\mathbf{r}'}\int_0^t d\tau\,\psi(\mathbf{r}-\mathbf{r}';t-\tau)R_0(\mathbf{r}',\tau)=\psi(\mathbf{r}-\mathbf{r},t) \, , \tag{5.3}$$

and hence

$$R_{n+1}(\mathbf{r},t)=\sum_{\mathbf{r}'}\int_0^t d\tau\,\psi(\mathbf{r}-\mathbf{r}';t-\tau)R_n(\mathbf{r}',\tau) \, . \tag{5.4}$$

Performing the summation over n and inserting the initial condition (5.2) with $\mathbf{r}_0=0$ gives

$$R(\mathbf{r},t)-\sum_{\mathbf{r}'}\int_0^t d\tau\,\psi(\mathbf{r}-\mathbf{r}',t-\tau)R(\mathbf{r}',\tau)=\delta_{\mathbf{r},0}\delta(t-0) \, . \tag{5.5}$$

Taking the Laplace transform of Eq. (5.5) reduces the integral equation (5.5) to an algebraic equation

$$\tilde{R}(\mathbf{r},s)-\sum_{\mathbf{r}'}\tilde{\psi}(\mathbf{r}-\mathbf{r}',s)\tilde{R}(\mathbf{r}',s)=\delta_{\mathbf{r},0} \, , \tag{5.6}$$

which in the case of an infinite lattice or by imposing periodic boundary conditions can be solved by means of Fourier transforms

$$\tilde{U}(\mathbf{k},s)=\sum_{\mathbf{r}}\tilde{R}(\mathbf{r},s)\exp(-i\mathbf{k}\cdot\mathbf{r}) \, . \tag{5.7}$$

The LT of $R(\mathbf{r},t)$, i.e.,

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$$\tilde{R}(\mathbf{r}, s) = N^{-3} \sum_{k} \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{1 - \Lambda(k, s)} , \tag{5.8}$$

where N is the number of lattice sites and $\mathbf{k}$ the lattice quasimomentum is then expressed in terms of the generalized structure factor for CTRW:

$$\tilde{\Lambda}(k, s) = \sum_{\mathbf{r}} \tilde{\psi}(\mathbf{r}, s) \exp(-i\mathbf{k} \cdot \mathbf{r}) . \tag{5.9}$$

To find the LT of $P(\mathbf{r}, t)$, we still have to specify the waiting time function [Eq. (4.19)], which can be expressed in the alternative form

$$\Phi(t) = 1 - \int_0^t d\tau\, \psi(\tau) , \tag{5.10}$$

where

$$\psi(t) = \sum_{\mathbf{r}} \psi(\mathbf{r}, t) \tag{5.11}$$

is the distribution function of hopping times.

Taking the LT of Eq. (5.1), one finally gets an explicit expression for the excitation probability

$$\tilde{P}(\mathbf{r}, s) = \tilde{R}(\mathbf{r}, s) \tilde{\Phi}(s) , \tag{5.12}$$

where

$$\tilde{\Phi}(s) = s^{-1}[1 - \tilde{\psi}(s)] . \tag{5.13}$$

The time development of the initial site-excitation probability is then simply given by

$$\begin{aligned} \tilde{P}(0, s) &= \tilde{R}(0, s) \tilde{\Phi}(s) \\ &= \tilde{\Phi}(s) \cdot N^{-3} \sum_{\mathbf{k}} [1 - \tilde{\Lambda}(\mathbf{k}, s)]^{-1} , \end{aligned} \tag{5.14}$$

where the sum gives the corrections due to the possibility that the excitation comes back to the site it initially started off after an arbitrary number of steps.

From Eqs. (5.12), (5.13), and (4.25), we also derive an explicit expression for the LT of the mean square displacement

$$\tilde{\Sigma}^2(s) = \sum_{\mathbf{r}} r^2 \tilde{\psi}(\mathbf{r}, s) / s^2 \tilde{\Phi}(s) . \tag{5.15}$$

The final step in this analysis requires the specification of the distribution function of the one-step hopping times which can be approximated in the form[28]

$$\psi(\mathbf{r}_1, t) = v\rho\, w(r_1) \exp[-w(r_1)t]\, \Phi(t) , \tag{5.16}$$

where $\Phi(t)$ is again the waiting time function [Eq. (4.19) or (5.10)], the exponential in Eq. (5.16) being the waiting time probability with respect to the jump to site $\mathbf{r}_1$, with $w(r_1)$ being the single-site jump probability to that site, and finally $v\rho$ with $v = V/N$ is the probability of site $\mathbf{r}_1$ being an accessible impurity site.

Equation (5.15) together with Eq. (5.16) results in the final form for $\tilde{\Sigma}^2(s)$ within the framework of the CTRW which is identical with the ADEA result [Eq. (4.39)]. This result establishes an important interrelationship between the ADEA, which starts from the master equation, and the CTRW, which rests on a stochastic, random walk picture. It should be noted that this exact correspondence between the two diverse approaches has been established for the mean square displacement and also for the time-dependent diffusion coefficient. On the other hand, the explicit expressions (4.17) and (5.14) derived for $P_0(t)$ in the framework of the ADEA and the CTRW, respectively, have similar structure, but the interrelationship between these results has not been established.

VI. APPLICATION OF THE AVERAGED DYSON EQUATION APPROACH TO MULTIPOLAR INTERACTIONS

In this chapter, we shall now give explicit expressions for the Laplace transforms of the initial site-excitation probability $P_0(t)$ and the mean square displacement $\Sigma^2(t)$ for a general class of multipolar interactions. For the time being, we shall confine ourselves to the orientationally averaged form of the interaction, neglecting any effects due to the possible anisotropy of the interaction. We then have for the transition probability

$$w(\mathbf{r}) = \tau^{-1}(R_0/r)^n , \quad n = 6, 8, 10, \ldots , \tag{6.1}$$

where τ is the lifetime of the electronic excitation and R_0 is the critical radius for EET.[12]

To perform the configurational averages in Eqs. (4.39) and (4.17), it turned out to be necessary to transform back to time variables, then to perform the averages, and finally do a LT on the result. The reason for this elaborate procedure lies in the nature of the vertex function, which is a nonlocal quantity with a LT which is not separable with respect to the spatial coordinates.

Assuming that the spatial coordinates can be treated as independent random variables homogeneously distributed in a volume V, the configurational average of the characteristic quantity in our description, the waiting time function (4.19) which is discussed in Appendix B, results in

$$\Phi_n(t) = \exp(-\lambda T^{\nu}) , \tag{6.2}$$

with

$$\begin{aligned} \lambda &= \bar{c}\Gamma(1 - \nu) , \\ \nu &= 3/n , \\ T &= t/\tau , \end{aligned} \tag{6.3}$$

where the effective number of impurities in the critical volume is $\bar{c} = \rho[(4\pi/3)R_0^3]$, with ρ being the impurity number density, T represents a reduced time, and n specifies the order of the multipolar interaction according to Eq. (6.1). It should be noted that Eq. (6.2) constitutes an asymptotic limit in the continuum approximation, so that corrections for the effects of discrete lattice structure, which are expected to be exhibited at extremely short times,[18] will be ignored in the present analysis.

