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Non-equilibrium transport of charge carriers in disordered organic materials

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Abstract

An analytic theory of non-equilibrium hopping charge transport in disordered organic materials is developed. It rests on the concept of effective transport energy and includes quasi-equilibrium (normal) and extremely non-equilibrium (dispersive) regimes of hopping transport as limiting cases at long and short times, respectively. Special attention is paid to the regime of moderately weak non-equilibrium transport. In this regime the quasi-equilibrium value of the mobility is nearly established, whereas the coefficient of field-assisted diffusion continues to increase at long times. Analytic expressions for relaxation times in the context of field-assisted diffusion and carrier drift have been obtained. The results of the theory are in agreement both with the data of time-of-flight experiments for molecularly doped polymers and the results of numerical simulations of the Gaussian disorder model. The impact of non-equilibrium effects on the transit time of charge carriers in thin organic films with a thickness of the order of 100 nm, which is typical for organic light-emitting diodes, is outlined.

1. Introduction

Charge transport in disordered organics has been intensively investigated in the last 30 years, both experimentally and theoretically. The Gaussian disorder model (GDM) [1] plays a dominant role in the understanding of the physical background of transport. The concept of the GDM is the temperature- and field-assisted tunnelling (hopping) of charge carriers between localized states (LSs). LSs are randomly distributed in their energies and mutual distances under the dominant role of energetic disorder. The latter is described by a Gaussian

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distribution function of energies of LSs. The transition rates of charge carriers have been assumed to follow the Miller and Abraham model [2]. The ubiquitous experimental option for investigating charge transport is the time-of-flight (TOF) experiment, the observable being the transient current in the organic layer. In general, the GDM model explains phenomena such as the field and temperature dependences of charge carrier mobility, the transition from the regime of normal (quasi-equilibrium) to dispersive transport with decreasing temperature, and the anomalously large field-dependent dispersion of the transient current signal under quasi-equilibrium conditions. The essential role of energy correlations of neighbour LSs in the Poole–Frenkel-type field dependence of mobility in low electric fields was the subject of subsequent theoretical works [3].

The main computational method in the GDM as well as in recent works [3] is the Monte Carlo numerical simulation. However, simulating the effect of positional disorder is a notoriously difficult and time-consuming task, especially at low field strengths and temperatures [1]. This problem can be overcome by analytic theories. Examples of such theories are the models of hopping transport that are based on the concept of effective transport energy [4–8]. These were applied successfully in recent years in order to calculate quasi-equilibrium carrier mobility [6] and injection currents [7]. The effective transport energy is analogous to the mobility edge in the multiple-trapping (MT) model [6], where deeper LSs can be considered as traps. This concept allows one to adapt the earlier results of the MT model [9–11] for the hopping. This hopping theory, however, has not been developed for the general case of non-equilibrium hopping transport. So far, only the asymptotic regimes of quasi-equilibrium [6, 12] and extremely non-equilibrium (dispersive) [13] hopping have been considered analytically.

The topic of recent works was the quasi-equilibrium transport in general, especially the charge carrier mobility [6, 8, 14–17]. However, it is an inherent feature of transport in disordered materials that shortly after their generation excess carriers are not yet in quasi-equilibrium, notably if there is an excess energy during excitation [1]. This circumstance, together with a strong variance of transition rate of carriers between LSs, causes a decrease of the average mobility with time, while the spatial dispersion of carriers relative to their mean position is anomalously large and time independent. This case is referred to as dispersive transport [1, 13, 18], whereas at long times, quasi-equilibrium transport is established, characterized by time-independent mobility and diffusion coefficients, implying that relative dispersion decreases with time. The later transport mode, referred to as quasi-equilibrium or Gaussian transport, is often realized in materials with moderate energetic disorder. Indeed, the TOF transients of $\geqslant 1$ μm thick samples at room temperature bear out a well developed plateau. This circumstance, however, does not always imply that the transport is completely normal, i.e. Gaussian. An unambiguous signature of the deviation from quasi-equilibrium is the anomalously large dispersion of formally non-dispersive TOF signals and the concomitant scaling of the tails of TOF signals as a function of sample thickness and electric field strength. This scaling was qualitatively explained in the works of Bässler *et al* [19–21] in terms of the increase of field-assisted diffusivity in the long-time domain after the relaxation of the carrier mobility.

