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Charge-carrier-trapping kinetics in a chain with chaotically distributed traps and broken bonds: Biased-random-walk model

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An exact expression for the Laplace transform of the configurationally averaged survival probability of a charged particle executing biased (asymmetric) random walks in a chain with traps and broken bonds (barriers) is derived. By inverting this expression, it has been shown that in high fields the charge-carrier density decays exponentially at the initial stage of the trapping process. For long times the decay law is of the logarithmic-power type $\propto [\ln(t)+\alpha^{-1}]t^{-\alpha}$, where α is a constant. This indicates the possibility of an anomalous slowing down of charge-carrier trapping in quasi-one-dimensional systems, e.g., in conducting polymers containing barrier-type defects. The asymptotic law obtained corrects the power-law asymptotics predicted recently by Burlatsky and Ovchinnikov. In the fast- and slow-trapping cases the full time-scale dependence of the charge-carrier density has been defined for low and high fields. Different intermediate asymptotics, the number and the form of which depend specifically on the trapping rate, the field, and the concentration of traps and barriers, are predicted.

I. INTRODUCTION

The problem of asymmetric random walks in a chain with traps treated as a model of nonstationary charge transfer in nonideal quasi one-dimensional (Q1D) structures in a biased field has been widely discussed in recent years.[1–6] The interest has been stimulated by a number of exact results that proved to be useful in describing the charge-transport properties of real objects. Photocurrent kinetics in polydiacetylene crystals,[7–9] in DNA crystals,[10] and some other experiments are in agreement with the theory developed by Movaghar, Pohlmann, and Würtz.[1,2] It is also worth noting that some predictions made for exactly solvable 1D models, e.g., the existence of an intermediate asymptotics in the case of slow trapping,[11] can easily be extended to 2D and 3D systems.[4,5]

A physical quantity of interest in the trapping problem is the survival probability of a random walker (here, of a charge carrier). For a chain with chaotically distributed traps, the survival probability, or more precisely the averaged survival probability (ASP) (see below), has been found using the following assumptions:[1] (i) The energy change, when the charge carrier makes a single jump along the bias, is small in comparison with the thermal energy of the particle; (ii) the charge-carrier and trap concentrations are small; (iii) the trapping rate is infinite.

The case of arbitrary trap concentrations and of arbitrary fields has been considered on the basis of a master-equation formalism using the image method by Aldea, Dulea, and Gartner.[3] The concentration and field dependence of the rate constant of the ASP exponential decay in high fields were obtained.

A more general (and more realistic) model of finite trapping rates has been employed by Burlatsky and Ovchinnicov,[4] by Burlatsky and Ivanov,[5] and by Onipko and Zozulenko.[6] It was shown that the main conclusions derived assuming an infinite trapping rate[1] hold also for the case of fast trapping.[6] Thus an important extension of the theory has been achieved. At the same time, the ASP decay kinetics, just as its concentration dependence, are qualitatively different when the condition of slow trapping is satisfied.[4–6]

Real physical systems contain not only traps, but also defects acting as scattering centers or barriers for charge carriers. In one dimension both types of defects "cage" moving particles in chain segments, here called clusters. A particle caged in a cluster with infinite barriers on its ends avoids trapping. In reality, the existence of barrier-type defects can increase considerably the survival probability. This effect is observed in the host-to-trap excitation-energy transfer in various Q1D crystals.[12–15] Symmetric random walks in a chain with traps and perfectly reflecting barriers[16,17] simulate appropriately the above case.

As far as we know, the caging effect has not been demonstrated directly in studies of charge-transfer processes, although the barriers, undoubtedly, play an important role. The most remarkable effect expected is that an anomalous slowing down of trapping should be observed in large fields.[4,5] This conclusion is confirmed here qualitatively, but we obtain another form of the ASP decay law that reads as $\ln(t)/t^{-\alpha}$. It differs from the power-law asymptotics $\propto t^{-\alpha}$, predicted recently,[4,5] especially for a large bias when $\alpha \ll 1$.

A more detailed comparison with previous results is made in the concluding part of the paper. In Sec. II the Laplace transform of the ASP is found using the model of asymmetric random walks in a chain with traps and barriers (equivalently broken bonds) without any restrictions on the trapping rate, bias, and defect concentration. Starting from this point, we get, in Sec. III, analytic expressions for the ASP valid for all times in some important particular cases. As intermediate steps we rederive or generalize some of the earlier results. Mathematical details are presented in two Appendixes.