The LT of Eq. (6.2), i.e.,

$$\tilde{\Phi}_n(s) = \tau\, \tilde{\Phi}_n(u) , \tag{6.4}$$

with

$$\tilde{\Phi}_n(u) = \int_0^{\infty} dT\, e^{-uT} \exp(-\lambda T^{\nu}) \tag{6.5}$$

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and $u = s\tau$, can then be given in terms of its asymptotic series expansions,[35] i.e., for large values of u,

$$\tilde{\Phi}_n(u) = u^{-1}\sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\Gamma(m\cdot\nu+1)z^m , \tag{6.6}$$

with

$$z = \lambda u^{-\nu} , \tag{6.7}$$

and for small values of u,

$$\tilde{\Phi}_n(u) = \left(\frac{1}{\nu}\right)\lambda^{-1/\nu}\sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\Gamma[(m/\nu)+(1/\nu)]z^m , \tag{6.8}$$

with

$$z = \lambda^{-1/\nu}u . \tag{6.9}$$

The short-time [Eq. (6.6)] and the long-time [Eq. (6.8)] asymptotic expansions of the waiting time function are valid for any multipolar interaction. Only for the case of dipole–dipole interaction, i.e., $n=6$, could we find a closed expression for the waiting time function in terms of the complementary error function[36]:

$$\tilde{\Phi}_6(u) = u^{-1}[1 - \pi^{1/2}z\exp(z^2)\operatorname{erfc}(z)] , \tag{6.10}$$

with

$$z = \lambda/(2u^{1/2}) . \tag{6.11}$$

After establishing the explicit form of the waiting time function, we are in a position to provide explicit results for $P_0(t)$ and for $\Sigma^2(t)$. To calculate now the LT of $P_0(t)$, we substitute Eq. (6.1) into Eqs. (4.17) and (4.22) and obtain the final result

$$\tilde{P}_0(s) = \tau\,\tilde{\Phi}(u)[1-\tilde{F}(u)]^{-1} , \tag{6.12}$$

where

$$\tilde{F}(u) = \nu(1-\nu)\Gamma(1-\nu)\bar{c}\int_0^{\infty} dT\, e^{-uT}T^{\nu-2}[\Phi(T)^*\Phi(T)] . \tag{6.13}$$

$\tilde{F}(u)$ could be evaluated analytically by means of a series expansion up to $\bar{c}=1$. The details of this procedure are outlined in Appendix C. For higher values of $\bar{c}$ (>1), we have evaluated $\tilde{F}(u)$ by applying numerical integration methods, which were checked by comparison with the analytical results for low $\bar{c}$ values.

To obtain in a similar manner an expression for the mean square displacement, we rewrite Eq. (4.39) in the form

$$\tilde{\Sigma}^2(s) = \left[\int_0^{\infty} dt\, e^{-st}C(t)\Phi(t)\right][s^2\,\tilde{\Phi}(s)]^{-1} , \tag{6.14}$$

with

$$C(t) = 4\pi\rho\int_0^{\infty} dr\, r^4 w(r)\exp[-w(r)t] . \tag{6.15}$$

Substituting now the general form of the interaction $w(r)$ [Eq. (6.1)], we finally get the result

$$\tilde{\Sigma}^2(s) = \nu\Gamma(1-\mu)\bar{c}R_0^2\tau\,\tilde{J}(u)/[u^2\tilde{\Phi}(u)] , \quad \mu = 5/n , \tag{6.16}$$

where

$$\tilde{J}(u) = \int_0^{\infty} dT\, e^{-uT}T^{\mu-1}\Phi(T) . \tag{6.17}$$

For the special case $n=6$, i.e., dipole–dipole interaction, Eq. (6.17) has a closed solution in terms of a parabolic cylinder function $D_\alpha(z)$ of a complex argument z[36]:

$$\tilde{J}_6(u) = 2^{1/6}\Gamma(5/3)u^{-5/6}\exp(z^2/4)D_{-5/3}(z) , \tag{6.18}$$

with $z = \lambda/(2u)^{1/2}$. In all the other cases, $\tilde{J}(u)$ is given by its asymptotic series expansions,[35] i.e., for large u,

$$\tilde{J}(u) = u^{-\mu}\sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\Gamma(m\cdot\nu+\mu)z^m , \tag{6.19}$$

with

$$z = \lambda u^{-\nu} , \tag{6.20}$$

and for small u values,

$$\tilde{J}(u) = \frac{1}{\nu}\lambda^{-\mu/\nu}\sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\Gamma\left(\frac{m+\mu}{\nu}\right)z^m , \tag{6.21}$$

with

$$z = \lambda^{-1/\nu}u . \tag{6.22}$$

Equation (6.16) is now amenable to numerical calculations which are given below. Before doing so, it will be instructive to consider two limiting cases of this final result.

A. Asymptotic behavior

Before discussing the asymptotic behavior, we present the relation between the LT's of the mean square displacement $\Sigma^2(t)$ and the time dependent diffusion coefficient $D(t)$ which has been defined in Eq. (1.2). The LT of Eq. (1.2) is obtained using the relation

$$\begin{aligned}\int_0^{\infty} dt\, e^{-st}\frac{\partial}{\partial t}P(\mathbf{r},t) &= s\tilde{P}(\mathbf{r},s) - P(\mathbf{r},0)\\ &= s\tilde{P}(\mathbf{r},s) - \rho\delta(r-r_0) ,\end{aligned} \tag{6.23}$$

being simply given by

$$\tilde{D}(s) = \frac{s}{6}\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_0)^2\tilde{P}(r,s) = \frac{s}{6}\tilde{\Sigma}^2(s) . \tag{6.24}$$

B. Short-time limit

The short-time limit corresponds to the short-time low concentration domain, where the pair approximation[21–23] is valid. If we take just the first few terms of the asymptotic expansions (6.6) and (6.19) for large values of u

$$\tilde{\Phi}(u) = u^{-1}[1 - \Gamma(\nu+1)\lambda u^{-\nu} + \tfrac{1}{2}\Gamma(2\nu+1)\lambda^2u^{-2\nu} - \cdots] \tag{6.25}$$

and

$$\tilde{J}(u) = u^{-\mu}[\Gamma(\mu) - \Gamma(\nu+\mu)\lambda u^{-\nu} + \tfrac{1}{2}\Gamma(2\nu+\mu)\lambda^2u^{-2\nu} - \cdots] , \tag{6.26}$$

respectively, we get the leading terms of an expansion of the mean square displacement in powers of the impurity concentration $\bar{c}$:

$$\begin{aligned}\tilde{\Sigma}^2(s) &= \nu\Gamma(1-\mu)\Gamma(\mu)\bar{c}R_0^2\tau\, u^{-1-\mu}\\ &\quad\times\{1 + [\Gamma(\nu+1) - \Gamma(\nu+\mu)/\Gamma(\mu)]\lambda u^{-\nu} + \cdots\} ,\end{aligned} \tag{6.27}$$

which for the special case of dipole–dipole interaction takes the explicit form

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TABLE I. Coefficients a_1 and a_2 in the expression for the short-time/low-density limit of the LT of the mean square displacement according to Eq. (6.28).

