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Equivalence of multiple-trapping model and time-dependent random walk

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A model of multiple trapping from a band of transport states is shown to be equivalent to the continuum limit of the continuous-time-random-walk description of anomalous dispersion developed by Scher and Montroll and the waiting-time distribution function $\psi(t)$ is expressed in terms of the parameters of the multiple-trapping model. Calculations of $\psi(t)$ as a function of temperature are presented for a-Se, using previously determined multiple-trapping parameters obtained from an extensive analysis of transient photocurrent data.

I. INTRODUCTION

The recent development of the multiple-trapping theory[1-3] has given a new perspective on the problem of charge transport in amorphous materials. Previously the continuous-time-random-walk (CTRW) model developed by Scher and Montroll[4] (SM) was the only formalism available for interpreting the kind of anomalous or extreme dispersion in charge transport observed in many materials.[5,6] It is now known that the multiple-trapping model can describe a wide range of dispersion in terms of a small number of transport parameters. In the preceding paper[3] (hereafter called I) an extensive analysis of photocurrent-transient data was carried out for a-Se. New results obtained included the superlinearity of the apparent transit time, the criteria for extreme dispersion, and the explanation for the disappearance of dispersion in terms of temperature-dependent trapping parameters.

At low temperature ($T \sim 140$ K), it was found that the anomalous dispersion previously described by the SM model[4,6] could be analyzed in terms of a homogeneous distribution of only three different types of traps. The same asymptotic value of the theoretical photocurrent transient was obtained as in the SM model,[4] indicating that there was a fundamental connection between the CTRW and multiple-trapping formalisms. In the present paper this connection is explored in more detail.

In Sec. II we derive the master equation for the total charge-carrier concentration, starting from generalized linear-transport equations. In Sec. III we carry out the same procedure for the multiple-trapping equations of I, and show that they are formally equivalent to the continuum limit of the SM master equation.[4] We obtain an expression for the Laplace transform of the SM relaxation function $\tilde{\phi}(s)$ and the corresponding waiting-time distribution function $\tilde{\psi}(s)$ in terms of the multiple-trapping parameters. We point out that an unkrown parameter $\tau = a_0\Delta/\mu_0 E$ must be specified independently before $\tilde{\psi}(s)$ is completely determined, where a_0 is the lattice spacing for the CTRW, Δ is the asymmetry factor in the transition probability between cells, and $\mu_0 E$ is the velocity of untrapped carriers in the multiple-trapping model. We argue that a reasonable choice is $\tau = (\sum_i \omega_i)^{-1}$, the average time for capture by any of the traps. With this choice for τ it can be shown that it is inappropriate to describe a small number of trapping events in terms of the SM model, whereas the multiple-trapping equations are always applicable.

We calculate $\psi(t)$ as a function of temperature in Sec. IV, using the a-Se trap parameters. At low temperatures good agreement with the asymptotic power-law behavior assumed by SM is obtained, and for higher temperatures we show the evolution of the distribution function to an exponential characteristic of nondispersive transport. The results are summarized in Sec. V.

II. MASTER EQUATION FOR GENERAL LINEAR-TRANSPORT PROCESS

We consider the following linear-transport equations, which have been applied to a variety of different problems[7]:

$$\frac{\partial p_n}{\partial t} = g_n + \sum_m \omega_{nm} p_m - \sum_\nu \omega_{\nu n} p_n - c_n \frac{\partial p_n}{\partial x}, \qquad (1)$$

where $p_n(x,t)$ is the concentration of "particles" in the nth state: $g_n(x,t)$ is the generation rate; and ω_{nm}, $\omega_{\nu n}$ are transition rates between the different levels. c_n is the proportionality coefficient between the flux of particles in the nth state, and the corresponding particle concentration. For charges moving under the influence of an electric field, $c_n = \mu_n E$, where μ_n is the mobility in the nth state and E is the electric field. The set of equations (1) have been written for one dimension, but the generalization of the results for three dimensions is straightforward. We consider a system of $N+1$ levels, so that $n, m, \nu = 0, 1, \ldots, N$. Terms with

$n=m$, $\nu=n$ are included in the summation since these terms cancel in any case.