II. GENERAL EXPRESSION FOR THE AVERAGE SURVIVAL PROBABILITY

The physical reasons for a specific kinetics of charge-carrier trapping in a chain with barrier-type defects are as follows. In the presence of barriers, some traps are in such a position that the field accelerates a particle in motion toward the nearest barrier and thus increases the probability for the particle to escape trapping. In all such clusters with a trap at, say, the left end and a barrier at the right one, the charge carrier will avoid trapping much longer than that in a cluster with two traps at its ends or with a barrier and a trap placed in the direction of the charge drift. Therefore, one can expect that the character of the charge-density decay will be very much different for short and long times.

Let us specify the model to be considered. It is assumed that the charge is transferred only between host sites which form four types of clusters: those with two traps at the ends denoted below as (t,t); with two barriers, as (b,b); with a trap at the left end and with a barrier at the right end, as (t,b); and with left and right interchanged, as (b,t). To describe the particle dynamics in any of the above types of clusters, we introduce the jumping rates of a particle between the nearest-neighbor host sites, $W^{\pm}=W\exp(\pm\eta)$, along $(+)$ a bias field E and in the opposite direction $(-)$; $\eta=eEa/2\Theta$, e is the magnitude of the electronic charge, a is the lattice constant, and Θ is the particle thermal energy. The trapping rate of a particle located on a site neighboring a trap at the right is denoted as ω_1 and at the left as ω_n.

Note that a finite value of the trapping rate means that the trapping event does not occur with a unit probability, when the particle reaches a site neighboring the trap: The particle may be reflected several times before being trapped. At the same time, it is supposed that the trapping is an irreversible process.

In the notation adopted, the equations defining $G_{r,r_0}(t)$—the probability of finding a particle on the rth site, $r=1,2,\dots,n$ at time t (in units of W^{-1}), given its initial position in the same cluster is the r_0-th site—take the form for any of the chain cluster

$$\frac{dG_{r,r_0}(t)}{dt}=\sum_{r'}L_{r,r'}G_{r',r_0}(t),\quad r,r',r_0\in(1,2,\dots,n)\ , \tag{1}$$

$$G_{r,r_0}(0)=\delta_{r,r_0}\ , \tag{2}$$

where

$$\begin{aligned}&-L_{1,1}=\exp(\eta)+\frac{\omega_1}{W},\quad -L_{r,r}=2\cosh(\eta),\quad -L_{n,n}=\exp(-\eta)+\frac{\omega_n}{W}\ ,\\ &L_{r,r+1}=\exp(-\eta),\quad L_{r,r-1}=\exp(\eta),\quad L_{r,r'}=0,\quad |r-r'|\geq 2\ .\end{aligned} \tag{3}$$

The solution of Eqs. (1) and (2) describes asymmetric random walks on a chain with arbitrary absorption rates on the chain ends, the first and the nth sites. In the model under consideration, they are

$$\begin{aligned}&\omega_1=\omega W^- \text{ and } \omega_n=\omega W^+ \text{ for } (t,t)\ ;\\ &\omega_1=\omega W^- \text{ and } \omega_n=0,\text{ for } (t,b)\ ;\\ &\omega_1=0 \text{ and } \omega_n=\omega W^+,\text{ for } (b,t)\ ;\\ &\omega_1=0 \text{ and } \omega_n=0,\text{ for } (b,b)\ ;\end{aligned} \tag{4}$$

where ω is the ratio of the jumping rate from a host to a trap site to the jumping rate between host sites in the absence of a bias.

The model formulated implies a fast transverse relaxation of the generated charge carriers and their small density.

In accordance with Eq. (4), the particle cannot leave a trap and meet a barrier as a broken bond between the host sites. Thus, in a chain defected in this way, any charge carrier generated belongs to a certain cluster, where it starts moving. The independence of particle motion in different clusters simplifies the configurational-averaging procedure, reducing it to averaging over the cluster-length distribution in a three-component randomly disordered chain.[16,18] The averaging of the survival probability should be performed both over the random distribution of defects and over the initial positions of a particle (also assumed to be random) on the host sites.

Denoting the trap concentration as c_t, the barrier concentration as c_b, and the concentration of defects as $c=c_b+c_t$, so that $1-c$ is the host-site concentration, we can write, for the ASP,[16,18]

$$\begin{aligned}\Delta\Omega(t)&=\langle\Omega(t)\rangle-\langle\Omega(\infty)\rangle\\ &=\frac{c_t^2}{c^2}\langle\Omega(t)\rangle^{(t,t)}+\frac{c_tc_b}{c^2}[\langle\Omega(t)\rangle^{(t,b)}+\langle\Omega(t)\rangle^{(b,t)}]\ ,\end{aligned} \tag{5}$$

where the partial averages related to different types of clusters are defined in such a way

$$\langle\Omega(t)\rangle^{\nu}=c^2\sum_{n=1}^{\infty}n(1-c)^{n-1}\Omega_n^{\nu}(t)\ , \tag{6}$$

$$\Omega_n^{\nu}(t)=n^{-1}\sum_{r,r_0=1}^{n}G_{r,r_0}^{\nu}(t)\ ,\nu=(t,t),(t,b),(b,t)\ , \tag{7}$$

that $\langle\Omega(0)\rangle^{\nu}=1$. For example, $\langle\Omega(t)\rangle^{(t,t)}$ is just the survival fraction in a chain with randomly distributed traps, the concentration of which is c.[1,3,6]

The structure of Eqs. (5) and (6) is quite transparent.