	a_1	a_2
DE[22]	2.7988	0.3892
SCDM[25]	2.799	0.5182
ADEA/CTRW	3.1416	0.5297
ADEA/CTRW(BT)	2.7988	0.3337

$$\tilde{\Sigma}_6^2(s) = a_1 \bar{c} R_0^2 \tau^{-5/6} s^{-11/6} + a_2 \bar{c}^2 R_0^2 \tau^{-4/3} s^{-7/3} + 0(s^{-17/6}) , \qquad (6.28)$$

with the numerical values of the coefficients a_1 and a_2 being given in Table I. The functional form of Eqs. (6.27) and (6.28) is identical with the results which have been previously obtained by Haan and Zwanzig from the solution of the master equation within the pair approximation and by means of a general scaling argument.[22] The present derivation of these old results by our ADEA/CTRW method inspires some confidence in the present approach, although we have to point out that the numerical values of the coefficients a_1 and a_2 are slightly different from those resulting of the density expansion of Haan and Zwanzig or from the recent SCDM of GAF (Table I). The reason for these deviations is quite simple. The semi-Markovian approach we have pursued corresponds to a self-avoiding walk approximation where only a *single* hop in the chain of hopping events is correlated. Thus, we allow only for the simplest contribution of interferences of the hopping process with the waiting time distribution and we completely discard interferences between actual jumps (backtransfer events).

Backtransfer can be taken into account in a heuristic manner, by including the effects of twofold exchange of excitation between impurity pairs as done by Huber *et al.*[37] This first order correction does not modify the time dependence of the waiting time probability, but just changes the numerical value of the exponent λ in Eq. (6.2). The waiting time function now is

$$\Phi_{\mathrm{BT}}(T) = \exp[-2^{\nu-1}\Gamma(1-\nu)\bar{c}T^{\nu}] \qquad (6.29)$$

and the corresponding hopping time distribution takes the form

$$\psi_{\mathrm{BT}}(\mathbf{r}, T) = \rho\nu\, w(r) \exp[-2\tau w(r) T] \Phi_{\mathrm{BT}}(T) \ . \qquad (6.30)$$

This empirical procedure, which leaves the functional form of $\Phi(t)$ invariant, just modifies the numerical coefficients in Eq. (6.28), which are again presented in Table I, being very close to the result reported by Haan and Zwanzig. Although this approach is not self-consistent, it is nevertheless quite remarkable that the short-time or low density features of dispersive transport are well established within our model. The importance of certain diagrams may also be understood in a more obvious way within our simple model than in the SCDM.

Equations (6.27) and (6.28) may easily be inverted term by term and we finally get for the short-time limit

$$\Sigma_6^2(T) = 1.063 a_1 \bar{c} R_0^2 T^{5/6} + 0.839 a_2 \bar{c}^2 R_0^2 T^{4/3} + 0(T^{11/6}) , \qquad (6.31)$$

$$D_6(T) = 0.147 a_1 \bar{c} \frac{R_0^2}{\tau} T^{-1/6} + 0.105 a_2 \bar{c}^2 \frac{R_0^2}{\tau} T^{1/3} + 0(T^{5/6}) \ . \qquad (6.32)$$

The validity condition for the short-time limit is $z = \lambda^{-1/\nu} u < 1$. Invoking Eqs. (6.3), (6.4), and (6.8), we get

$$(t/\tau) < [\Gamma(1-3/n)\bar{c}]^{-n/3} \ . \qquad (6.33)$$

Setting $\bar{c} = x(4\pi/3\delta)(R_0/d)^3$, where d is the lattice constant, δ (~1) a numerical coefficient depending on the lattice structure, and x the impurity mole fraction, we get

$$(t/\tau) < [(4\pi/3\delta)\Gamma(1-3/n) \times (R_0/d)^3]^{-n/3} \ . \qquad (6.34)$$

Three general features of this result should be noted. First, $(t/\tau) < x^{-n/3}$ and the short-time limit prevails for low concentrations, as expected. Second, for the common case of a long-range dipole–dipole interaction where $n = 6$ and where common values of R_0/d are in the range 5–10, the validity range of the pair approximation which exhibits the short-time limit is rather limited. Thus, for $x = 0.01$ and $R_0/d = 5$, we get $(t/\tau) < 3 \times 10^{-2}$. Third, the upper time limit for the validity of the pair approximation strongly depends on (R_0/d). For high-order short range multipolar interactions, or for short range exchange interactions $R_0/d \sim 1$ and in this case for sensible values of $x = 0.01$–10, the upper limit for (t/τ) will be large. For example, taking $n = 12$, $x = 0.01$, and $R_0/d = 2$, we get the astronomical upper limit $(t/\tau) < 10^4$ and transport will never become diffusive. We thus conclude that, for short-range interactions, dispersive diffusion effects will prevail over a broad concentration and time domain.

Our formalism is not limited to the short time region and we proceed to consider the second extreme case.

C. Long-time limit

Now we consider the small frequency limit where the leading terms of Eqs. (6.8) and (6.21) are

$$\begin{aligned} \tilde{\Phi}(u) &= 1/\nu\, \lambda^{-1/\nu} \Gamma(1/\nu) , \\ \tilde{J}(u) &= 1/\nu\, \lambda^{-\mu/\nu} \Gamma(\mu/\nu) , \end{aligned} \qquad (6.35)$$

respectively and $u \to 0^+$, from which we obtain for the mean square displacement

$$\tilde{\Sigma}^2(s) = \alpha(\mu, \nu) R_0^2 \tau u^{-2} , \qquad (6.36)$$

with

$$\alpha(\mu, \nu) = \nu \frac{\Gamma(1-\mu)}{\Gamma(1/\nu)} \Gamma(\mu/\nu) \times \Gamma(1-\nu)^{(1-\mu)/\nu} \bar{c}^{(1+\nu-\mu)/\nu} \ . \qquad (6.37)$$

Equation (6.36) as well as Eq. (6.24) for the diffusion coefficient are immediately inverted resulting in

$$\Sigma^2(t) = \alpha(\mu, \nu) R_0^2 T ; \qquad (6.38)$$

and we find that the long-time result exhibits the characteristics of a conventional diffusion process where

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TABLE II. Long-time diffusion coefficient $D = D^{\infty} \cdot \bar{c}^{(n-2)/3} R_0^2 \tau^{-1}$ for multipolar interactions with $n = 6-12$ and $\bar{c} = 1$.

n	6	8	10	12
D^{∞}	0.5068	0.1275	0.0445	0.0154
D^{∞} (BT)	0.4022	0.0638	0.0140	0.0031

$\Sigma^2(T) \propto T$ and $D(T) = \alpha(\mu, \nu) R_0^2/6\tau$ is independent of T.

Table II gives the long-time diffusion coefficients for various multipolar interactions with and without backtransfer being taken into account. Our result for long time EET in an impurity band is characterized by the same functional form as that obtained for the diffusion coefficient of the electronic excitation on a superlattice. For example, for the special case of dipole–dipole interaction ($n = 6$), the long-time diffusion coefficient (Table II) is quite close to that for a regular lattice, e.g., for a SC lattice, $D/(\bar{c}^{4/3} R_0^2/\tau) = 0.409$.

The validity condition for the onset of long-time behavior is, according to Eq. (6.9), $z = \lambda^{-1/\nu} u < 1$, which implies that

$$(t/\tau) > [\Gamma(1 - 3/n)\bar{c}]^{-n/3}. \tag{6.39}$$

This result is complementary to Eq. (6.33).

