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Diffusion and relaxation of energy in disordered organic and inorganic materials

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In this paper we examine the following problem: Given a band of localized states randomly distributed in space and obeying a distribution function for energies, how does an excitation diffuse as a function of time and initial energy? This question is encountered in luminescence, photoconductivity, and transport work in organic and inorganic semiconductors and in novel quantum-well structures. We also allow random processes which do not conserve excitation number (radiative and nonradiative recombination). We present analytic solutions and exact Monte Carlo simulations and discuss the validity of approximation procedures focusing in this paper on Gaussian energy distributions appropriate to organic materials.

I. INTRODUCTION

In a previous paper (Grünewald *et al.*[1]), which we shall hereafter refer to as I, we examined the following problem: Given a band of localized eigenstates, how does an excitation diffuse as a function of time t and initial energy ϵ? This question is of considerable interest for a great number of problems in the field of disordered organic and inorganic semiconductors. Knowledge of the time- and energy-dependent diffusivity $D(\epsilon,t)$ is necessary for a wide range of topics including charge and exciton transport,[2,3] dispersive transport,[4-7] luminescence[3] and photoconductivity,[8,9] and the recent direct observations of energy relaxation in organic materials.[10,11] A new and fascinating topic which can be added to the above class of phenomena is the photoluminescence and exciton transport and energy relaxation in semiconductor quantum-well structures.[12-14]

From a theory point of view the basic quantity of interest is the probability function $G_{ij}(t)=\bar{G}[\mathbf{R}_i,\mathbf{R}_j,\epsilon_i,\epsilon_j,t]$, which describes the probability of finding an excitation at site $\mathbf{R}_j$ with energy ϵ_j at time t, given that it started at site $\mathbf{R}_i$ with energy ϵ_i at time $t=0$. The function $G_{ij}(t)$ is in principle dependent on all $2N$ energy and position coordinates in the system. In practice it is only the configurationally averaged quantity $\langle G_{ij}\rangle_{ij}=\bar{G}_{ij}$ with $(\mathbf{R}_i,\epsilon_i,\mathbf{R}_j,\epsilon_j)$ fixed, which is of physial relevance.

Let us now briefly recall the physical model situation that we are trying to describe. The "system" in question consists of a network of sites with positional and energetic disorder, each site can in general be characterized by three variables, and i therefore will from now on always denote $(\mathbf{R}_i,\epsilon_i,\lambda_i)$ where λ_i is the recombination rate at site i. The recombination rate λ_i is a sum of all excitation loss processes, i.e., radiative and nonradiative channels. The position of the "molecule," or cluster, or localized site $\mathbf{R}_i$ will obey some distribution function $P(\mathbf{R}_1-\mathbf{R}_N)$ usually taken as random, the energy ϵ_i is distributed according to some density of states functions $\rho(\epsilon)$ and λ_i has the distribution $P_\lambda(\lambda_i)$. The density of states of excitations $\rho(\epsilon)$ depends very much on the material under consideration. For an amorphous semiconductor[8,9,15] the localized band tail states are well described by an exponential distribution, the corresponding $\rho(\epsilon)$ for a disordered organic semiconductor is well described by a Gaussian model; see I. In paper I we were only concerned with the diffusion problem and $\lambda_i\equiv 0$ for all i. In this case (I) the excitation number was conserved. In the present paper we generalize our formalism to include λ_i, thus we are now explicitly able to deal with luminescence and photoconductivity in the most general situations encountered.

As described in I the theoretical difficulties are formidable. In solving this problem analytically one is forced to resort to approximation techniques. The most successful one is the effective-medium approximation (EMA). This approximation has been described and applied to incoherent transport in a series of papers.[16-18] These transport problems can be separated into three classes: (i) equilibrium transport properties, in which we put $\lambda_i=0$ and evaluate the configurational average, ac and dc conductivities, and Hall mobility. The theory and results have been described in detail in a set of papers and review articles.[16-18] Class (ii) includes nonequlibrium transport processes where we need to keep the information on the initial energy of the excitation such as energy relaxation and diffusion in a band of states $p(\epsilon)$. The theory and solution to this problem has been described within the EMA in I. The memory of the initial energy makes the solution of the transport problem considerably more difficult as shown in I. (iii) Finally, in the third class of transport problems we want both to keep the memory of the initial energy and to allow randomly distributed loss rates λ_i (recombination rates). This will then allow us to deal with essentially every situation: pulsed and steady-state luminescence and photoconductivity, energy relaxation with random loss rates, etc. The present paper will attempt a solution of class (iii).

Next we ask: How do we know that the approximation techniques applied are valid? The best verification of a theory is a direct comparison with computer simulation. The simulation actually solves the model as it stands; a real experiment can include processes not accounted for in the model. There is yet another advantage: If theory and computer experiments agree and both disagree with experiment one can locate the error to be in the model assumption rather than in the approximation techniques. For equilibrium transport we have compared our EMA theory with the extensive resistor network simulations of McInnes and Butcher.[19] The agreement was found to be excellent. For nonequilibrium transport we had the possibility of comparing our work directly with the Monte Carlo simulations of Schönherr *et al.*[20,21] and more recently Richert *et al.*[22] We have compared energy and time dependence of diffusion and energy relaxation and thus verified the nonequilibrium theory given in I. The comparison with Monte Carlo is included partly in paper I and partly in this paper. An interesting exception to the validity of the EMA occurs at sufficiently low temperatures where the approximation method breaks down for energy relaxation; this will be illustrated in the present paper. The Monte Carlo work shows that at low T the excitation tends to freeze-in because its relaxation to lower energies is seriously impeded by the absence of suitable lower energy sites in the neighborhood. This effect is particularly serious in either exponential or Gaussian-type tails. As $T \to 0$ an excitation with start energy ϵ at $t=0$ undergoes diffusion processes to sites of lower energy only. If such sites are not spatially accessible to it, the relaxation process gets blocked and equilibrium cannot be reached or is only reached in the very-long-time limit, depending on whether the transfer rates have finite or infinite range. An approximation which averages over the environment can then of course drastically overestimate the potentiality for relaxation. The precise nature of the environment and percolation property is crucial in this limit. The blocking of relaxation has been demonstrated by the elegant recent experiments of Richert *et al.*[12] on benzophenone and directly verified in the same paper, by the Monte Carlo work of Ries. Agreement with the analytic EMA theory has been shown to be excellent down to about 50 K; from here the deviations start.