The weight factor $c_t^2(1-c)^{n-1}$ implies the probability that a cluster, chosen in an *ad hoc* manner from all possible nonequivalent configurations of a three-component chain (consisting of host, trap, and barrier sites distributed at random), has n host sites and two traps at its ends. The weight factor $c_t c_b(1-c)^{n-1}$ related to clusters of the types (t,b) and (b,t) and also $c_b^2(1-c)^{n-1}$ has a similar meaning. The term in Eq. (5) which contains the latter factor represents the contributions to the ASP coming from (b,b) clusters, resulting in a nonzero ASP limit for infinite times,

$$\langle \Omega(\infty)\rangle = c_b^2/c^2 \ . \tag{8}$$

To obtain the survival probability of a particle in a given cluster, it is necessary to use in Eq. (7) the solution of Eqs. (1) and (2) with ω_1,ω_n taken in accordance with Eq. (4). Exact expressions of the survival probabilities can be found in the Laplace-transform space (see Appendix A). Summing the Green's function

$$\tilde{G}_{r,r_0}(s)=\int_0^\infty \exp(-st)G_{r,r_0}(t)dt \ ,$$

over r and r_0, one immediately gets Eq. (A10), resulting in

$$\tilde{\Omega}_n^{(t,t)}(s)=s^{-1}-\frac{\omega}{ns^2}\frac{Q_{n+1}(\xi)-\sinh[(n+1)\xi]s+(\omega-1)\{Q_{n-1}(\xi)+\sinh[(n-1)\xi]s\}}{[s(1-\omega+\frac{1}{2}\omega^2)+\omega^2\cosh(\eta)]\sinh(n\xi)+\omega(2-\omega)\sinh(\xi)\cosh(n\xi)} \ , \tag{9a}$$

where

$$Q_n(\xi)=4\sinh(\xi)\sinh\left[\frac{n}{2}(\xi+\eta)\right]\sinh\left[\frac{n}{2}(\xi-\eta)\right] ,$$

$$\exp(\pm\xi)=\frac{s}{2}+\cosh(\eta)\pm\left[\left[\frac{s}{2}+\cosh(\eta)\right]^2-1\right]^{1/2} ,$$

and

$$\tilde{\Omega}_n^{(t,b)}(s)=s^{-1}-\frac{\omega}{ns^2}\frac{e^{-\eta}\sinh[(n+1)\xi]-2\sinh(n\xi)+e^{\eta}\sinh[(n-1)\xi]+2e^{-n\eta}\sinh(\eta)\sinh(\xi)}{\sinh[(n+1)\xi]-e^{\eta}\sinh(n\xi)+(\omega-1)e^{-\eta}\{\sinh(n\xi)-e^{\eta}\sinh[(n-1)\xi]\}} \ , \tag{9b}$$

$$\tilde{\Omega}_n^{(b,t)}(s)=\tilde{\Omega}_n^{(t,b)}(s)|_{\eta\to-\eta} \ . \tag{9c}$$

The inverse Laplace transform of Eqs. (9) together with Eqs. (5) and (6) define an exact expression of the ASP. It is a good starting point for numerical calculations which can be useful in studying the charge-density temporal behavior for particular values of the parameters η, ω, and c. For some particular cases, we are able to get the time dependence $\Delta\Omega(t)$ in an explicit form.

III. LIMITING CASES OF THE ASP TIME DEPENDENCE

In accordance with Eq. (5), the definition of the ASP divides into three survival fractions, the partial averages $\langle\Omega(t)\rangle^{(t,t)}$, $\langle\Omega(t)\rangle^{(b,t)}$, and $\langle\Omega(t)\rangle^{(t,b)}$. Since for the first of them the time dependence is known (for $\eta,c\ll 1$, $\omega=\infty$;[1] for arbitrary values of η,c and $\omega=\infty$;[3] for $\eta,c\ll 1$, $\omega\gg c$, and $\omega\ll c$[4–6]), our task is to find the inverse Laplace transform for the partial averages over (t,b) and (b,t) clusters. The details of the inversion procedure are given in Appendix B.