We wish to derive an equation for the total concentration of particles in all levels $\rho(x,t)$, where

$$\rho(x,t)=\sum_n p_n(x,t)\,. \tag{2}$$

We first add the set of equations (1) giving

$$\frac{\partial p}{\partial t}=\sum_n g_n-\frac{\partial}{\partial x}\left(\sum_n c_n p_n\right)\,, \tag{3}$$

where all the terms corresponding to transitions between the various levels cancel since we have neglected recombination processes. Next we express the flux term on the right-hand side of Eq. (3) in terms of ρ. The simplest way to proceed is to express N of the $N+1$ concentration variables in terms of the remaining variable, and to express the remaining variable in terms of ρ. Without loss of generality we choose to express $p_1, \ldots, p_N$ in terms of p_0. We introduce the Laplace transform (LT)

$$L(p_n(x,t))=\tilde{p}_n(x,s)$$

$$=\int_0^\infty e^{-st}p_n(x,t)\,dt\,, \tag{4}$$

and write the equation for $\tilde{p}_1, \ldots, \tilde{p}_N$ in matrix form

$$\frac{\partial \underline{p}}{\partial x}=\underline{A}\underline{p}+\underline{h}\,, \tag{5}$$

where $\underline{p}$ is a vector with components $\tilde{p}_1, \ldots, \tilde{p}_N$, $\underline{h}$ is a vector with components $\tilde{h}_1, \ldots, \tilde{h}_N$, where $\tilde{h}_n=\tilde{f}_n+a_{n0}\tilde{p}_0$, and $\underline{A}$ is a matrix with components A_{nm}, where

$$A_{nm}=a_{nm}-\delta_{nm}\left(\sum_\nu b_{\nu n}\right) \tag{6}$$

and

$$\begin{aligned} a_{nm}&=\omega_{nm}/c_n\,,\\ b_{\nu n}&=[\omega_{\nu n}+s/(N+1)]/c_n\,,\\ \tilde{f}_n&=[\tilde{g}_n+p_n(x,0)]/c_n\,. \end{aligned} \tag{7}$$

Equation (5) can be solved easily to give

$$\underline{p}(s)=\int_0^x \exp[(x-x')\underline{A}(s)]\underline{h}(x',\tilde{p}_0)\,dx'\,, \tag{8}$$

where the $p_n(x,t)$ are assumed to vanish outside a finite interval $0\le x\le L$. The inverse LT can be obtained from Eq. (8),

$$\underline{p}(t)=L^{-1}(\underline{p}(s))\,. \tag{9}$$

Equation (2) can now be written

$$\rho=p_0+\sum_{n\neq 0} p_n=F[p_0]\,, \tag{10}$$

and using the fact that ρ is a unique functional of p_0, Eq. (10) can be inverted formally to give

$$p_0=G_0[\rho]\,. \tag{11}$$

Using Eqs. (8) and (11) we may write, in general,

$$p_n=G_n[\rho]\,, \tag{12}$$

and Eq. (3) becomes

$$\frac{\partial \rho}{\partial t}=\sum_n g_n-\sum_n c_n\frac{\partial}{\partial x}G_n[\rho]\,, \tag{13}$$

which is the desired master equation for ρ. In Sec. III we show how the above formal procedure can be carried out for a specific model of charge conduction in an amorphous medium.

III. EQUIVALENCE OF MULTIPLE-TRAPPING MODEL TO CTRW

The multiple-trapping model, defined by Eqs. (1)–(3) of I is a special case of the general linear-transport equations (1). In this model direct transitions between trap states are neglected, and it is assumed that the motion of free carriers can be characterized by a single mobility μ_0 for the band of transport states. In I it was shown that this simple model could describe a broad range of dispersion in photocurrent transients, using a small number of different types of traps. Here we show that the multiple-trapping equations are equivalent to the master equation of SM, using the general method described in Sec. I.[8] Another derivation of this equivalence has been presented by Schmidlin.[9]