Fortunately it has been possible to examine the problem analytically in the $T \to 0$ limit. We have in fact succeeded in obtaining an exact solution to the problem at $T \to 0$, and can now therefore approach the problem starting from the low-T limit. The theory confirms the "freezing-in" of the excitation and will be presented in detail in the next paper of the present series. The fact that this freezing-in of the excitation has been observed in a real system is fascinating and warrants a systematic search for this effect in other materials. Indeed, nonexponential slow relaxation of energy has been observed in $\mathrm{GaAs/Al}_x\mathrm{GaAs}_{1-x}$ and other semiconductor quantum wells by several groups; see, in particular, Ref. 14. Takagahara[13] has attempted to give a theoretical description of this phenomenon. We plan to discuss his approximation in detail in the next paper of this series. Takagahara's work includes a detailed evaluation of exciton-phonon transfer-matrix elements in quantum wells.

The metastability associated with the freezing in the excitation is very much analogous to the spin-glass freezing-in phenomenon,[23] except that in the latter the "barriers" are associated with many-body relaxation whereas in our problems it is a single-particle percolation effect. Note that for charged particles a large electric field will further reduce the number of pathways and can under certain circumstances lengthen the relaxation path.

In the present paper we extend the work in I to allow for random loss rates $\{\lambda_i\}$. The random rates λ_i introduce a new category of difficulty, and we discuss various ways of dealing with it. We also calculate the energy- and time-dependent diffusivity $D(\epsilon,t)$ and energy relaxation function $E(\epsilon,t)$ as a function of initial energy and time using Monte Carlo simulation and analytically methods for Gaussian density of states models appropriate to organic disordered semiconductors.

II. THEORETICAL FORMULATION AND METHODS

In the present context we are interested in motion which is purely incoherent, i.e., where phase memory is lost after every step. The dynamics can therefore be described using the Master equation

$$\frac{dn_i}{dt} = -\sum_j W_{ij} n_i(t) + \sum_j W_{ji} n_j(t) - \lambda_i n_i(t) , \qquad (1)$$

where $n_i(t)$ is the occupational density of site i characterized by position $\mathbf{R}_i$, energy ϵ_i, and loss rate λ_i at time t. The index i will be hereafter always abbreviated $(\mathbf{R}_i, \epsilon_i, \lambda_i)$. The form of the transfer rates and loss rates depends very much on the problem under consideration. Most situations however fall under the two categories

$$W_{ij} = \begin{cases} \nu_0 F(|\mathbf{R}_{ij}|)\exp[-(\epsilon_j - \epsilon_i)/kT], & \epsilon_j > \epsilon_i \\ \nu_0 F(|\mathbf{R}_{ij}|), & \epsilon_j < \epsilon_i \end{cases} \qquad (2)$$

with

$$F(|\mathbf{R}_{ij}|) = \exp(-2\gamma |\mathbf{R}_{ij}|) \qquad (3)$$

for charge transport and triplet (exchange) exciton transport or

$$F(|\mathbf{R}_{ij}|) = \frac{1}{|\gamma \mathbf{R}_{ij}|^6}, \quad \gamma |\mathbf{R}_{ij}| > 1 \qquad (4)$$

applicable to single exciton transport and where γ^{-1} denotes the localization length of the localized state and can in principle be energy dependent, and ν_0 is the prefactor in s^{-1}. The model (4) is also called the Förster[3] rate (dipole-dipole transfer).

The transfer rates W_{ij} can be formally symmetrized:

$$\exp(-\epsilon_i/kT)W_{ij}=\exp(-\epsilon_j/kT)W_{ji} \ . \tag{5}$$

The loss rates λ_i will depend on the recombination process and can in general be summarized by

$$\lambda(\mathbf{R}_i,\epsilon_i)=\sum_n \lambda_i^{(n)} , \tag{6}$$

i.e., a sum of different energy- and position-dependent processes.

The formal solution of the master equation can be conveniently written in the form of a Green function $G_{ij}(t)$ which in the present context is directly the probability function sought, namely, the probability of finding the excitation at time t at the site j, given that it started at time $t=0$ at site i. In the space of the Laplace variable p

$$G_{ij}(p)=\int_0^\infty e^{-pt}G_{ij}(t)dt \ . \tag{7}$$

$G_{ij}(p)$ obeys the exact integral equation

$$G_{ij}(p)=\frac{\delta ij}{p+\sum\limits_\mu W_{iu}+\lambda_i}+\frac{1}{p+\sum\limits_\mu W_{iu}+\lambda_i}\sum_l W_{il}G_{lj}(p) \ . \tag{8}$$

Thus the exact $G_{ij}(p)$ will in general depend on the $3N$ coordinates $\{R_u,\epsilon_u,\lambda_u\}$ of the system. The quantity of interest, however, is the configurationally averaged probability $\overline{G}_{ij}(p)$ given by

$$\overline{G}_{ij}(p)=\int\prod_{u\neq i,j} d\mathbf{R}_u d\epsilon_u d\lambda_u \frac{1}{\Omega^{N-2}} \times\rho(\epsilon_u)P(\lambda_u)G_{ij}(p) , \tag{9}$$

with the sites i and j held fixed, ρ and P are normalized energy and λ distribution function, and Ω is the volume. When $\{\lambda_u=0\}$, we have shown (in I) that $G_{ij}(p)$ satisfies within the EMA the effective integral equation

$$\overline{G}_{ij}(p)=\frac{\delta_{ij}}{p+\sum\limits_u \overline{g}_{iu}}+\frac{1}{p+\sum\limits_u \overline{g}_{iu}}\sum_{l\neq i,j}\overline{g}_{il}\overline{G}_{lj}(p) , \tag{10}$$

where the renormalized frequency-dependent transfer rates $\overline{g}_{ij}(p)$ are given by (see I)

$$f_i\overline{g}_{ij}=1\bigg/\left[\frac{1}{f_iW_{ij}}+\frac{1}{f_j(p+\sigma_j)}+\frac{1}{f_i(p+\sigma_i)}\right] , \tag{11}$$

where

$$\sigma_i=\left\langle\sum_u g_iu\right\rangle_i \tag{12}$$

and is given by the self-consistency relation

$$f(\epsilon_i)\sigma(\epsilon_i,p)=na_p\int\int dE_j\,d\mathbf{R}\rho(\epsilon_j)\bigg/\left[\frac{1}{\tau(\epsilon_i,\epsilon_j,R)}+\frac{1}{f(\epsilon_j)[p+\sigma(\epsilon_j,p)]}\right] , \tag{13}$$

where

$$\tau(\epsilon_i,\epsilon_j,R_{ij})=f_iW_{ij} \tag{14}$$

and $n=N/\Omega$ is the site density, a_p a percolation factor $a_p\sim(2.7)^{-1}$, and f_i is the Fermi function approximated to a Boltzmann function.