VII. NUMERICAL CALCULATIONS

We have conducted a series of numerical model calculations for the three pertinent experimental observables: the initial site-excitation probability $P_0(t)$, the mean square displacement of the excitation $\Sigma^2(t)$, and the time dependent diffusion coefficient $D(t)$. These calculations were performed using our ADEA/CTRW scheme where $P_0(t)$ was expressed by Eqs. (6.12) and (6.13) while $\Sigma^2(t)$ and $D(t)$ are given in terms of Eqs. (6.16) and (6.21), respectively. The LT's from the frequency to the time domain were calculated using the numerical procedure by Stehfest.[38] The ADEA/CTRW results were compared with the Haan and Zwanzig results which originate from a density expansion and with the recent results of GAF who utilized the self-consistent diagrammatic method (Appendix A). Numerical data will be reported to explore the dependence of energy transport on the range of the multipolar interaction varying n in Eq. (6.1) in the range $n = 6-12$, and to investigate the concentration dependence of the EET process varying the reduced concentration of the impurity in the range $\bar{c} = 1-10$, so that the impurity mole fraction is $x = \bar{c}(3\delta/4\pi)(d/R_0)^3$. The time dependence of the observables was investigated in the range $T = t/\tau = 0-2$ as due to the finite lifetime of the excitation longer times are of no interest.

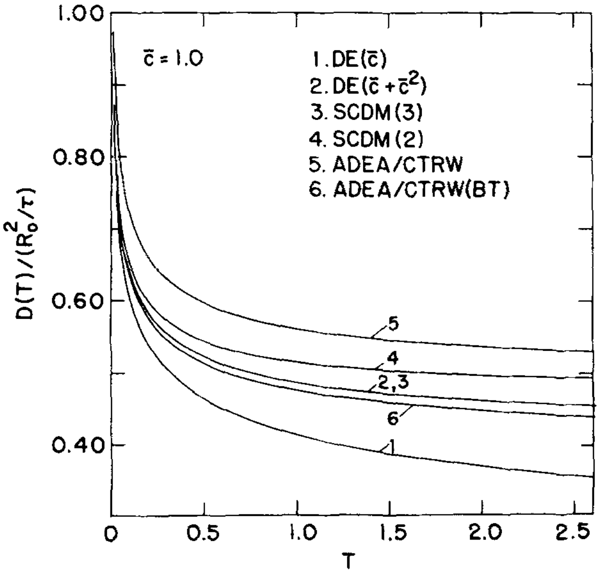

FIG. 1. The time dependent diffusion coefficient $D(T)$ for dipole–dipole coupling ($n = 6$) and impurity concentration $\bar{c} = 1.0$. In this figure, a comparison is given of the results obtained within three different schemes: the first order DE($\bar{c}$) [curve (1)] and the second order DE($\bar{c} + \bar{c}^2$) [curve (2)] density expansion (Ref. 22), the three-body SCDM(3) [curve (3)] and the two-body SCDM(2) [curve (4)]. SCDM results (Ref. 25) and the results obtained by the ADEA/CTRW method without [curve (5)] and with [curve (6)] backtransfer taken into account.

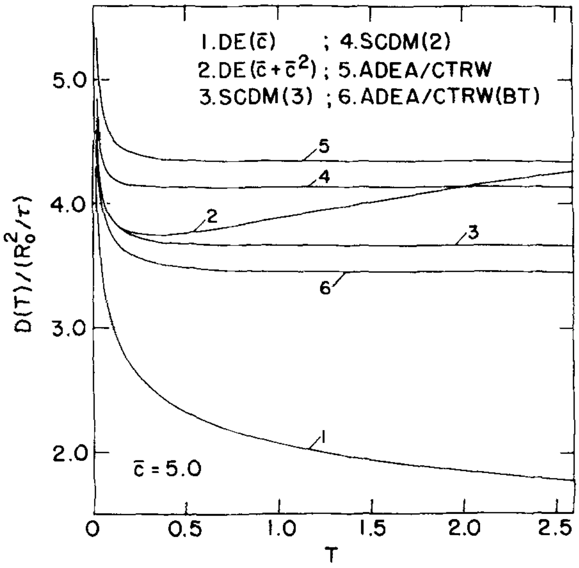

FIG. 2. The time-dependent diffusion coefficient $D(T)$ for dipole–dipole coupling ($n = 6$) and impurity concentration $\bar{c} = 5.0$. Figure 2 presents again a comparison of the results obtained by the three methods DE, SCDM, and ADEA/CTRW demonstrating the behavior in the crossover region between dispersive and diffusive transport. Notation identical with that of Fig. 1.

First, we confront the results of our method with results obtained by other methods. In Figs. 1 and 2, we have compared our results for the time-dependent diffusion coefficient for $n = 6$ to the two low-order results from a density expansion as well as to those recently obtained by the SCDM. For $\bar{c} = 1$, dispersive transport occurs over the whole range of 3τ. All the curves of ADEA/CTRW and SCDM differ remarkably from the simple pair approximation. The ADEA/CTRW curve modified for backtransfer is close to the three-body corrected result of Haan and Zwanzig which is practically indistinguishable from the best approximation in SCDM. The result in SCDM, which uses the pair approximation for the self-energy, turns out to be of quite similar

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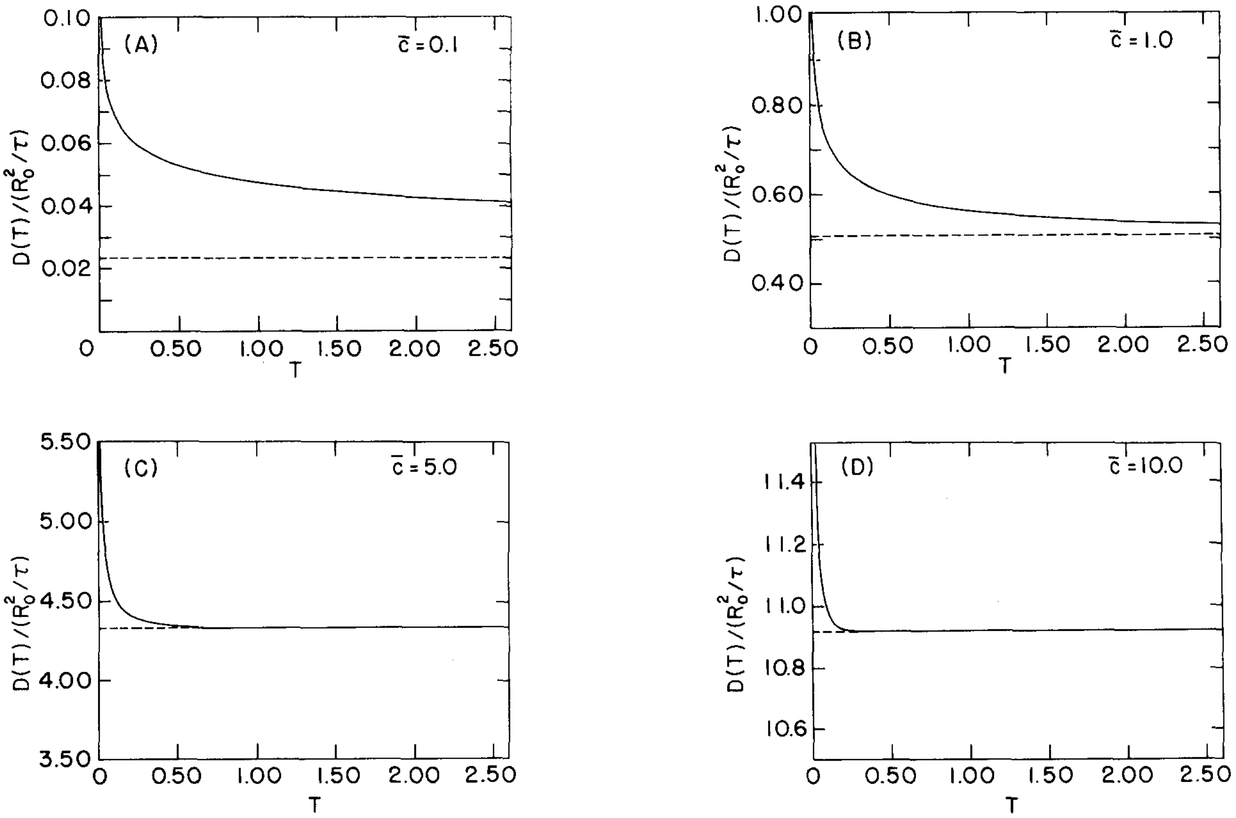