Using the relation between the flux of mobile carriers, and the free-carrier concentration, we write Eq. (1) of I as

$$\frac{\partial \rho}{\partial t}=g-\vec{\nabla}\cdot\vec{\nabla}p\,, \tag{14}$$

where $\vec{\nabla}$ is the velocity of the free carriers. In order to obtain an equation for the total carrier concentration $\rho(\vec{x},t)$ from Eq. (14), it is necessary to obtain a relation between $p(\vec{x},t)$ and $\rho(\vec{x},t)$. This can be done using Eq. (2) of I and introducing the Laplace transform, giving

$$s\tilde{p}_i-p_{i0}=\tilde{p}\omega_i-\tilde{p}_i r_i\,, \tag{15}$$

where

$$p_{i0}=p_i(\vec{x},0)\,. \tag{16}$$

Hence

$$\tilde{\rho}=\tilde{p}+\sum_i\tilde{p}_i=\left(1+\sum_i\frac{\omega_i}{s+r_i}\right)\tilde{p}+\sum_i\frac{p_{i0}}{s+r_i} \tag{17}$$

or

$$\tilde{p} = \tilde{Q}\tilde{\rho} - \sum_i p_{i0}\tilde{Q}(s+r_i)^{-1}\,, \tag{18}$$

where

$$Q = \left(1 + \sum_i \frac{\omega_i}{s+r_i}\right)^{-1}. \tag{19}$$

Using the convolution theorem, the inverse transform of Eq. (18) is given by

$$p(t) = \int_0^t Q(t-t')\rho(t')\,dt' - \sum_i p_{i0}\int_0^t e^{-r_i t'}Q(t-t')\,dt'\,. \tag{20}$$

The second term in Eq. (20) corresponds to an initial distribution of trapped charge, and would be important in an analysis of thermally stimulated currents, say. Here we assume $p_{i0}=0$, and substituting Eq. (20) in Eq. (14) we get

$$\frac{\partial\rho}{\partial t} = g - \int_0^t Q(t-t')\vec{\nabla}\cdot\vec{\nabla}\rho(t')\,dt'\,. \tag{21}$$

Equation (21) is to be compared with the generalized master equation which is the starting point for the SM theory of anomalous dispersion[4]

$$\frac{dP(l,t)}{dt} = \int_0^t \phi(t-t')\sum_{l'}[\eta(l-l')P(l',t') - \eta(l'-l)P(l,t')]\,dt'\,. \tag{22}$$

SM superimpose a simple cubic lattice, lattice constant a_0, on the material and denote the cells by an index l. $P(l,t)$ is the probability that a cell is occupied by a carrier at time t. The quantities $\eta(l-l')$ are transition probabilities between cells, and $\phi(t)$ is a relaxation function. The $\eta(l-l')$ are dimensionless, and $\phi(t)$ has dimension t^{-2}. The effects of space charge are neglected in Eq. (22), as well as in the multiple-trapping model. The generation term was not included by SM in the master equation, but was discussed separately as a boundary condition. In general, however, a term $g(l,t)$ must be added to Eq. (22), and $P(l,0)$ must be given before the set of equations (22) can be solved.

We multiply Eq. (22) by the total number of carriers, and proceed to show the equivalence of CTRW to the multiple-trapping equations by taking the continuum limit of Eq. (22). We assume that $\eta(l-l')$ is different from zero only for nearest neighbors, and taking the electric field in the x direction, we have[10]

$$\eta(\pm1,0,0) = \tfrac{1}{6}\pm\tfrac{1}{2}\Delta\,,\qquad \eta(0,\pm1,0) = \eta(0,0,\pm1) = \tfrac{1}{6}\,, \tag{23}$$

where Δ corresponds to the small asymmetry in the transition probability between cells, in the x direction, caused by the electric field. In the continuum limit we get

$$P(l,t) \Rightarrow \rho(x,t)\,,\qquad P(l\pm 1_x,t) \Rightarrow \rho(x,t) \pm a_0\frac{\partial\rho}{\partial x}\,, \tag{24}$$

and

$$\int_0^t \phi(t-t')\sum_{l'}[\eta(l-l')P(l',t') - \eta(l'-l)P(l,t')]\,dt' \Rightarrow -\int_0^t \phi(t-t')(a_0\Delta)\frac{\partial\rho(t')}{\partial x}\,dt'\,, \tag{25}$$

where in obtaining Eq. (25) the term corresponding to diffusion has been neglected.[10] We equate Eq. (25) to the integral in Eq. (21), and find if $\tilde{Q}$ and $\tilde{\phi}$ are holomorphic,

$$\tilde{\phi} = \tilde{Q}/\tau\,, \tag{26}$$

where

$$\tau = a_0\Delta/\mu_0 E\,. \tag{27}$$

In order to complete the basic equivalence relation equation (26), the quantity τ must be specified. In other words the parameters of the CTRW model, specifically the product $a_0\Delta$, must be specified before the multiple-trapping model can "mapped" onto the CTRW model. We will argue that a reasonable choice for τ is the mean time for capture by any of the traps