The diffusion coefficient $D_i(t)$ is defined as the derivative of the mean-square displacement of an excitation at time t, given that it started at time $t=0$ at site i with energy ϵ_i. In the space of the Laplace variable p we define

$$D_i(p)=\tfrac{1}{6}p^2\sum_j R_{ij}^2\overline{G}_{ij}(p) , \tag{15}$$

so that

$$D_i(t)=\hat{L}^{-1}\left\{\frac{D_i(p)}{p}\right\} , \tag{16}$$

where $\hat{L}^{-1}$ is the inverse Laplace transform. Using Eqs. (10) and (15) we obtain

$$D_i(p)=\frac{p}{6}\sum_j R_{ij}^2\overline{g}_{ij}\bigg/\sum_u \overline{g}_{iu}+p+\sum_l \overline{g}_{il}D_l\bigg/\sum_u \overline{g}_{iu}+p \ . \tag{17}$$

This is an integral equation for the energy- and frequency-dependent diffusion coefficient, which we can also rewrite as

$$D(\epsilon,p)=\frac{p}{6}\frac{n\int\int dR\,d\epsilon'\rho(\epsilon')R^2\overline{g}(\epsilon,\epsilon';R)}{p+\sigma(\epsilon)}+\frac{n}{p+\sigma(\epsilon)}\int\int dR\,d\epsilon'\rho(\epsilon')\overline{g}(\epsilon,\epsilon',R)D(\epsilon',p) , \tag{18}$$

where

$$\sigma(\epsilon)=n\int\int dR\,d\epsilon'\rho(\epsilon')g(\epsilon,\epsilon',R) \ . \tag{19}$$

In order to solve this equation for $D(\epsilon,p)$ it is useful to consider a pseudoequilibrium diffusion coefficient $D_0(p)$ defined as

$$D_0(p)=\sum_i f_iD_i(p)\bigg/\sum_i f_i , \tag{20}$$

which, from Eq. (17), has a particularly simple solution given by

$$D_0(p)=\tfrac{1}{6}\sum_{i,j} f_i R_{ij}^2 \bar{g}_{ij}(p) \Big/ \sum_i f_i \ . \tag{21}$$

In the long-time limit ($p\rightarrow 0$), $D_i(p)$ must be independent of the initial energy, so

$$\lim_{p\rightarrow 0} D_i(p)=D_0(p=0) \tag{22}$$

for all values of the initial energy ϵ_i. We can use these exact relations (21) and (22) as constraints on the integral equation for $D(\epsilon,p)$. In the limit $p\rightarrow 0$, Eq. (19) becomes a homogeneous integral equation which can be solved only with the constraints (21) and (22). The diffusion coefficient in the long-time limit is trivially evaluated using Eq. (21) for any distribution of the site energies $\rho(\epsilon)$.

For small fields E we can compute the current produced by a charged particle with initial energy ϵ as

$$j(\epsilon,t)=\hat{L}^{-1}\left\{\frac{e^2E}{kT}\frac{D(\epsilon,p)}{p}\right\} . \tag{23}$$

The corresponding mobility $\mu(\epsilon,t)$ is given by

$$\mu(\epsilon,t)=j(\epsilon,t)/eE \ . \tag{24}$$

To describe for example, a white-light pulse at $t=0$, the corresponding current can be written

$$j(t)=\hat{L}^{-1}\int_{-\infty}^{\infty}\frac{e^2E}{kT}\frac{d\epsilon\rho(\epsilon)D(\epsilon,p)}{p} \tag{25}$$

with $\mu(t)=j(t)/eE$.

In computer simulation work (Silver *et al.*[20] and Schönherr *et al.*[21]) it is also possible to register the energy of the particles as they relax in time from a given initial value. We define the mean energy of the excitations at time t by the relation

$$E(\epsilon_i,t)=\tilde{\epsilon}_i(t)=\sum_j \bar{G}_{ij}(t)\epsilon_j \ , \tag{26}$$

which in Laplace space can be obtained from the integral equation

$$\tilde{\epsilon}_i(p)=\frac{\epsilon_i}{p+\sigma_i}+\frac{1}{p+\sigma_i}\sum_u \bar{g}_{iu}\tilde{\epsilon}_u(p) \ . \tag{27}$$

Again, we have the exact relation

$$\sum_i f_i\tilde{\epsilon}_i(p)=\left[\sum_i f_i\epsilon_i\right]\Big/p \ , \tag{28}$$

which is a constraint on Eq. (27). In the long-time limit, the system reaches thermodynamic equilibrium and thus

$$\lim_{t\rightarrow\infty}\tilde{\epsilon}_i(t)=\sum_i f_i\epsilon_i \Big/ \sum_i f_i \ , \tag{29}$$

which is simply the thermally averaged energy and is readily evaluated for a given density-of-states function.

Finally, by analogy with Eq. (25), there is also the averaged quantity

$$\langle\epsilon(t)\rangle=\int_{-\infty}^{\infty}d\epsilon\rho(\epsilon)E(\epsilon,t) \ . \tag{30}$$

This completes the discussion of the energy- and time-dependent diffusion problem when $\lambda_i=0$. The solution of these equations has been compared with the Monte Carlo simulations for a class of situations described in I and for amorphous semiconductors in a more recent article, hereafter referred to as II.[15] In II we have considered an exponential density of states model and have computed $D(\epsilon,t),E(\epsilon,t),D_0(t),\langle\epsilon(t)\rangle$. We have compared that model with the multiple-trapping model and the experimental work on amorphous semiconductors by Monroe[24] and Monroe *et al.*[9]

III. DIFFUSION AND ENERGY RELAXATION IN THE PRESENCE OF RECOMBINATION

In order to extend the theory to include recombination processes we recall that when $\lambda_i=0$, the probability function $\bar{G}_{ij}(p)$ satisfies the particle conservation rate

$$\sum_j G_{ij}(p)=\frac{1}{p} \ . \tag{31}$$

This relation no longer holds when $\lambda_i\neq 0$, and we can now define a trapping self-energy $\Sigma(\lambda_i,\ldots,\lambda_N,p)$ such that

$$\bar{n}_i(p)=\sum_j \bar{G}_{ij}(p)=\frac{1}{p+\Sigma_i(\lambda,p)} \ . \tag{32}$$

The left-hand side now denotes the survival fraction $n_{\rm i}(p)$ [number of excitation surviving of time t, given that $n_{\rm i}(t)=1$ at $t=0$].