Being completely identical in the case of a zero bias, $\langle\Omega(t)\rangle^{(b,t)}$ and $\langle\Omega(t)\rangle^{(t,b)}$ make essentially different contributions to the ASP when $\eta\neq 0$. The physical reasons for this are outlined in the preceding section. Mathematically, the difference results from the fact that $\tilde{\Omega}_n^{(t,b)}(s)$ has, as a function of s, an exponentially small pole in a complex plane, when $n\eta\gg 1$, and $\tilde{\Omega}_n^{(b,t)}(s)$ has none. The existence of such a pole results in the following asymptotics for the (t,b) survival fraction:

$$\langle\Omega(t)\rangle^{(t,b)}\propto\left[\ln\left[\frac{t}{\tau}\right]-\psi(\alpha)\right]\left[\frac{t}{\tau}\right]^{-\alpha} , \tag{10}$$

where

$$\psi(\alpha)=\frac{d\ln\Gamma(\alpha)}{d\alpha}=\begin{cases}\ln(\alpha)-(2\alpha)^{-1}+O(\alpha^{-2}), & \alpha\gg 1\\ -\alpha^{-1}-\gamma+O(\alpha), \quad \gamma=0.5772\ldots, & \alpha\ll 1 \ ,\end{cases}$$

$\alpha=c/2\eta$, $\Gamma(\alpha)$ is the gamma function, and the time-scale constant τ is defined by

$$\tau^{-1}=\frac{2\omega\sinh(\eta)}{1+\omega\exp(-\eta)/2\sinh(\eta)} \ , \tag{11}$$

for arbitrary values of the bias and trapping rate (in units of W). Equations (10) and (11) represent the main result of the paper.

In low fields, $\eta \ll c$, it is easy to show[6,17] that

$$\langle \Omega(t) \rangle^{(b,t)}_{\tau_1/4 \geq 1} = \frac{8}{\pi} \left[\frac{\tau_1}{6\pi} \right]^{1/2} \left[1 + \frac{17}{18} \left[\frac{\tau_1}{4} \right]^{-1/3} + \frac{205}{648} \left[\frac{\tau_1}{4} \right]^{-2/3} \right] \exp \left[-\eta^2 t - \frac{3}{2} \left[\frac{\tau_1}{4} \right]^{-1/3} \right] ,$$
$$\langle \Omega(t) \rangle^{(t,t)} = \langle \Omega(4t) \rangle^{(b,t)} , \tag{12}$$

where $\tau_1 = 2\pi^2 c^2 t$.

In high fields, $\eta \gg c$, we have, for these survival fractions,

$$\langle \Omega(t) \rangle^{(b,t)} = \langle \Omega(t) \rangle^{(t,t)} = \exp(-Kt) , \tag{13}$$

with the rate constant being dependent on the trapping rate

$$K = \begin{cases} 2c \sinh(\eta), & \omega \gg c \\ 2\omega \sinh(\eta), & \omega \ll c . \end{cases} \tag{14}$$

Equation (13) shows that the contributions to the ASP coming from the partial averages over (b,t) and (t,t) clusters are equivalent in high fields. It is quite natural and was to be expected. The upper equation of Eqs. (14) has initially been obtained for an infinitely fast trapping,[3] and the lower one represents a generalization of the formula $K = 2\omega\eta$ (Refs. 5 and 6) to the case of arbitrary biases. Both results are included in the following definition of K:

$$K = \frac{2c\omega \sinh(\eta)}{c + \omega} . \tag{15}$$

Comparing the results (10), (12), and (13), it is seen that the long-time behavior of the ASP obeys the logarithmic-power law (10). This dependence differs sharply from the exponential one expected for a classic trapping model (i.e., in a noninterrupted chain).

The quantities α and τ in Eq. (10) are field dependent. The latter dependence is especially remarkable, since it is trapping controlled. In the case $\omega = \infty$,

$$\tau^{-1} = 4 \exp(\eta) \sinh^2(\eta) = 4\eta^2, \text{ for } \eta \ll 1 . \tag{16}$$

But for sufficiently small trapping rates, we have

$$\tau^{-1} = 2\omega \sinh(\eta) = 2\eta, \text{ for } \eta \ll 1 . \tag{17}$$

This result is very much different from the corresponding prediction of a classic trapping model: The field dependence of the rate constant K is not sensitive to the trapping rate [Eqs. (14) and (15)].

As mentioned in the Introduction, the character of the ASP time behavior depends on ω. This dependence is pronounced in low fields.[6] This is also true for the model under consideration. Calculations of the (b,t) and (t,t) survival fractions in accordance with Eq. (12) and with exact formulas show that in the case of fast trapping, $\omega \gg c$, one gets practically the same results for $\langle \Omega(t) \rangle^{(b,t)}$ for times $\tau_1/4 \geq 1$ and for $\langle \Omega(t) \rangle^{(t,t)}$ for times $\tau_1 \geq 1$. For the (t,b) fraction, Eq. (12) is valid up to times $\tau_1 \ll (nc/\eta)^3$ only.