$$\tau^{-1} = \sum_i \omega_i\,. \tag{28}$$

From Eq. (27) the quantity $\mu_0\tau E$ is then an "effective" schubweg, or distance travelled between trapping events. The definition of τ by Eq. (28) is consistent with the interpretation of the asymmetry factor Δ, which is given in terms of τ by Eq. (27), only if $\Delta \ll 1$, or $\mu\tau E \ll a_0$. Hence if there are only a couple of trapping events as the carrier crosses the sample, then the maximum cell parameter possible (the sample thickness L) will still not satisfy the condition $\mu_0\tau E \ll a_0$. In this case it is clearly inappropriate to establish an equivalence between the SM and multiple-trapping theories, although a small number of trapping events can still be described using the multiple-trapping equations. We would also like to point out that it may be possible to introduce definitions for τ other than Eq. (28). However, our definition is justified to some extent by the reasonable results of the calculation of the SM waiting-time distribution function $\psi(t)$ for a-Se as described in Sec. IV.

IV. WAITING-TIME DISTRIBUTION FUNCTION

According to SM, the relation between the relaxation function $\tilde{\phi}(s)$, and the waiting-time distribu-

tion $\tilde{\psi}(s)$, is[4]

$$\tilde{\psi}(s)=[1+s\tilde{\phi}(s)^{-1}]^{-1}. \tag{29}$$

Using Eqs. (19) and (26), and defining $\bar{s}=s\tau$, $\bar{\omega}_i=\omega_i\tau$, $\bar{r}_i=r_i\tau$, Eq. (29) becomes

$$\tilde{\psi}(\bar{s})=[1+b(\bar{s})]^{-1}, \tag{30}$$

where

$$b(\bar{s})=\bar{s}\left(1+\sum_{i=1}^{n}\frac{\bar{\omega}_i}{\bar{s}+\bar{r}_i}\right). \tag{31}$$

It can easily be shown that for n traps, $\tilde{\psi}(\bar{s})$ has $n+1$ real poles, denoted by

$$\bar{s}_i=-\alpha_i, \quad i=1,\ldots,n+1. \tag{32}$$

Equation (30) can then be rewritten

$$\tilde{\psi}(\bar{s})=\prod_{i=1}^{n}(\bar{s}+\bar{r}_i)\Big/\prod_{i=1}^{n+1}(\bar{s}+\alpha_i)$$

$$=\sum_{i=1}^{n+1}\frac{A_i}{\bar{s}+\alpha_i} \tag{33}$$

and

$$A_i=\prod_{j=1}^{n}(\bar{r}_j-\alpha_i)\Big/\prod_{j\neq i}^{n+1}(\alpha_j-\alpha_i). \tag{34}$$

It should be noted that this expression for the A_i is valid only when the r_i are all different. By taking the limit $\bar{s}\to\infty$, the sum rule

$$\sum_{i=1}^{n+1}A_i=1 \tag{35}$$

is obtained from Eq. (33). The inverse transform of Eq. (33) gives immediately

$$\tau\psi(t)=\sum_{i=1}^{n+1}A_i\exp\left(\frac{-\alpha_i t}{\tau}\right). \tag{36}$$

A simplification of this general formula can be obtained for $\bar{s}\ll 1$. Expanding Eq. (30) gives

$$\tilde{\psi}(\bar{s})\simeq 1-\bar{s}\left(1+\sum_{i=1}^{n}\frac{\bar{\omega}_i}{\bar{s}+\bar{r}_i}\right) \tag{37}$$

$$\simeq 1-\sum_{i=1}^{n}\bar{\omega}_i+\sum_{i=1}^{n}\frac{\bar{\omega}_i\bar{r}_i}{\bar{s}+\bar{r}_i}. \tag{38}$$

With τ given by Eq. (28), Eq. (38) becomes

$$\tilde{\psi}(\bar{s})=\sum_{i=1}^{n}\frac{\bar{\omega}_i\bar{r}_i}{\bar{s}+\bar{r}_i} \tag{39}$$

and

$$\tau\psi(t)=\sum_{i=1}^{n}\bar{\omega}_i\bar{r}_i\exp(-r_i t), \tag{40}$$

which is a special case of Eq. (36).