In the present work, an analytic theory for non-equilibrium hopping charge transport in disordered organics is being developed with special emphasis on transport in thin samples, e.g. such as those used in light-emitting diodes. It includes previously investigated quasi-equilibrium (normal) [6] and extremely non-equilibrium (dispersive) [13] regimes at long and short times, respectively. The equations introduced in section 2.1 allow adapting analytic results, which has been obtained earlier in the MT model [9–11], to the case of hopping transport. In section 2.2, analytic estimations of relaxation times of carrier mobility, t_{eq_μ},

and field-induced diffusivity, $t_{\mathrm{eq\_}D}$, $t_{\mathrm{eq\_}\mu} \ll t_{\mathrm{eq\_}D}$, are obtained, where $t_{\mathrm{eq\_}D}$ is the time of ultimate establishment of quasi-equilibrium. In section 2.3 the time dependence of the TOF current is analysed and a simple approximate analytic expression is obtained. The results are in good agreement with both TOF experiments for molecularly doped polymers and Monte Carlo simulations of the GDM [1, 19–22], as shown in section 3.

2. Theory

2.1. Equation of non-equilibrium hopping transport

An inherent feature of disordered materials is a broad distribution of LSs in energy and mutual distances. The energy distribution of LSs is described in terms of the distribution function $g(E)$, $\int_{-\infty}^{\infty} \mathrm{d}E\, g(E) = 1$. The appropriate choice for organic materials is the Gaussian energy distribution of LSs,

$$g(E) = \exp(-E^2/2\sigma^2)/\sqrt{2\pi\sigma^2}. \tag{1}$$

Analyses of transport in disordered materials can be greatly simplified by the concept of transport energy [4–8]. It rests on the notion that (i) for the typical case $\sigma/kT \gg 1$ charge transport is controlled by thermally activated jumps from LSs in a deep tail of $g(E)$, and (ii) for these jumps the energy of the target state E_{trans} does not depend on the energy of the initial state E, if $E \ll E_{\mathrm{trans}}$, since $g(E)$ decreases drastically to lower energies. The states around E_{trans} (the latter is usually called 'transport energy') contribute mostly to the transport process, while the great majority of charge carriers are localized at deeper states, $E \ll E_{\mathrm{trans}}$. The deep states, $E < E_{\mathrm{trans}}$, can be considered as traps, while E_{trans} and LSs with $E > E_{\mathrm{trans}}$ are mobility edge and 'conductive states', respectively. The method of calculating E_{trans} is introduced here.

The transition rate of charge carrier from the LS of energy E to the LS of energy E', which are separated by the distance r, is described in this work in terms of the Miller–Abraham expression, i.e. $\nu(r, E, E') = \nu_0 \exp[-u(r, E, E')]$, where $u(r, E, E') = \eta(E' - E)(E' - E)/kT + 2\gamma r$ is the hopping parameter, $\eta(x)$ is the unit step function, ν_0 is the frequency prefactor, γ is the inverse localization length, k is the Boltzmann constant and T is the temperature. The steep dependence of the transition rate on u together with positional disorder implies that a carrier jumps to that neighbour LS that is characterized by a minimal value of the hopping parameter $u = u_0$. The jump, followed by a return to the initial LS, does not contribute to transport, however. Consequently, the parameters of numerous neighbours of the initial LS must be included in order to determine the value of u_0. A rigorous formalism is provided by the percolation theory [23, 24]. This approach encounters problems, however, if a non-uniform and non-stationary distribution of charge carriers is considered. On the other hand, if transport is dominated by energetic rather than by positional (off-diagonal) disorder, i.e. if the energy distribution of LSs is rather broad, one can assume that the typical release frequency of a carrier from an LS with energy E, $\omega(E) = \nu_0 \exp[-u_0(E)]$, depends only on the energy of this LS, E. This assumption will be justified by comparing of theoretical results with data of experiments, Monte Carlo simulations in the GDM and results of percolation theory (see below). Following [5, 6], one can define the typical release frequency $\omega(E)$ by the condition

$$n\{E, \ln[\nu_0/\omega(E)]\} = 1, \tag{2}$$

where $n(E, u_0)$ is the mean number of neighbours for the LS of energy E having hopping parameters $u \leqslant u_0$. An approximate approach to calculate $\omega(E)$ will be introduced below.