In the absence of energetic and spatial disorder we can use the powerful coherent-potential approximation (CPA) which gives us an approximation to $\Sigma(p)$. The technique as applied to the trapping problem has been described in detail by Movaghar.[25] The CPA in the trapping problem can be justified in the same way as in the usual case: It can be also derived using the t-matrix expansion technique and summing the class of mean-field diagrams self-consistently; see also Refs. 26 and 27. The CPA is the corresponding single-site self-consistent effective-medium approximation when we have diagonal disorder. In the long-time limit and for infinitely deep traps we found that the CPA agreed with the first passage time (FPT) approach of Montroll and Weiss[28] except in one dimension, where the FPT is superior to the CPA. In the FPT, one computes the average number of new sites visited by the particle in a time t. In Laplace space and for a disordered system this quantity $S_{\rm i}(p)$ can be approximately written as

$$S_{\rm i}(p)=\frac{1}{p^2}(\langle G_{ii}^{-1}-p\rangle_i) \ . \tag{33}$$

For infinitely deep traps the distribution function of the λ's can be written

$$P(\lambda)\sim x\delta(\lambda-\lambda_0)+(1-x)\delta(\lambda),\ \ \lambda_0\rightarrow\infty \tag{34}$$

and the survival fraction in FPT becomes

$$\bar{n}_{\rm i}(t)=\exp[-xS_{\rm i}(t)] \ , \tag{35}$$

where $S_{\rm i}(t)=L^{-1}\{S_{\rm i}(p)\}$ and x is the trap concentration. Both CPA and FPT are only useful when energetic disorder is absent, though formally in the FPT method the memory of the initial energy could be kept as shown in (35). The energetic disorder case, however, has not been tested within the FPT and we shall now propose a better alternative which we shall now proceed to derive.

Energetic disorder makes the recombination problem much more difficult; to see this let us expand in the rates λ_i and write

$$G_{ij}(p,\lambda)=G_{ij}^{0}(p,\lambda=0)+\sum_{u} G_{iu}^{0}\lambda_u G_{uj} \ , \tag{36}$$

where

$$G_{ij}^{0}(p)=G_{ij}^{0}(p,\lambda=0) \ . \tag{37}$$

The t-matrix renormalization of (36) becomes

$$G_{ij}=G_{ij}^{0}+\sum_{u} G_{iu}^{0}t_u G_{uj}^{0} + \sum_{u\neq 1} G_{iu}t_u G_{ul}^{0}t_l G_{lj}^{0}+\cdots \ , \tag{38}$$

where

$$t_u=\frac{-\lambda_u}{1+\lambda_u G_{uu}^{0}} \ . \tag{39}$$

Assuming that the initial site i is not a trap, a reasonable approximation to (38) which is exact within the single recombination center limit would be

$$\bar{n}_i(p)=\frac{1}{p}+\sum_{u\neq i}\bar{G}_{iu}^{0}\bar{t}_u\bar{n}_u(p) \ , \tag{40}$$

where

$$\bar{t}_u=\frac{-\lambda_u}{1+\lambda_u\bar{G}_{uu}^{0}} \ . \tag{41}$$

Note that despite the EMA, Eq. (40) is an integral equation which is very difficult to solve because we first have to compute $\bar{G}_{iu}^{0}$ using (10). The full solution to the two-site probability function $\bar{G}_{iu}^{0}$ is a very difficult problem in itself despite the EMA. In the absence of energetic disorder, (40) can be solved immediately for infinitely deep traps. Using (12), we find

$$\bar{n}(p)=\frac{1}{p+x\sigma(p)} \ , \tag{42}$$

where the self energy $\Sigma(p)=x\sigma(p)$ is simply the trap density x multiplied by what is essentially, from (13), the $\bar{R}$-hopping frequency-dependent effective-transfer rate. Note that (42) is identical to the FPT as $p\rightarrow 0$ (long times) and that the CPA solution differs from the average t-matrix solution (40) only by a renormalization of $p\rightarrow p/(1-x)$ and $x\rightarrow x/1-x$. For a detailed analysis of the energy-independent problem the reader is referred to Ref. 25.

Returning now to the energy-dependent problem, we propose to bypass the full solution of (40) by adapting the following procedure: Map the true discrete network onto a continuum with an effective energy and time-dependent diffusivity $D(\epsilon,t)$ evaluated by the procedure described in Sec. II. Introduce an effective time- and energy-dependent trapping self-energy (rate) $\Sigma(\epsilon,t)$; thus the particle density $n(\epsilon,\mathbf{r};t)$ now obeys the diffusion equation

$$\frac{\delta n(\epsilon,\mathbf{r};t)}{\delta t}=\int_0^t D(\epsilon,t')\nabla^2 n(\epsilon,\mathbf{r};t-t')dt' - \int_0^t \Sigma(\epsilon,t-t')n(\epsilon,\mathbf{r};t')dt' \ . \tag{43}$$

The solution of (43) with initial condition $n(\epsilon,\mathbf{r};t=0)=\delta(\mathbf{r})$ is the usual probability function which in Fourier and Laplace space becomes

$$G(\mathbf{k};\epsilon,p)=\frac{1}{p+D(\epsilon,p)k^2+\Sigma(\epsilon,p)} \ . \tag{44}$$

In the limit of no energetic disorder (44) is the usual continuum limit of a continuous-time random walk mapping in the small-k limit.[6] Thus we could have also, for example, mapped our network into an ordered cubic lattice with effective-transfer rates $D(\epsilon,p)/R_0^2$, where again $D(\epsilon,p)$ is evaluated as in Sec. II and R_0 is the lattice constant. This would have given for $G(\mathbf{k};\epsilon,p)$ the form

$$G(\mathbf{k};\epsilon,p)=\frac{1}{p+[D(\epsilon,p)/R_0^2](\epsilon_{\mathbf{k}=0}-\epsilon_{\mathbf{k}})+\Sigma(p,\epsilon)} \ , \tag{45}$$

where in d dimensions

$$\epsilon_{\mathbf{k}}=\sum_{u=1}^{d}\cos(k_u R_0) \ . \tag{46}$$

Equations (44) and (45) represent powerful approximations and are physically very appealing. We have bypassed the random network problem and we now have to solve for $\Sigma(p,\epsilon)$ given that the particle is moving on an effective ordered lattice with effective diffusivity. This effective lattice changes with time and initial energy of the particle, but in the long-time limit the memory of the initial energy disappears and a quasi-steady-state is reached, as shown by Eq. (22).