The calculated waiting-time distribution function for a-Se is shown in Fig. 1 for $T=143$ K. As discussed previously,[3] a three-trap model was found adequate to analyze the shapes of photocurrent transients in a-Se over a wide range of temperature and dispersion. The parameters determined from this analysis were used to evaluate $\psi(t)$ according to Eq. (36). The solid line in Fig. 1 shows the result of this calculation, and the dotted line shows the approximation to $\psi(t)$ given by Eq. (40). As expected, the approximation is good for long times, corresponding to $s\tau\ll 1$, and deviates from the exact result for shorter times. The straight line in Fig. 1 is drawn to indicate the power-law behavior $\psi(t)\sim t^{-\gamma}$ over two decades in time.

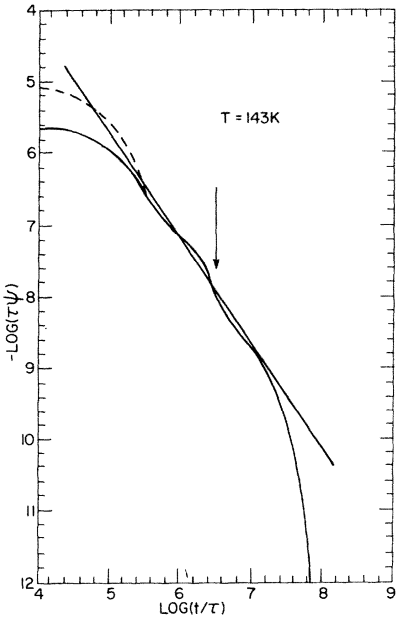

FIG. 1. Solid line—Scher-Montroll waiting-time distribution $\psi(t)$ calculated for a-Se using Eq. (36) and previously determined trap parameters for $T=143$ K, $E=10$ V/μm, $L=79$ μm. The straight line indicates the power-law behavior of the distribution function $\psi(t)\sim t^{-(1+\alpha)}$, and the dashed line shows the approximation to $\psi(t)$ calculated using Eq. (40), for $s\tau\ll 1$. The proportionality constant τ is defined by Eq. (28). The arrow indicates the apparent transit time t_m.

According to the SM theory of extreme dispersion $\gamma=1+\alpha$, where α is a disorder parameter, and the exponent of the power law for the distribution function should be the same as the exponent obtained directly from the $\log_{10}I$-$\log_{10}t$ plot of the photocurrent transient. From Fig. 1 we get $\alpha\simeq 0.5$, and the same value of α is obtained from the corresponding photocurrent transient shown in Fig. 1 of I, where $I\sim t^{-(1-\alpha)}$ for $t<t_m$ (apparent transit time) and $I\sim t^{-(1+\alpha)}$ for $t>t_m$. The small oscillations which appear both in the calculated $\psi(t)$ shown in Fig. 1 and the calculated photocurrent transient shown in Fig. 1 of I (dashed line) are due to the assumption of purely discrete trap

levels. These oscillations disappear when a distribution of trap release and capture rates is included in the model. The good agreement of the slopes in Fig. 1 of this paper and Fig. 1 of I is a powerful check on the validity of the multiple-trapping formalism, and also illustrates the usefulness of knowing the multiple-trapping parameters for a given material. For higher temperatures, the photocurrent transients in a-Se can no longer be characterized by a single parameter, α (Ref. 6) and the SM theory becomes difficult to apply, since a temperature-dependent order parameter must be introduced *a priori* into the waiting-time distribution function. However the multiple-trapping model can be used to analyze shapes of photocurrent transients over a wide range of temperature, and the corresponding waiting-time distribution function can then be calculated directly from Eq. (36) and the multiple-trapping parameters. A knowledge of $\psi(t)$ in turn can give information about the importance of various transport mechanisms in an amorphous material.