FIG. 3. The time dependence of the generalized diffusion coefficient $D(T)$ for dipole–dipole interaction ($n=6$) is shown for various impurity concentrations $\bar{c}$.

functional form as the CTRW curve except to a uniform shift along the vertical axis. For somewhat higher concentrations $\bar{c}=5$, the density expansion technique breaks down and both the pair approximation and the three-body density expansion result are inadequate. Both fail to give any meaningful result at long times ($t>\tau$) and high densities. ADEA/CTRW and SCDM again differ only with respect to the magnitude of the diffusion coefficient but not with respect to the general characteristics of its time dependence. We conclude that both our ADEA/CTRW method as well as the SCDM of GAF are adequate to establish the gross features of dispersive diffusion for EET determined by dipole–dipole coupling ($n=6$) over the entire time and concentration domains.

Second, we shall consider the cardinal problem of the crossover from the dispersive to the pure diffusive behavior. Numerical calculations were conducted using the ADEA/CTRW method over a broad concentration range $\bar{c}=0.1$–10. Typical results for the $n=6$ case are portrayed in Fig. 3. At very low concentration $\bar{c}=0.1$–1.0 [or $x=2\times10^{-4}$–2×10^{-3} for $(d/R_0)=1/5$], pure dispersive diffusion is exhibited over the entire time region of interest. Unfortunately, at these low concentrations, the diffusion length is rather low being of the order of $L\sim R_0\bar{c}^{4/3}$ so that for $\bar{c}=1.0$ $L\sim R_0$. Deviations from conventional diffusive behavior due to dispersive transport will be extremely difficult to observe. At higher densities $\bar{c}=5$–10, the diffusion coefficients for $n=6$ reach a constant, time-independent limiting value at $t/\tau>0.3$. This result is in accord with the qualitative predictions of Eqs. (6.34) and (6.39). For large densities $\bar{c}>10$ ($x>0.02$ for $d/R_0=1/5$), the dipole–dipole induced EET exhibits essentially only diffusive transport. The experimental verification of the theoretical results for the effects of dispersive diffusion in the case of long-range dipole–dipole coupling will require very careful experimental work to establish small deviations from conventional diffusive transport at the intermediate concentration range $\bar{c}\sim5$–10 ($x\sim0.01$).

The second relevant physical variable which might influence the crossover point from dispersive to diffusive transport is the range of the interaction potential and the excitation transition probability [Eq. (6.1)] between the impurities. As shown in Figs. 4 and 5 for the densities $\bar{c}=1$ and $\bar{c}=5$, respectively, the crossover to diffusive transport is shifted to larger times the more short ranged the interaction becomes, which is in accord with the predictions of Eq. (6.34). To explain this interesting feature, we assert that spatial inhomogeneity due to the random distribution of impurities is more easily averaged out in the case of long-ranged interactions like dipole–dipole ($n=6$) than in the case of short-ranged interactions like higher multipoles ($n>6$) or exchange. The effects of dispersive diffusion should become more pronounced for EET dominated by short-range interactions and this novel and interesting feature should be amenable to experimental observation.

To provide some quantitative predictions regarding the effects of dispersion of $D(t)$ on EET in an impurity band, we have calculated the diffusion length $L=[\Sigma^2(t)]^{1/2}$ at $t=\tau$ for $n=6$ and for $n=10$ as a function of the im-

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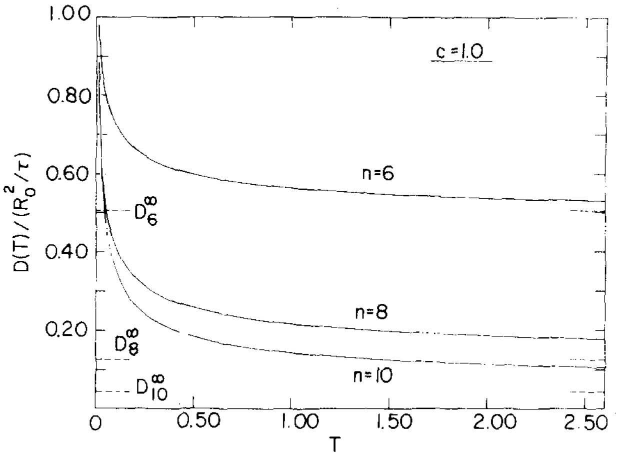

FIG. 4. Time dependence of $D(T)$ at $\bar{c}=1.0$ for multipolar interactions of order $n=6$, 8, 10.

purity concentration $\bar{c}$. In Fig. 6, we present the $\bar{c}$ dependence of L together with the values of the conventional diffusion length obtained from the relation $L=(6D\tau)^{1/2}$, where D is the long time diffusion coefficient of Table II. The deviations from ordinary diffusion are much more pronounced in the case of short-ranged interactions, as expected.

Finally, after considering the mean square displacement and the time-dependent diffusion coefficient, we turn to consider the third experimental observable, the initial site-excitation probability $P_0(t)$. P_0 is of considerable interest as it can be experimentally determined from laser fluorescence line narrowing experiments and, moreover, the combination of picosecond optical excitation techniques with ultrafast fluorescence interrogation methods using streak cameras will enable the monitoring of this observable on the psec time scale where effects of dispersive transport will be prominent. In this context, it is important to note that $P_0(t)$ can be monitored on a much shorter time scale than $\Sigma^2(t)$ and $D(t)$. In Fig. 7, we present the time dependence of P_0 for the $n=6$ case. As $P_0(t)$ is related to the waiting time function $\Phi(t)$ as is evident from Eq. (6.12), we have found it convenient to plot also $\ln P_0(t)$ vs $t^{3/n}$ (Fig. 8) according to Eq. (6.2). For $\bar{c}=1$, the simple waiting time distribution (6.2) exhibits the same time dependence $\exp(-\lambda T^{1/2})$ as the result of the SCDM with three-

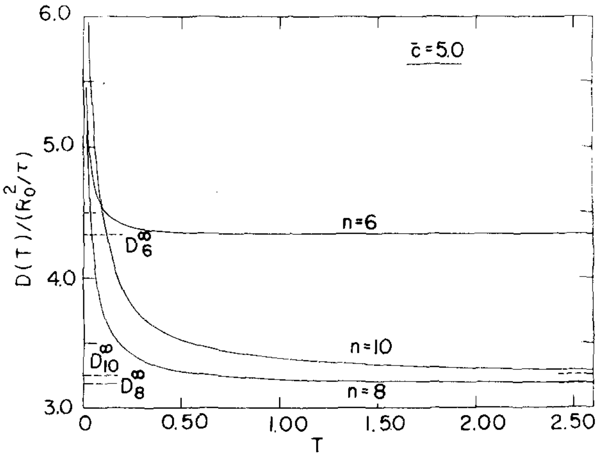

FIG. 5. Time dependence of $D(T)$ at $\bar{c}=5.0$ for $n=6$, 8, and 10.