To evaluate $\Sigma(p,\epsilon)$ we can now make use of the CPA, and thus $\Sigma(p,\epsilon)$ is determined from the self-consistency condition (26)

$$\int d\lambda P(\lambda)\left[\frac{\Sigma(p,\epsilon)-\lambda}{1-[\Sigma(p,\epsilon)-\lambda]G_{00}[p+\Sigma,\epsilon]}\right]=0 \ , \tag{47}$$

where the local Green function G_{00} is given by

$$G_{00}(p+\Sigma(\epsilon))=\sum_{\mathbf{k}}\left[p+\Sigma(p,\epsilon)+(\epsilon_{\mathbf{k}=0}-\epsilon_{\mathbf{k}})\frac{D(p,\epsilon)}{R_0^2}\right]^{-1} \tag{48a}$$

and

$$\bar{n}(\epsilon,t)=\hat{L}^{-1}\{G(\mathbf{k},\epsilon;p)\}_{\mathbf{k}=0} \ . \tag{48b}$$

Equations (45), (47), and (48) now represent the full solution to the energy-dependent trapping problem on a disordered network. The approximations are reliable except in the very-long-time limit where we know the CPA to become inaccurate. For example, with $P(\lambda)$ given by (34) (deep traps), the true asymptotic decay of $n(t)$ is known to be[27]

$$n(\epsilon,t)\sim\exp[-\gamma_d(x^{2/d}t)^{d/(d+2)}] \text{ as } t\to\infty \qquad (49)$$

where d is the dimensionality of the lattice.[31] For fractal lattices $d\to\tilde{d}$ the spectral dimensionality of the lattice. The CPA, on the other hand, gives us a pure exponential law. It is still not entirely clear when the asymptotic solution (49) becomes relevant when $d>2$, but it has been suggested[27] that $n\leq 10^{-13}$ $(d>2)$ before (49) applies. From this it follows that the deviations of (49) from the CPA or FPT theories are not of practical significance when $d>2$.

Note that a decay law of the type

$$n(t)\sim\exp[-(t/t_0)^{\alpha}],\quad 0<\alpha<1 \qquad (50)$$

can be expected for a completely different reason in the intermediate time domain as a result of the time dependence of $D(t)$. As shown by Richert *et al.*,[22] when $D(t)\sim t^{\alpha-1}$, the effective trapping rate $k(t)$ goes as

$$k(t)\sim xt^{\alpha-1} \qquad (51)$$

and thus (50) applies over the domain where $D(t)$ is time dependent. The asymptotic form is exponential here, of course, because $D(t)\to D_0(T)$ as $t\to\infty$.

The decay law (50) is observed in a wide class of excitation decays in organic and inorganic systems and even in the relaxation of two-level systems in glasses. It is associated with time-dependent diffusion and has no relation to the exact asymptotic forms which are associated with fluctuations [Eq. (49)]. We shall show that (50) can be obtained rigorously from the CPA solution in the intermediate time domain. As it turns out, the "intermediate" time domain very often spans essentially all of the physically relevant time domain.

IV. RESULTS AND DISCUSSIONS

In this paper we shall now focus the application of the formalism of Secs. I and II to transport and energy relaxation in organic materials. In disordered organic solids the density of excited states is well described by a Gaussian model,

$$\rho(\epsilon)=\frac{1}{(2\pi a^2)^{1/2}}\exp(-\epsilon^2/2a^2)\ . \qquad (52)$$

The Gaussian spread results from the statistical fluctuations of the polarization energy and is well established experimentally and theoretically.

The nonequilibrium diffusivity obtained from (25) is plotted as a function of time in Fig. 1 for different values of the Gaussian bandwidth a/kT. The crossover time t_r to long-time behavior D_∞ is denoted by an arrow on each curve; t_r can be verified to roughly obey the relation

$$t_r^{\alpha}D_\infty\sim\text{const}\ \ (\alpha\sim 0.45)\ , \qquad (53)$$

and from paper I,

$$\log_{10}D_\infty\sim T^{-2},\ \ D_\infty\sim e^{-(T_0/T)^2}\ . \qquad (54)$$

Temperature dependences of D_∞ and t_r are plotted in the inset of Fig. 1.

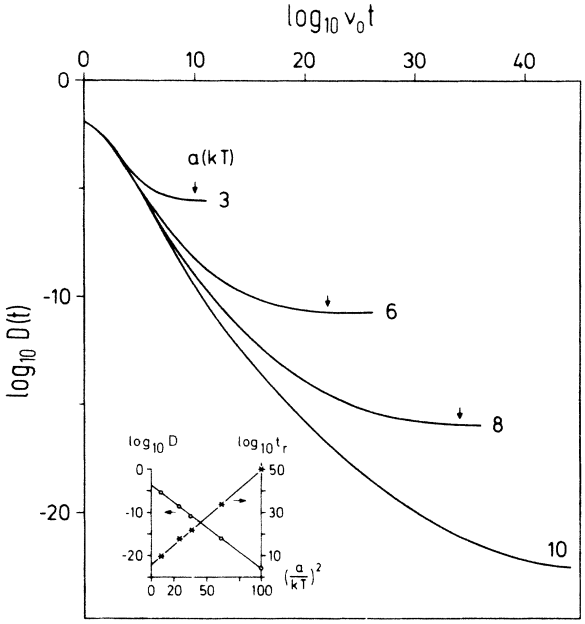

FIG. 1. The $\log_{10}$ of the diffusivity $D(t)$ as defined by Eq. (21) for the Gaussian model is plotted against $\log_{10}$(time) for different values of a/kT. The inset shows the long-time (equilibrium) value $D_\infty(T)$ and the relaxation time t_r plotted versus $(a/kT)^2$.