When the condition of slow trapping is satisfied, $\omega \ll c$, a generalization of the solution of the trapping problem[6] to include the (b,t) and (t,b) fractions is trivial and gives (for $\eta \ll c$)

$$\langle \Omega(t) \rangle^{(b,t)} = \langle \Omega(t) \rangle^{(t,b)}$$
$$= \tau_2 K_2[(2\tau_2)^{1/2}] \exp(-\eta^2 t) ,$$
$$\langle \Omega(t) \rangle^{(t,t)} = \langle \Omega(2t) \rangle^{(b,t)} , \quad \tau_2 = 2c\omega t \ll (\pi c/\omega)^2 , \tag{18}$$

where $K_2(t)$ is the modified Bessel function. At times $\tau_2 \gg (\pi c/\omega)^2$, the time dependencies of the survival fractions take the form of Eq. (12). For the fraction (t,b), the dependence (12) transforms into the asymptotics (10).

Combining the above results, we can write

$$[\Delta\Omega(t)]_{\eta \ll c} = \exp(-\eta^2 t) \Delta\Omega_{\eta=0}(t), \quad \tau_1 \ll (\pi c/\eta)^3 ;$$
$$\alpha\Gamma(1+\alpha)[\ln(t/\tau) - \ln(\alpha) + (2\alpha)^{-1}](t/\tau)^{-\alpha}, \quad \tau_1 \gg (\pi c/\eta)^3 , \tag{19}$$

and

$$[\Delta\Omega(t)]_{\eta \gg c} = \frac{c_t}{c} \exp\left[-\frac{2c\omega \sinh(\eta)}{c+\omega} t \right] + \frac{c_t c_b}{c^2} \alpha\Gamma(1+\alpha) \frac{\ln(t/\tau) + \alpha^{-1} + 0.5772}{(t/\tau)} , \tag{20}$$

where $\Delta\Omega_{\eta=0}(t)$ is the solution of the problem for zero bias.[17]

IV. DISCUSSION AND CONCLUSIONS

The results obtained can, in our opinion, be instrumental in studies of charge-carrier trapping processes in Q1D organic crystals. Therefore, we summarize the main expectations concerning the charge-density decay kinetics predicted in the model.

(i) In high fields, $\eta \gg c$, the decay law of the ASP in the interval of $\langle \Omega(t) \rangle$ from 1 to $(1 - c_t/c)$ is very close to an exponential one, with the rate constant defined in Eq. (15). Further changes in the ASP [in the interval from

$(1-c_t/c)$ to c_b^2/c^2] are extremely slow [Eq. (20)]. Thus, if a Q1D crystal contains barrier-type defects, the decay of the charge-carrier density due to trapping can be appreciably slowed up by applying a sufficiently high electric field. This expectation is quite realistic. For instance, polydiacetylenes are very likely to be built of finite polymer segments.[19] In this respect it is important that Eq. (10) define not only the asymptotic dependence proper, but under certain conditions, also that it describe the charge-carrier density decay in a time interval available for observations.

It is appropriate to recall the well-known power decay law $t^{-\mathrm{const}}$ associated with dispersive transport[20] (the constant is a parameter of disorder). It is often observed in time-resolved experiments in conducting polymers.[21,22] The power-law and the logarithmic-power dependencies are not easily distinguished experimentally. To choose an adequate interpretation, the specific field dependence, prescribed by Eqs. (10) and (11), can be used.

(ii) The field dependence of the exponential-decay rate constant K is not sensitive to the trapping rate. In contrast, the dependence $\tau(\eta)$ is modified by the parameter ω [see Eq. (11)] and therefore is informative in this respect. It is important also that measurements of $\tau(\eta)$ can be performed when the charge density is not too small (if c_b and c_t are of the same order of magnitude) and thus are, in principle, available. For example, for $c_b=c_t$ the ASP decay is exponential up to 0.5 only. Then the stage of slow, logarithmic-power decay follows.

(iii) The asymptotics of $\Delta\Omega(t)$ has been obtained earlier in the form $\propto(t/\tau)$.[4,5] The absence of a logarithmic factor, which is especially important when $\alpha\ll 1$, is due to the fact that the factor x in the averaging formula (B8) has been omitted.[5] There are other discrepancies between the Burlatsky-Ivanov results and ours. The field dependencies of the time scale τ have been given for limiting cases only ($\tau^{-1}\propto\eta^3$, $\eta\ll\omega$ [Eq. (109)] and $\tau^{-1}\propto\eta^2$, $\eta\gg\omega$ [Eq. (111)]; compare with Eqs. (16) and (17)). Moreover, this quantity turns out to be dependent on the defect concentration[5] for reasons not yet clarified.