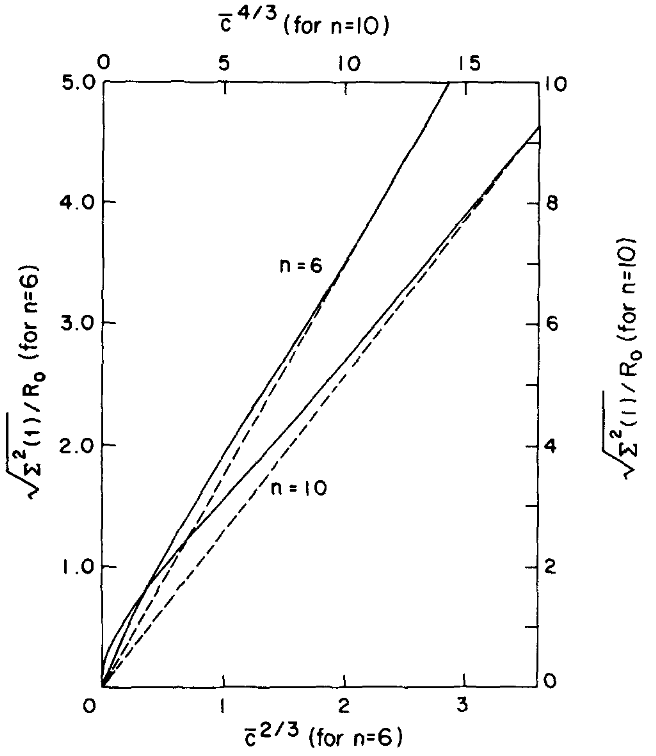

FIG. 6. The diffusion length $L=[\Sigma^2(t)]^{1/2}$ at $t=\tau$ as a function of the impurity concentration $\bar{c}$. The solid curves describe L vs $(\bar{c}^{(n-2)/3})^{1/2}$ for $n=6$ and $n=10$. The dashed curves represent the long-time diffusion length $L=(6D\tau)^{1/2}$, where D is the long time diffusion coefficient of Table II. The left vertical scale and the scale at the bottom are for the curves with $n=6$, while the right vertical scale and the scale at the top are for the curves with $n=10$.

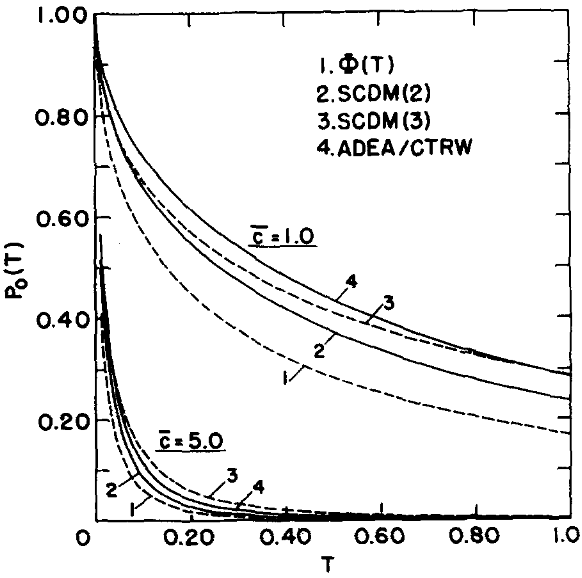

FIG. 7. The time dependence of $P_0(t)$ is shown for $n=6$ and impurity densities $\bar{c}=1.0$ and $\bar{c}=5.0$. The figure presents a comparison between the simple waiting time function $\Phi(t)$ [Eq. (4.19)], the two-body and the three-body SCDM results, and the result by the ADEA/CTRW method.

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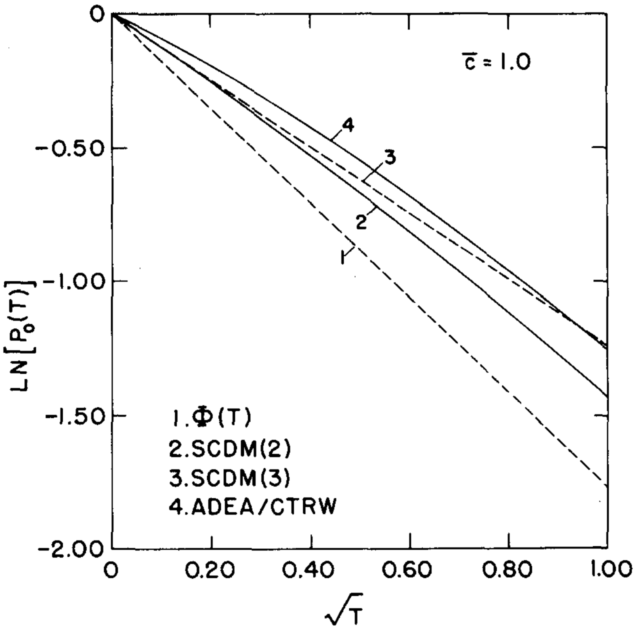

FIG. 8. The time dependence of the natural logarithm of $P_0(t)$ is displayed versus $T^{1/2}$.

body interactions taken into account in the self-energy, but the numerical value of λ is different in the two cases. This SCDM result also coincides with the heuristic initial site-excitation probability of Huber *et al.*,[37] which contains corrections for effects of back transfer. The perfect agreement may be fortuitious. Our ADEA result at $\bar{c}=1$ shows a time dependence which is quite similar to that exhibited by the SCDM when the pair approximation is applied to the self-energy; this time dependence, however, reveals some deviations from the $\exp(-\lambda T^{1/2})$ law. At higher values of $\bar{c}$, a fast decrease of $P_0(t)$ vs t is revealed and the relevant time scale for monitoring the t dependence of this quantity is shifted to shorter times.

VIII. CONCLUDING REMARKS

Four theoretical methods were recently developed to explore the characteristics of dispersive energy transport in an impurity band:

(1) the density expansion method originally advanced by Sakun[21] and by Haan and Zwanzig[22];

(2) the self-consistent diagrammatic method (SCDM) proposed by Gouchanour, Andersen, and Fayer (GAF),[25] who studied the two lowest approximations for the self-energy (pair approximation and three-body interactions) in a Dyson type equation for the average density of excitation;

(3) the stochastic continuous time random walk (CTRW) method adopted by us[26] and further developed in the present paper;

(4) the average Dyson equation approach (ADEA) proposed and explored in the present work.