The strong temperature dependence of t_r and $D_\infty(T)$ are characteristic of transport in Gaussian bands with no lower cutoff. The relation (54) can be derived analytically. The relaxation time grows very rapidly as $T\to 0$ and the value $\alpha\sim 0.45$ appears to be connected with the Gaussian density of states and the fact that $D(t)$ does not strictly obey a $t^{-\beta}$ law for a Gaussian model. This question has been discussed in detail in I and II. Strictly speaking we find that $\beta(t)$ is itself time dependent and a constant β is only valid for a limited time regime, in sharp contrast to an exponential density of states where β is a constant almost throughout the entire time domain.

Figure 2 illustrates the energy dependence of the diffusivity as a function of time for different start energies, for the Gaussian model. Figure 2 illustrates the remarkable property shown at low energies, namely, the fact that $D(\epsilon,t)$ first decreases to a value below its equilibrium value. This is related to the fast initial thermalization of the excitation at low T. It is only at long times that an effective-transport level establishes itself. The quasiequilibrium is established roughly when the total upward rate matches the downward rate, i.e.,

$$\int_{\epsilon}^{\infty}d\epsilon'\rho(\epsilon')e^{-\epsilon'/kT}\sim\int_{\epsilon}^{-\infty}\rho(\epsilon')d\epsilon'\ . \qquad (55)$$

This effect has also been demonstrated by the Monte Carlo simulations (not shown here).

Figure 3 is a plot of the energy relaxation $\langle\epsilon(t)\rangle$ defined by (30) as a function of time for $T=80$ K and $\rho(\epsilon)$ given by (52). The analytical theory is compared with the Monte Carlo result in a cubic lattice with lattice constant c (dashed line). The agreement is remarkable; almost per-

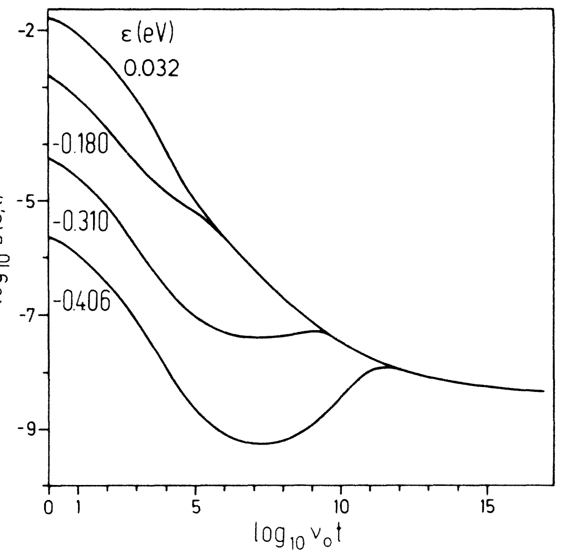

FIG. 2. The log of the energy- and time-dependent diffusivity $D(\epsilon,t)$ for a Gaussian with $a=0.1$ eV and $kT=\frac{1}{50}$ eV plotted versus $\log_{10}$(time) with different start energies. $n=8.10^{18}/\text{cm}^3$ [from Eq. (19)].

fect agreement is obtained by introducing a minimum distance of approach between the localized states (cutoff) as shown.

Figures 4(a) and (4b) illustrate the EMA to $\langle\epsilon(t)\rangle$ for different temperatures and the corresponding Monte Carlo results for a Gaussian band. Agreement is excellent down to 80 K; below 50 K the EMA and the "exact" simulations begin to differ rather strongly. Whereas the Monte Carlo shows a freezing in effect, i.e., a saturation of the relaxation curve at long times, the effective-medium approximation still exhibits a relatively fast relaxation down to lower energies. From a simple thermodynamic argument it follows that the exact long-time energy is given by

$$\langle\epsilon(\infty)\rangle=\frac{\int_{-\infty}^{\infty}\rho(\epsilon)\epsilon e^{-\epsilon/kT}d\epsilon}{\int_{-\infty}^{\infty}\rho(\epsilon)e^{-\epsilon/kT}d\epsilon}=-\frac{a^2}{kT}\,. \tag{56}$$

At low temperatures this value cannot be reached (finite-range hopping) in a Gaussian band or can only be reached strictly at $t=\infty$ (infinite-range hopping). In other words it is clear that percolation effects (the depletion of possible hop sites after each jump) seriously impedes further relaxation in energy and we get a freezing-in of the excitation. Clearly any approximate solution can be very misleading

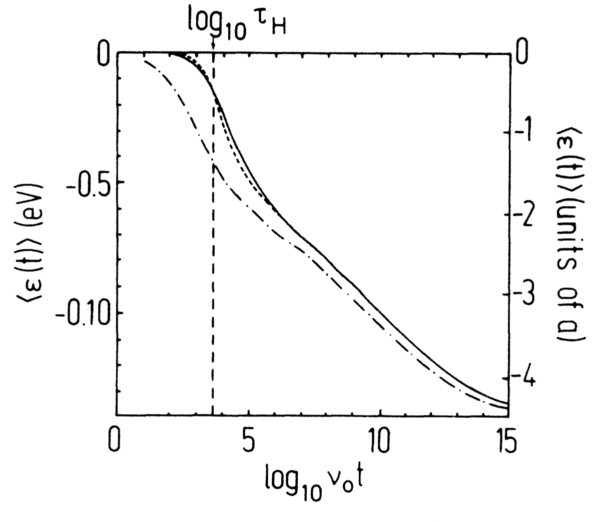

FIG. 3. The energy relaxation function $\langle\epsilon(t)\rangle$ for a white-light pulse plotted versus $\log_{10}$(time) using Eq. (30) (solid line with $r_{\min}=0.8n^{-1/3}$; dashed-dotted line with $r_{\min}=0$ continuum, Monte Carlo results; dashed line, $T=80$ K, $a=31$ meV, $2\gamma n^{-1/3}=10$).