(iv) In low fields, $\eta\ll c$, the time dependence of the ASP is qualitatively different at an early stage of the decay for the cases of fast and slow trapping. For $\omega\gg c$, in accordance with Eqs. (5), (10), and (12), one can expect the following changes in charge-density decay kinetics when the time increases:

$$\begin{aligned}
&\Delta\Omega(t)\propto J_1(t)\to J_2(t)\to J_3(t)\ ,\\
&J_1(t)\propto c_t^2\exp\left[-\frac{3}{2}\tau_1^{1/3}\right]+2c_tc_b\exp\left[-\frac{3}{2}\left[\frac{\tau_1}{4}\right]^{1/3}\right]\ ,\\
&J_2(t)\propto\exp(-\eta^2t)\ ,\\
&J_3(t)\propto\frac{\ln(t/\alpha\tau)+(2\alpha)^{-1}}{(t/\tau)^{\alpha}}\ ,
\end{aligned}\tag{21}$$

whereas for $\omega\ll c$,

$$\begin{aligned}
&\Delta\Omega(t)\propto J(t)\to J_1(t)\\
&\qquad\to J_2(t)\to J_3(t)\ ,\\
&J(t)\propto c_t^2\exp[-2(\tau_2)^{1/2}]+c_tc_b\exp[-(2\tau_2)^{1/2}]\ ,
\end{aligned}\tag{22}$$

if $\eta\ll\omega$, and

$$\Delta\Omega(t)\propto J(t)\to J_2(t)\to J_3(t)\ ,\tag{23}$$

if $\eta\gg\omega$ (but still $\eta\ll c$).

All the above dependencies except $J_2(t)$ show the trapping slowing down with increasing time due to fluctuations of the defect density. The difference between the powers in the exponents of $J(t)$ and of $J_1(t)$ is the direct consequence of the fact that the capture of particles is trapping-rate controlled in the first case and diffusion-rate controlled in the second. In its turn, the dependence $J_3(t)$ shows that the microscopic picture of the capture process at long times differs from that mentioned above. This regime may be called a field-suppressing trapping. The slowing down observed at this stage is the most dramatic and, in a sense, anomalous.

Note that the intermediate asymptotics (21)–(23) is more or less pronounced, depending on the parameters. For certain relations between trap and barrier concentrations, the dependence $J_2(t)$ will not manifest itself at all as an intermediate asymptotics.

To conclude, it is to be mentioned that if we follow the arguments of previous works,[4,5] our asymptotics is valid for a three-component (host molecules, trap molecules, and molecules of an inert solvent) randomly disordered system of any dimensionality d, which is below the percolation threshold. In such a system the charge carriers are supposed to diffuse and to drift in closed cavities formed by host molecules in the solvent ($c_t\ll c_b, 1-c$). In high fields the asymptotic approach to the steady-state limit of the ASP is governed by the survival probability in those cavities which have the form of a long thick cylinder with its axis parallel to the field and where the charge drift is directed from the base containing traps to that containing no traps. Thus the problem of finding an asymptotics is in essence of the kind solved here. At the same time it is clear that for $d>1$ the transition to the asymptotic decay law will not be as sharp as it is for $d=1$ in high fields. The question of when the asymptotics is "switched on" remains so far unanswered for $d>1$.

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APPENDIX A: RANDOM WALKS IN A CHAIN WITH ARBITRARY ABSORPTION ON ITS ENDS: SOLUTION AND SURVIVAL PROBABILITY IN THE LAPLACE-TRANSFORM SPACE

Using in Eqs. (1) and (2) the substitution

$$\tilde{G}_{r,r_0}(s)=\exp(r-r_0)g_{r,r_0}(s)\ ,\tag{A1}$$

we get

$$\begin{aligned}
&[s+2\cosh(\eta)]g_{1,r_0}(s)=\delta_{1,r_0}-\beta_1g_{1,r_0}(s)+g_{2,r_0}(s)\ ,\\
&[s+2\cosh(\eta)]g_{r,r_0}(s)=\delta_{r,r_0}+g_{r-1,r_0}(s)\\
&\qquad\qquad+g_{r+1,r_0}(s),\quad 2\le r\le n-1\ ,\\
&[s+2\cosh(\eta)]g_{n,r_0}(s)=\delta_{n,r_0}-\beta_ng_{n,r_0}(s)+g_{n-1,r_0}(s)\ .
\end{aligned}\tag{A2}$$

These equations coincide formally, up to the replacement $s+2\cosh(\eta)\to s+2$, with the ones describing dynamics of symmetric random walks in an n-site chain with the rate of absorption β_1+1 on the first site and β_n+1 on the nth site,

$$\left.\begin{matrix}\beta_1\\ \beta_n\end{matrix}\right\}=\frac{\omega_{1(n)}}{W}-\exp\left\{\begin{matrix}-\eta\\ +\eta\end{matrix}\right\}. \tag{A3}$$