The density expansion method has been extremely important in establishing the effects of dispersive, i.e., time dependent, diffusion in the short-time, low concentration domain. From the technical point of view, this approach is based on a partial summation of all diagrams in the expansion for the mean square displacement which are of first and second order in the impurity density $\bar{c}$. From the point of view of general methodology, this formalism rests on general scaling arguments. However, as demonstrated by our model calculations in Sec. VII, even the second-order density expansion fails for long times, as expected. It is apparent that the long-time behavior of $\Sigma^2(t)$ and of the diffusion coefficient cannot be deduced using the density expansion technique. Both the SCDM and the CTRW lead to the important conclusion that for long times an ordinary diffusion process is exhibited for EET in the impurity band. The SCDM of GAF and our CTRW method seem to be unrelated, as the former starts from the Haan–GAF solution to the master equation for incoherent EET while the latter rests on a description of a stochastic random walk process which simulates the energy hopping among randomly distributed impurity sites in terms of a distribution of hopping times. The interrelationship between the stochastic CTRW approach to EET and the general treatment of EET in terms of a Dyson type equation for the average density of excitation was provided in the present work by the ADEA method. Starting from the master equation for EET, we established the close relationship between the ADEA and the CTRW, demonstrating that $\Sigma^2(t)$ and $D(t)$ are identical, while $P_0(t)$ has a similar structure in both schemes.

Both our ADEA/CTRW formalism and the SCDM were utilized for numerical calculations of the pertinent experimental observables. The qualitative and quantitative information emerging from these two schemes is very similar. At the present stage of development of the theory, our ADEA/CTRW formalism seems to be more transparent as compared to the SCDM, particularly since it demonstrates how the long-time behavior is related to interference effects between direct hopping events and the contributions of the waiting time function in our approximation, or in general the diagonal part of the Green's function and to interferences of individual direct hopping steps of the exciton. From the technical point of view, it should be noted that while both our ADEA/CTRW and the SCDM can be used for numerical calculations of dispersive transport induced by dipole–dipole interactions ($n=6$), the SCDM cannot be easily adopted to study transport induced by high-order ($n>6$) multipolar interaction while our ADEA/CTRW scheme yields general results for any order of the multipolar coupling.

Several comments regarding future extensions of the SCDM and of the ADEA/CTRW schemes are now in order. From the point of view of general methodology, the SCDM (for $n=6$) can be systematically extended, in principle, to include higher-order effects, although we suspect and expect that upgrading of this method beyond the three-body approximation for the self-energy in the SCDM will be a formidable task. The ADEA/CTRW approach seems to us to be terminal as far as basic extensions of this formalism is concerned as it is practically impossible to systematically relax the approxima-

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tions (i.e., rerandomization after each hopping event) inherent in these two schemes. On the other hand, the ADEA/CTRW approach can be extended in several practical directions, which are of physical interest: (a) Technical improvements of the scheme: One may consider the possibility of using better formalisms for the waiting time function which are superior to the continuum approximation [Eq. (5.2)] utilized herein.[39] (b) Extensions to lower dimensionality: All the formalism presented herein pertains to dispersive diffusion in three-dimensional systems where the hopping probability is spatially isotropic. Incoherent EET between impurity states in systems where the exciton band structure is essentially determined by one-dimensional ($1D$) and two-dimensional ($2D$) interactions are of interest. Extensive theoretical studies[40] and computer experiments[41] were recently conducted to explore the features of incoherent EET in $1D$. Regarding $2D$ systems, we would like to emphasize that this state of affairs prevails for triplet EET in naphthalene. The ADEA/CTRW formalism can be extended in a straightforward manner for the $2D$ situation.[39]

The present formalism of dispersive transport provides a comprehensive framework for a detailed analysis of experimental data which pertain to the direct interrogation of $P_0(t)$ and of $\Sigma^2(t)$ or $D(t)$. Spectral diffusion studies as well as spatial diffusion studies provide such experimental information. Another class of interesting experimental data involves luminescence quenching of the emission from the impurity band induced by a chemical trap. The effect of dispersive transport on energy trapping from an impurity band is yet unknown. Blumen and Silbey[42] have provided a treatment of such a trapping process. However, their analysis essentially considers a diffusion controlled trapping process with the trapping rate being proportional to the long time diffusion coefficient $D \propto \bar{c}^{\gamma}$, with $\gamma = (1+\nu-\mu)/\nu = (n-2)/3$, thus disregarding the effects of dispersive diffusion. The problem of trapping from an impurity band is of considerable inherent and practical interest and deserves further study.

Dispersive EET in an impurity band falls into the broad class of dispersive transport in disordered materials, bearing a close analogy to dispersive mobility in amorphous semiconductors.[28] Experimental studies of dispersive incoherent EET, where the transition probability is determined by a power law, are amenable to a complete interpretation in terms of our theory. On the other hand, in the case of dispersive mobility for which the transition probability is exponential, some difficulties arise in the detailed derivation of the LT of the waiting time function. Thus, experimental and theoretical studies of EET in substitutionally disordered molecular solids will serve as a touchstone for the understanding of the general problem of dispersive transport.

ACKNOWLEDGMENTS

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APPENDIX A. COMMENT ON THE SELF-CONSISTENT DIAGRAMMATIC METHOD (SCDM)

For the sake of completeness, we present a brief analysis of the diagrammatic method utilized by GAF for the EET problem.[25] Starting from Eq. (4.9), we can readily write down the corresponding Dyson equation for the microscopic Green's function $\mathbf{g}$:

$$\mathbf{g} = \mathbf{g}^0 + \mathbf{g}^0 \mathbf{W} \mathbf{g} \ , \tag{A1}$$

where now the vertex function $\mathbf{g}^0$ is local, i.e., a diagonal matrix of the simple structure

$$(g^0)_{jk} = s^{-1}\delta_{jk} \ . \tag{A2}$$

Applying successively the operator identity Eq. (4.5) to Eq. (A1) results in the following identity for g_{jk}:

$$\begin{aligned} g_{jk} &= s^{-1}\tilde{g}_{jk} \ , \\ \tilde{g}_{jk} &= \delta_{jk} + s^{-1}W_{jk} + s^{-2}\sum_n W_{jn}W_{nk} + \cdots \ , \end{aligned} \tag{A3}$$

which can be expressed in the concise form

$$g_{jk} = \sum_{n=0}^{\infty} B_n(j,k) s^{-(n+1)} \ . \tag{A4}$$

The first few B_n coefficients, as well as their appropriate diagrammatic expansion, can easily be obtained and have been given in Refs. 23, 25, and 43. In performing the configurational average on Eq. (A4), approximations of a different level of sophistication have been made.