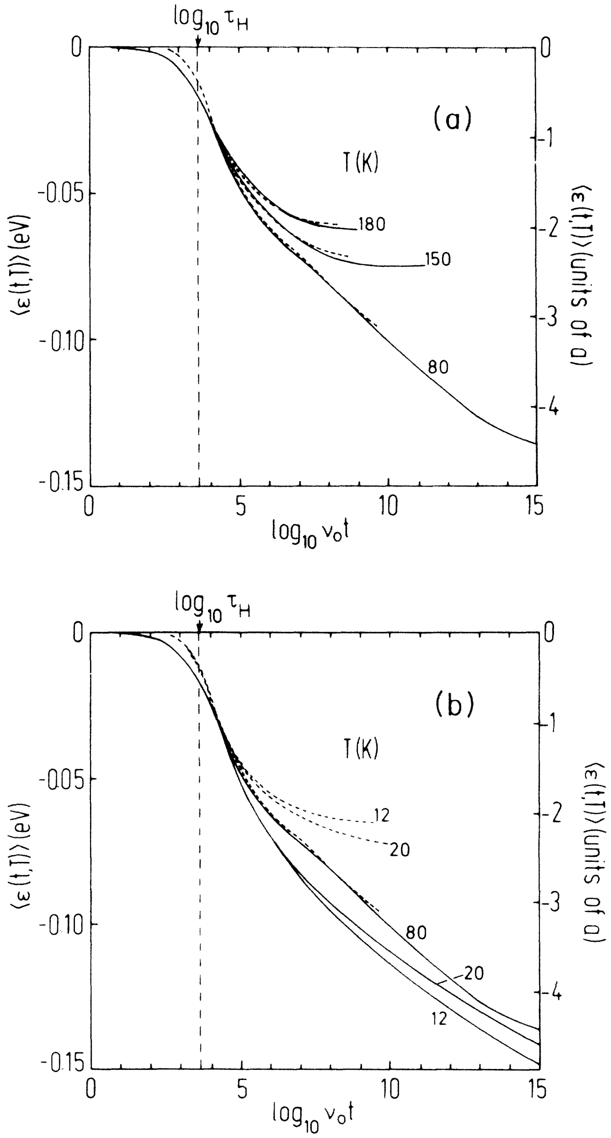

FIG. 4. The energy relaxation function $\langle\epsilon(t,T)\rangle$ from Eq. (20), with Gaussian $\rho(\epsilon)$ plotted versus $\log_{10}(\nu_0 t)$ for different temperatures (solid line). The corresponding Monte Carlo results are shown by the dashed lines. Notice the freezing in at $T=20$ and 12 K in (b); the deviations from analytic theory at low T are rather evident.

as $T \rightarrow 0$. The EMA must necessarily by its very logic overestimate the number of potential hop sites. We can illustrate this by a direct calculation. Consider the limit $T \rightarrow 0$ and the local-stay probability $G_{00}(t)$. The configurational average in the EMA becomes

$$\langle G_{00}(p) \rangle = 1 \Big/ \left[p + \left\langle \sum_u g_{iu} \right\rangle \right] , \tag{57}$$

and thus

$$\langle G_{00}(t) \rangle = e^{-t\sigma(\epsilon_0)} , \tag{58}$$

where from (13) and in the limit $T=0$, we have

$$\sigma(\epsilon_0) = \nu_0 n \int_{\epsilon_0}^{-\infty} \rho(\epsilon')d\epsilon' \int F(|\mathbf{R}|)d\mathbf{R} . \tag{59}$$

The exact evaluation of $\langle G_{00}(t) \rangle$, however, yields

$$\langle G_{00}(t) \rangle = \left\langle \exp \left[- \sum_{\epsilon_k \le \epsilon_0} W_{0k} t \right] \right\rangle \tag{60a}$$

and for infinite-range hopping we obtain (see also Ref. 28)

$$\langle G_{00}(t) \rangle = \exp \left[n n(\epsilon_0) \int d\mathbf{R}_k (e^{-F(|\mathbf{R}_{0k}|)t} - 1) \right]$$

with

$$n(\epsilon) = \int_{\epsilon}^{-\infty} \rho(\epsilon')d\epsilon' . \tag{60b}$$

This gives approximately (α_n is constant)

$$\langle G_{00}(t) \rangle_{t\rightarrow\infty} \sim \begin{cases} 1/(\nu_0 t)^{\alpha_0 n(\epsilon)} \rightarrow F(|\mathbf{R}|) = e^{-2\gamma|\mathbf{R}|} , \\ e^{-(\nu_0 t)^{1/2}\alpha_1 n(\epsilon)} \rightarrow F(|\mathbf{R}|) = \dfrac{1}{(|\mathbf{R}|\gamma)^6} . \end{cases} \tag{61}$$

The effect is rather drastic as a comparison between (58) and (61) shows.[6,32] The EMA must considerably overestimate the relaxation as $T \rightarrow 0$ and $t \rightarrow \infty$.

We pursue our analysis by considering $E(\epsilon,t)$ as a function of the initial energy for the EMA and Monte Carlo simulations. The results are shown in Fig. 5. The analytical treatment is the solid line and the Monte Carlo simulation corresponds to the dashed line. It can be seen that at 80 K the agreement is still extremely good, in fact this applies down to $T \sim 50$ K. One can see that the relaxation curves eventually all join up to a single curve; the time involved depends on the initial start energy.

The influence of the start energy is even more pronounced when we look at the survival fraction $n(\epsilon,t)$ evaluated according to Sec. III [Eq. (48b)]. For a deep trap concentration $x=10^{-3}$ the results are illustrated in Fig. 6. We have not used the fully self-consistent CPA solution given by (47) but only the average t-matrix approximation which is sufficient for the present purposes (see Ref. 25). We have also approximated the cubic lattice local propagator $G_{00}(p)$ by the Hubbard truncated form. Both approximations lead to errors in the very-long-time limit. However, here we know that the effective-medium theories are not valid in any case. Figure 6 shows $n(\epsilon,t)$ for two values of $\nu_0 t = 2\times10^9$ and 10^{10} (dashed line) as a function of energy and for different values of the Gaussian "width" (a/kT). As can be seen, the change in $n(\epsilon,t)$

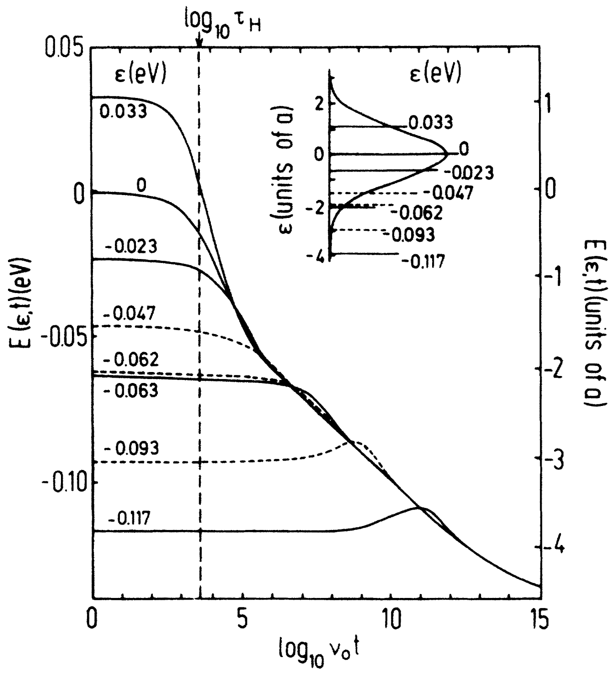

FIG. 5. The energy-dependent (pulse) relaxation function $E(\epsilon,t)$ from Eq. (26) is plotted versus $\log_{10}(\nu_0 t)$ for different start energies. The Monte Carlo results are shown by the dashed lines. The inset shows the position of the energies on the density of states diagram $T=80$ K, $a=31$ meV, $2\gamma n^{-1/3}=10$, and $a/kT=4.5$.