In Fig. 2 $\psi(t)$ is shown for a-Se at $T=188$ K. The slope of the straight-line portion is now steeper, and at $T=250$ K (Fig. 3) the distribution function has evolved to an exponential, characteristic

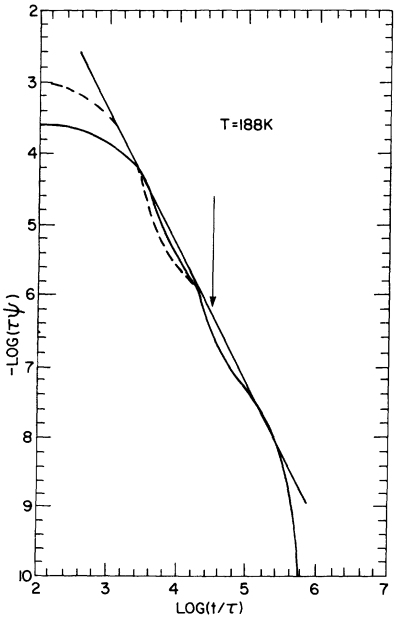

FIG. 2. Solid line—Scher-Montroll waiting-time distribution function $\psi(t)$ calculated for a-Se using Eq. (36) and previously determined trap parameters for $T=188$ K and same sample as in Fig. 1. The straight line shows the power-law behavior of $\psi(t)$, and the dashed line shows the approximation to $\psi(t)$ calculated using Eq. (40). The arrow indicates the apparent transit time t_m.

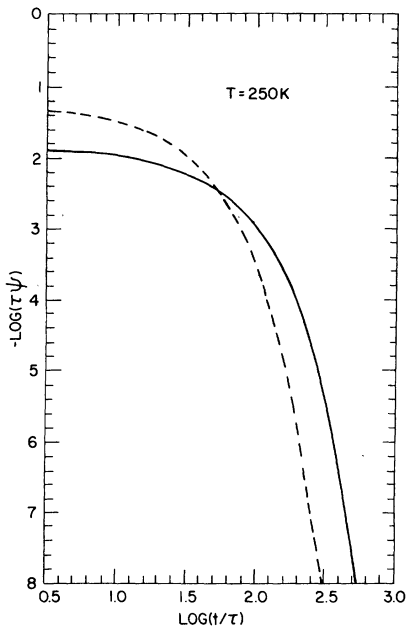

FIG. 3. Solid line—Scher-Montroll waiting-time distribution function $\psi(t)$ calculated for a-Se using Eq. (36) and previously determined trap parameters for $T=250$ K and same sample as in Figs. 1 and 2. The dashed line shows the approximation to $\psi(t)$ calculated using Eq. (40).

of nondispersive charge transport. The corresponding photocurrent transients are shown in the two panels of Fig. 2 of I. The method of calculating $\psi(t)$ outlined here is valuable in studying the transition between disperse and nondisperse charge transport, as illustrated by the behavior of the photocurrent transients in a-Se at $T\sim 188$ K. A discussion of various physical mechanisms in a-Se, using the present results, will be given in a future publication.[11]

V. CONCLUSIONS

A method of deriving the master equation for the total particle or charge carrier concentration, starting from generalized linear-transport equations, has been presented and applied to the multiple-trapping model. The multiple-trapping equations were shown to be formally equivalent to the continuum limit of the SM master equation, provided that the parameter τ, given by Eq. (27), was defined independently. Using the formal equivalence of the two theories, it was possible to represent the SM waiting-time distribution function $\psi(t)$ in terms of trapping parameters, and the quantity τ.

$\psi(t)$ was calculated for a-Se as a function of temperature, assuming $\tau^{-1}=\sum_i \omega_i$, and using previously

determined trapping parameters. The calculated curves showed the evolution of $\psi(t)$ from a power-law characteristic of extreme dispersion to an exponential characteristic of nondispersive transport.

In general, the multiple-trapping model has been found to be useful in several ways. It is a relatively simple model which can be used to analyze photocurrent transient data in terms of a small number of transport parameters, and to obtain significant trends in these parameters with temperature, electric field, and sample properties. However, the multiple-trapping formalism also affords a way of calculating $\psi(t)$ for the SM model. Although the CTRW formalism is very general, it is still necessary to specify the distribution function before quantities of interest can be calculated. In some cases, e.g., the transition to nondispersive transport in a-Se, it is not clear what form of $\psi(t)$ should be assumed. Using the parameters from an analysis in terms of multiple trapping allows us to calculate the detailed shape of $\psi(t)$, which can be compared to the results of model calculations. Knowledge about $\psi(t)$ obtained via a multiple-trapping analysis can thus be valuable in determining the underlying physical mechanisms involved in the charge transport.

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