Introducing a generating function

$$\Phi_{r_0}(s,z)=\sum_{r=1}^{n} g_{r,r_0}(s)z^r , \qquad g_{r,r_0}(s)=\frac{1}{r!}\left.\frac{d\Phi_{r_0}(s,z)}{dz^r}\right|_{z=0} , \tag{A4}$$

we find

$$\Phi_{r_0}(s,z)=z\frac{(1+\beta_1 z)g_{1,r_0}(s)+z^n(\beta_n+z)-z^{r_0}}{(z-z_+)(z-z_-)}, \tag{A5}$$

where

$$z_\pm=\frac{s+2\cosh(\eta)}{2}\pm\left\{\frac{[s+\cosh(\eta)]^2}{4}-1\right\}^{1/2} .$$

Taking into account the analyticity of the generating function at $z=z_+$ and $z=z_-$, we obtain

$$\begin{aligned} g_{1,r_0}(s)&=D_n^{-1}(\xi)\{\sinh[(n-r_0+1)\xi]\\ &\quad+\beta_n\sinh[(n-r_0)\xi]\} ,\\ g_{n,r_0}(s)&=D_n^{-1}(\xi)\{\sinh(r_0\xi)+\beta_1\sinh[(r_0-1)\xi]\} . \end{aligned} \tag{A6}$$

where $\sinh(r\xi)=\frac{1}{2}(z_+^r-z_-^r)$ and

$$\begin{aligned} D_n(\xi)&=\sinh[(n+1)\xi]+(\beta_1+\beta_n)\sinh(n\xi)\\ &\quad+\beta_1\beta_n\sinh[(n-1)\xi] . \end{aligned} \tag{A7}$$

Substituting Eqs. (A5) and (A6) into Eq. (A4), we get the solution of Eq. (A2):

$$\begin{aligned} [g_{r,r_0}(s)]_{r\le r_0}&=\frac{\{\sinh(r\xi)+\beta_1\sinh[(r-1)\xi]\}\{\sinh[(n-r_0+1)\xi]+\beta_n\sinh[(n-r_0)\xi]\}}{\sinh(\xi)D_n(\xi)} ,\\ [g_{r,r_0}(s)]_{r\ge r_0}&=[g_{r_0,r}(s)]_{r\le r_0} , \end{aligned} \tag{A8}$$

and hence the solution of Eqs. (1) and (2) in the Laplace-transform space.

The relation

$$s\sum^{n}\tilde{G}_{r,r_0}(s)=1-\frac{\omega_1}{W}\tilde{G}_{1,r_0}(s)-\frac{\omega_n}{W}\tilde{G}_{n,r_0}(s) \tag{A9}$$

simplifies finding the expression for the Laplace transform of the survival probability

$$\begin{aligned} \tilde{\Omega}_n(s)&=n^{-1}\sum_{r,r_0=1}^{n}\tilde{G}_{r,r_0}(s)\\ &=s^{-1}-\frac{1}{ns^2D_n(\xi)}\left\{\frac{\omega_1+\omega_n}{W}\sinh[(n+1)\xi]-2\frac{\omega_1\exp(\eta)+\omega_n\exp(-\eta)}{W}\sinh(n\xi)\right.\\ &\qquad+\frac{\omega_1\exp(2\eta)+\omega_n\exp(-2\eta)}{W}\sinh[(n-1)\xi]\\ &\qquad+2\frac{\omega_1\exp[-(n-1)\eta]-\omega_n\exp[(n-1)\eta]}{W}\sinh(\eta)\sinh(\xi)\\ &\qquad\left.+2\frac{\omega_1\omega_n}{W}\{\sinh(n\xi)-\cosh(\eta)\sinh[(n-1)\xi]-\sinh(\xi)\cosh[(n-1)\eta]\}\right\} . \end{aligned} \tag{A10}$$

Putting in Eq. (A10) ω_1 and ω_n in accordance with Eq. (4), one gets the expressions for the survival probabilities in clusters (t,t), (b,t), and (t,b) given in the text.

APPENDIX B: TIME DEPENDENCIES $\Omega_n^\nu(t)$ IN HIGH FIELDS

It can be verified that the function $\tilde{\Omega}_n(s)$ is not singular at $s=0$, except the trivial case $\omega_1=\omega_n=0$. Thus all poles of this function in a complex s plane are defined by the equation

$$D_n(\xi)=0 . \tag{B1}$$

Using the identity

$$\frac{\sinh[(n+1)\xi]}{\sinh(\xi)}=\sum_{k=0}^{n}\frac{s^k}{k!}f_{n,k}(\eta) , \tag{B2}$$

where

$$f_{n,k}(\eta)=\frac{d^k}{d[2\cosh(\eta)]^k}\,\frac{\sinh[(n+1)\eta]}{\sinh(\eta)}\;, \tag{B3}$$

Eq. (B1) can be rewritten in an equivalent form

$$\sum_{k=0}^{n}\frac{s^k}{k!}[f_{n,k}(\eta)+(\beta_1+\beta_n)f_{n-1,k}(\eta)+\beta_1\beta_n f_{n-2,k}(\eta)]=0\;. \tag{B4}$$

The latter is more convenient for an analysis of the limit $s\to 0$, i.e., of the long-time behavior of $\Omega_n(t)$.