The simplest approximation is to expand the averaged Green's function in a power series in the density, which corresponds to a partial summation of Eq. (A4) by summing up all graphs of first and second orders (or even higher orders) in the impurity density. The validity of this approach is limited to short times or low densities, and nothing can be learned about the long-time behavior. The second approach is to perform a reduction of the appearing diagrams by exploiting topological equivalences and to calculate only the irreducible graphs. The first attempt along this line is due to Moore[43] in the context of electronic conduction in amorphous systems. His reduction scheme was incomplete in the sense that he did not exploit the special role of the diagonal part of the microscopic Green's function, which itself corresponds to a partial summation of irreducible diagrams. Taking advantage of this feature of the diagrammatic expansion (A4), GAF recently managed to derive a Dyson type equation for the averaged Green's function. The topological reduction they performed consisted of removing all loops which did not interfere with the path of migration by renormalizing the vertex by the averaged diagonal Green's function. The simplified path, which still contained loops and which however interfered with the path of migration, was then further reduced to a simple connection of irreducible graphs. These irreducible graphs are diagrams which cannot be further divided along an interaction line. The sum of these irreducible

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graphs represents the self-energy of the problem and is due to the renormalization of the vertices itself a function of the averaged diagonal Green's function $G^s(s)$. The pseudo-Dyson equation then reads

$$G(k,s)=\frac{G^s(s)}{1-\rho G^s(s)\tilde{\Sigma}[k,G^s(s)]} . \tag{A5}$$

Although this has been an important step forward to the solution of the problem, there still remained the task to solve for the diagonal averaged Green's function. Haan and Zwanzig were the first who pointed out the important sum rule

$$\lim_{k\to 0} G(k,s)=1/s , \tag{A6}$$

which just indicates the conservation of probability. By means of this sum rule, GAF found the relation between the self-energy and the diagonal Green's function

$$G^s(s)=\frac{1}{s+\rho\hat{\Sigma}[0,G^s(s)]} . \tag{A7}$$

Equation (A7) allowed one to obtain good solutions to $G^s(s)$ which is identical to the LT of initial site-excitation probability $P_0(t)$, while staying in a reasonable low approximation for Σ (pair or three-body approximations).

As will become obvious by comparing the numerical results, there are only slight differences between this self-consistent scheme and the ADEA/CTRW described in Secs. IV and V.

APPENDIX B. THE WAITING TIME FUNCTION $\Phi(t)$

In this Appendix, we shall derive the waiting time function $\Phi(t)$ [Eq. (4.19)] within the continuum approximation. The physical situation we consider is a single excited donor in the presence of N_A acceptors distributed at random around the donor site. The question we ask then is as follows: What is the probability $Q(t)$ to find the excitation still localized at the donor site at some time t? $Q(t)$ obeys a simple linear differential equation

$$\frac{\partial}{\partial t}Q(r=0,t)=-\sum_{k=1}^{N_A} w_{0r_k}Q(r=0,t) , \tag{B1}$$

with the initial condition

$$Q(r=0,t=0)=1 . \tag{B2}$$

The solution of this initial value problem for a fixed configuration of acceptors is

$$Q(t)=\exp\left(-\sum_{k=1}^{N_A} w_{0r_k}t\right)$$
$$=\prod_{k=1}^{N_A}\exp(-w_{0r_k}t) . \tag{B3}$$

The macroscopic time evolution of $Q(t)$ is then obtained by performing a configurational average on Eq. (B3).

In the following, we make the assumption that the $\mathbf{r}_k$ are statistically independent variables with a distribution function $f(r_k)$. Neglecting the detailed lattice structure, we obtain in the continuum approximation for the average of Eq. (B3):

$$\Phi(t)=\lim_{\substack{R\to\infty\\ N_A\to\infty\\ N_A/v=\rho=\text{const.}}}\prod_{k=1}^{N_A}\int_0^R \exp(-w_{0r_k}t)f(r_k)dr_k . \tag{B4}$$

We now assume that the random variable $\mathbf{r}_k$ is homogeneously distributed in the volume V_R, i.e., we take the distribution function

$$f(r)=4\pi r^2/V_R . \tag{B5}$$

Due to the specific form of $f(r)$, Eq. (B4) can easily be rewritten as

$$\Phi(t)=\lim_{\substack{R\to\infty\\ N_A\to\infty\\ \rho_A=\text{const.}}}\left\{1-\int_0^R dr f(r)[1-\exp(-w_{0r}t)]\right\}^{N_A}$$

$$=\exp\left\{-4\pi\rho_A\int_0^\infty dr\, r^2[1-\exp(-w_{0r}t)]\right\} . \tag{B6}$$

The same result would have been obtained if we would have assumed that $f(r)$ describes a Poisson distribution.[16] In the case of multipolar interactions of order n, Eq. (B6) reduces finally to

$$\Phi(t)=\exp[-\bar{c}\Gamma(1-3/n)T^{3/n}] . \tag{B7}$$

A derivation of a formula for $\Phi(t)$ without invoking the continuum approximation has been given by Yonezawa and Matsubara[44] and independently by Leath and Goodman.[45] These authors exploited the cumulant technique in performing the configurational average on Eq. (B3) and found the general result

$$\Phi(t)=\exp\sum_k \ln\{1-c[1-\exp(-w_{0r_k}t)]\} , \tag{B8}$$

which has recently been reconsidered by Blumen and Manz[18] in a numerical study of the time evolution of $\Phi(t)$.

APPENDIX C. EVALUATION OF $\tilde{F}(s)$

According to Eq. (6.13), we can write $\tilde{F}(s)$ in the form

$$\tilde{F}(s)=ks^{-\nu}\int_0^\infty dy\, e^{-y}y^{\nu-2}\int_0^y dx\exp\{-[x(x^\nu+(y-x)^\nu]\} , \tag{C1}$$

where we have changed variables by means of the substitution $y=sT$ and where $k=\bar{c}\nu(1-\nu)\Gamma(1-\nu)$ and $\alpha=\lambda/s^\nu$. The convolution integral is then rewritten by expanding the exponential into a power series

$$\int_0^y dx\exp\{-\alpha[x^\nu+(y-x)^\nu]\}$$
$$=\sum_{m=0}^\infty\sum_{n=0}^\infty\frac{(-\alpha)^{m+n}}{m!n!}y^{\nu n}\int_0^y dx\, x^{\nu m}\left(1-\frac{x}{y}\right)^{\nu n} . \tag{C2}$$

Using the identity

$$(1-z)^r=1+\sum_{l=1}^\infty(-1)^l\frac{r(r-1)\cdots(r-l+1)}{l!}z^l , \qquad |z|<1 , \tag{C3}$$

we end up with a pure algebraic expression for the con-

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volution (C2):

$$\int_0^y dx \exp\{-\alpha[x^\nu + (y-x)^\nu]\}$$
$$= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \frac{(-\alpha)^{m+n}}{m!n!} y^{\nu\cdot(n+m)+1} \Bigg[(\nu\cdot m+1)^{-1} + \sum_{l=1}^{\infty}(-1)^l \frac{r(r-1)\cdots(r-l+1)}{!(\nu\cdot m+l+1)}\Bigg] , \qquad \text{(C4)}$$

where $r=\nu\cdot n$. Substituting Eq. (C4) into (C1) and performing the integration with respect to y, we obtain the final result

$$\tilde{F}(s) = k\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-\lambda)^{m+n}}{s^{\nu(m+n+1)}}\frac{\Gamma[\nu(m+n+1)]}{m!n!}$$
$$\times\Bigg[(\nu\cdot m+1)^{-1} + \sum_{l=1}^{\infty}(-1)^l \frac{r(r-1)\cdots(r-l+1)}{l!(\nu\cdot m+l+1)}\Bigg] . \qquad \text{(C5)}$$

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