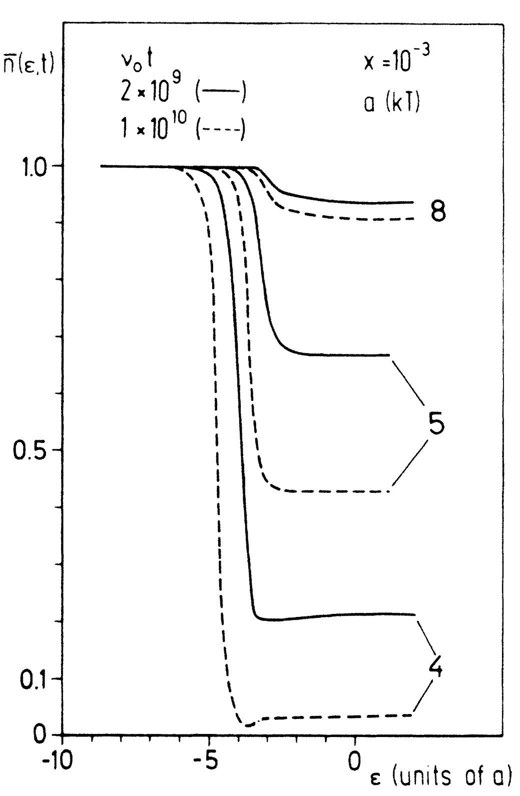

FIG. 6. The survival fraction $n(\epsilon,t)$ plotted versus ϵ/a from Eq. (48b) for a deep trap concentration $x=10^{-3}$ at two different times: solid line, $\nu_0 t = 2\times10^9$; dashed lines, $\nu_0 t = 10^{10}$. Curve 4 corresponds to $T=9.35$ K; curve 8, $T=47$ K; curve 5, $T=75$ K if $a=0.0322$ eV.

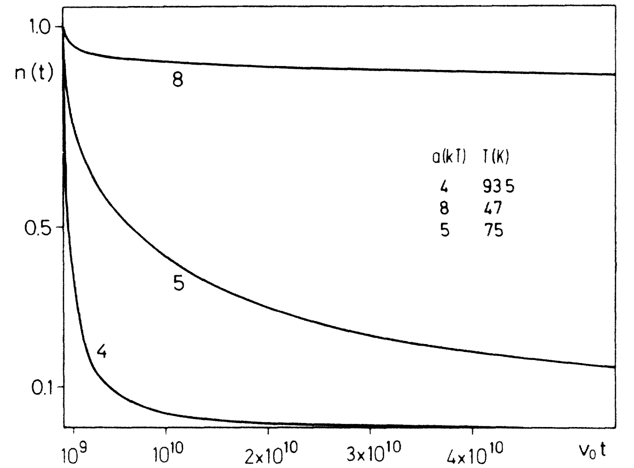

FIG. 7. The survival fraction $n(t)$ for a white-light pulse from Eq. (62) plotted versus $\nu_0 t$ for a Gaussian $\rho(\epsilon)$ with $a=0.0322$ eV with $\gamma n^{-1/3}=5$, $x=10^{-3}$ (deep traps) and various temperatures. Curve 4, $T=93.5$ K; curve 8, $T=47$ K; curve 5, $T=75$ K.

takes place in a rather narrow energy range. One can almost define a critical energy ϵ_c which acts as a kind of mobility edge below which the excitations are almost immobilized and have therefore not had a chance to reach a trap. Experimentally this behavior was observed in polyvinylcarbazole by Rockwitz and Bässler.[10] The critical energy is of course not a true mobility edge since it does not separate extended states from localized states in the sense of the Anderson localization at $T=0$. The sharpness of the change in $n(\epsilon,t)$ is a consequence of the strong energy dependence of the Gaussian $\rho(\epsilon)$ and the strong dependence of $D(\epsilon,t)$ on ϵ in a Gaussian band (see Fig. 2).

Figure 7 is a plot of $n(t)$ given by

$$n(t)=\int_{-\infty}^{\infty} n(\epsilon,t)\rho(\epsilon)d\epsilon \qquad (62)$$

versus time for different values of a/kT. The time decay can be well approximated by an $\exp[-(t/t_0)^{\alpha}]$ law in agreement with (50). The nonexponential behavior is here a consequence of the dispersive (time-dependent) nature of the diffusion process and not due to exact fluctuation effects [Eq. (49)].

V. CONCLUSIONS

We have presented analytical and Monte Carlo results for the problem of diffusion and recombination in transport problems that can be described by the master equation. We have shown how to evaluate the diffusivity, the energy-dependent diffusivity $D(\epsilon,t)$, and the energy-dependent relaxation function $E(\epsilon,t)$, with and without recombination centers. Recombination processes are defined as processes which do not conserve particle density. The theory and the Monte Carlo techniques can be applied to a vast number of experimental data ranging from organic and inorganic semiconductors to the novel quantum wells and superlattices.

The analytic effective-medium description has been tested against the "exact" Monte Carlo work. The theory is excellent down to about $T\sim50$ K. Below this temperature we find that mean-field theory overestimates the decay channels available after every jump. This applies in particular to density of states distribution which change rapidly with energy (i.e., Gaussian and exponential).

In the limit $T\rightarrow0$ we can solve the problem exactly. The reason for this is that no back jumps are allowed and thus the diffusion process has a pure "tree like" structure. The Monte Carlo results are confirmed; the excitations "freeze-in" at low T, giving rise to extremely weak relaxation functions. This analysis will be presented in the next paper of the present series which will be devoted to the very-low-temperature situation in organic systems and quantum wells.

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