For clusters (t,b), $\omega_n=0$, $\omega_1/W=\omega\exp(-\eta)$, it follows, from the above two equations,

$$\omega\exp(-n\eta)+\frac{s}{2\sinh^2(\eta)}\{2\sinh(\eta)\sinh(n\eta)+\omega[\exp(-\eta)\sinh(n\eta)-n\sinh(\eta)\exp(-n\eta)]\}+O(s^2)=0\;. \tag{B5}$$

Under the condition $n\eta\gg 1$, one of the solutions of Eq. (B5) is

$$s_{\min}=-\frac{2\omega\sinh(\eta)}{1+\dfrac{\omega\exp(-\eta)}{2\sinh(\eta)}}\times[\exp(-2n\eta)+O(\exp(-3n\eta))]\;. \tag{B6}$$

The rest of the $n-1$ poles of $\tilde{\Omega}_n^{(t,b)}(s)$ are not smaller in magnitude, than n^{-2} or ωn^{-1}. Moreover, it can be shown that a factor before the exponent $\exp(s_{\min}t)$ in a standard representation of the original of the rational function $\tilde{\Omega}_n^{(t,b)}(s)$ is close to unity. Thus we can write

$$\Omega_n^{(t,b)}(t)=\exp\left[-\frac{t}{\tau}\exp(-2n\eta)\right]\;, \tag{B7}$$

with τ defined in Eq. (11).

The use of Eq. (B7) in Eq. (6) yields, for $c\ll 1$,

$$\langle\Omega(t)\rangle_{t\to\infty}^{(t,b)}=\int_{2\alpha}^{\infty}x\exp\left[-x-\frac{t}{\tau}\exp\left[-\frac{x}{\alpha}\right]\right]dx=\alpha\Gamma(1+\alpha)\frac{\ln(t/\tau)-\psi(\alpha)}{(t/\tau)^{\alpha}},\quad\text{for } t\gg\alpha\tau \tag{B8}$$

This expression, with the lower integral limit equal to zero, can be used for a description of the full time dependence of the survival fraction (t,b) in high fields, $\alpha=c/2\eta\ll 1$.

We turn now to the clusters (t,t) and (b,t). Changing in Eq. (B5) the sign of η and retaining the terms with the powers s^0 and s^1 only, we get

$$s'_{\min}=-\frac{2\omega\sinh(\eta)}{1+\omega n},\quad\text{for } n\eta\gg 1\;. \tag{B9}$$

This equation defines the smallest pole of $\tilde{\Omega}_n^{(b,t)}(s)$ if $\omega n\ll 1$. Just the same result is valid for $\tilde{\Omega}_n^{(t,t)}(s)$. Following the way of calculations,[6] one gets Eq. (13) with the rate constant $K=2\omega\sinh(\eta)$.

To obtain expressions for $\langle\Omega(t)\rangle^{(b,t)}$ and $\langle\Omega(t)\rangle^{(t,t)}$ in the case of fast trapping, the contributions coming from all poles of the functions $\tilde{\Omega}_n^{(b,t)}(s)$ and $\tilde{\Omega}_n^{(t,t)}(s)$ should be taken into account.[1,3,6] A generalization of the calculation procedure[6] into the case of arbitrary biases is straightforward and gives the result presented in Eqs. (13) and (14).

It is interesting to note that, using the exponent with the rate constant defined by Eq. (B9), i.e.,

$$\Omega_n^{(b,t)}(t)=\Omega_n^{(t,t)}(t)=\exp\left[-\frac{2\omega\sinh(\eta)}{1+\omega n}t\right]\;, \tag{B10}$$

for all values of ω and n, we get (in the mean-field approximation)

$$\langle\Omega(t)\rangle_{\eta\gg c}^{(b,t)}=\langle\Omega(t)\rangle^{(t,t)}=\exp\left[-\frac{2c\omega\sinh(\eta)}{c+\omega}t\right]\;. \tag{B11}$$

This derivation is not strict, but it gives surprisingly good coincidence with exact calculations in the limit cases, $\omega\gg c$ and $\omega\ll c$. Thus it seems reasonable to use Eq. (B11) for a description of the charge-carrier density decay in high fields for arbitrary trapping rates.

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