The number $n(E, u_0)$ is a sum of two terms, $n(E, u_0) = n_{\downarrow}(E, u_0) + n_{\uparrow}(E, u_0)$, the latter and former accounting for upwards and downwards jumps, respectively. For the limit of deep

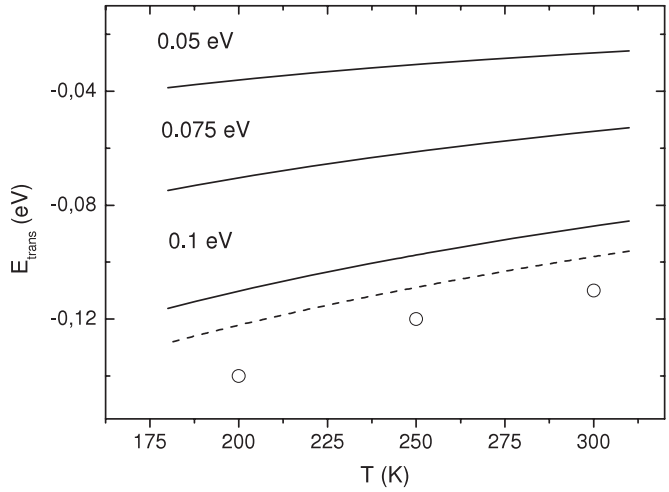

Figure 1. Temperature dependences of the transport energy $E_{\rm trans}$ for different values of σ, as shown in the figure. The solid lines are calculated from equations (A.1), (4) and (5). The dashed line is calculated under the assumption that return jumps are absent, in order to compare this result with the data from [8] ($\sigma = 0.1$ eV); see circles. $N = 10^{21}$ cm^{-3}, $\gamma^{-1} = 0.2$ nm.

LSs, $E \to -\infty$, one can replace $n(E, u_0)$ by $n_\uparrow(E, u_0)$ in (2). The calculation of $n_\uparrow(E, u_0)$ is described in appendix A. The result is [6] $u_0 \approx (E_{\rm tr} - E)/kT$, and hence

$$\omega(E) \approx \nu_0 \exp[-(E_{\rm tr} - E)/kT], \qquad E < E_{\rm trans}, \tag{3}$$

where the formal transport energy $E_{\rm tr}$ was defined as [6]

$$\lim_{E\to-\infty} \{n_\uparrow[E, (E_{\rm tr} - E)/kT]\} = 1. \tag{4}$$

Obviously, for $n_\uparrow[E, u_0(E)] > 1/2$, jumps are preferably upwards in energy and, hence, the upper limit of traps, i.e. the transport energy, can be defined by the condition

$$n_\uparrow\{E_{\rm trans}, (E_{\rm tr} - E_{\rm trans})/kT\} = 1/2. \tag{5}$$

One should remember that the formal transport energy $E_{\rm tr}$ as defined in [6] cannot be considered as the upper energetic limit of sites that can act as traps because the respective hopping parameter $u_0 = (E_{\rm tr} - E)/kT$ does not contain the tunnelling term $\widetilde{=}2\gamma a$ included in the Miller–Abrahams model. Considering u_0 as $u_0 = (E_{\rm trans} - E)/kT + 2\gamma a$, one obtains following equation for the typical hopping distance a:

$$a = (E_{\rm tr} - E_{\rm trans})/2\gamma kT. \tag{6}$$

Since jumps from the LSs with energies $E \geqslant E_{\rm trans}$ occur preferably downwards in energy, $\omega(E) \approx \nu_0 \exp(-2\gamma a) \equiv \tau_0^{-1}$. In other words, τ_0 is the lifetime of carriers in 'conductive' LSs with energies above $E_{\rm trans}$. It should be noted that the condition $2\gamma N^{-1/3} kT/\sigma > 1$, where N is the spatial density of LSs, is usually fulfilled in organic materials even at moderately low temperatures. For $2\gamma N^{-1/3} kT/\sigma \gg 1$, equations (4) and (5) yield $E_{\rm trans} \approx 0$. This is plausible because the jump rate to the neighbour LS is defined by the spatial distance rather then by the energy difference. For the same case, $E_{\rm tr}$ is well above the centre of $g(E)$, $E_{\rm tr} \approx 1.2kT(6\gamma^3/\pi N)^{1/3} \gg \sigma$ [6]. For this limit, (6) yields $a \approx E_{\rm tr}/2\gamma kT \approx 1.2(3/4\pi N)^{1/3} \approx 0.745N^{-1/3}$.

Figure 1 shows the temperature dependences of the transport energy $E_{\rm trans}$ calculated from (1), (4) and (5) for different values of the energy variance σ. Obviously, $|E_{\rm trans}| < \sigma$

for the case $\sigma < 0.1$ eV, $T > 200$ K, and $|E_{\text{trans}}| \to 0$ in the high-temperature limit. Note that in [8] the transport energy was defined differently, i.e. as the maximum of the energy-dependent 'differential conductivity', that describes the contribution of states with given energy E to the total conductivity. The dashed line shows $E_{\text{trans}}(T)$, calculated under the assumption that returns to the initial states are absent (see appendix A), as in [8]. The circles show the transport energy at several temperatures as it have been calculated in [8]; see figure 2 of that paper. These values differ by less than kT, if $T > 200$ K. This supports the notion that the definition of E_{trans} by (5) is in good agreement with the statement that LSs with energies around E_{trans} contribute mostly to the transport and hence E_{trans} is in analogy with 'mobility edge' of the MT model. Thus, both release and capture of charge carriers for LSs with energies $E < E_{\text{trans}}$, which are characterized by the typical frequency $\omega(E)$, see (3), and by energy-independent capture time $\tau_0 = \nu_0^{-1} \exp(2\gamma a)$, respectively, can be described in complete analogy with the MT model, E_{trans} being the mobility edge.

One has to remember that, in a real TOF experiment, charge carriers are not generated under quasi-equilibrium, but, rather, are generated in the upper portion of the density of states. That implies energetic relaxation (thermalization) of charge carriers. It occurs simultaneously with transport, and should be considered as a two-step process [4, 5, 13]. The first step is a sequence of fast jumps downwards in energy right after a carrier was started at $t = 0$. However, the characteristic time of this process cannot considerably exceed the time τ_0 under the presumed condition $2\gamma N^{-1/3} kT/\sigma > 1$. Upwards jumps to the transport energy, which are described above, are the rate-limiting step for transport at $t \gg \tau_0$; hence under this condition the concept of transport energy is valid. The moment $t = \tau_0$ often will be referred to as $t = 0$ below, because τ_0 is much shorter than all other characteristic times mentioned below.

One has to recall also the approximation made when distinguishing between deep and shallow traps, that greatly simplify the analytic modelling of energetic relaxation of charge carriers in course of non-equilibrium transport [9–11]. In this approximation all the traps (i.e. LSs with energies $E < E_{\text{trans}}$) are considered as being either currently deep or either currently shallow, defined by the condition that release of a previously captured carrier from a currently deep trap is not probable up to time t, and vice versa. In the simplest approximation [9, 10], all traps are deep, if $E < E_{\text{d}}(t)$, and vice versa. The demarcation energy $E_{\text{d}}(t)$ is defined from the condition $\omega[E_{\text{d}}(t)]t = 1$ and equation (3) as

$$E_{\text{d}}(t) = E_{\text{tr}} - kT \ln(\nu_0 t) = E_{\text{trans}} - kT \ln(t/\tau_0), \qquad t > \tau_0. \tag{7}$$

Obviously, $E_{\text{d}}(t) < E_{\text{trans}}$ at $t > \tau_0$.

On the basis of the formal analogy between MT and hopping at $t \gg \tau_0$, as discussed above, one can describe the time- and coordinate-dependent density of charge carriers $p(x, t)$ by the following differential equation, which was derived previously in the framework of the MT model [9, 11],

$$\frac{\partial p(x,t)}{\partial t} + \mu(t) F_0 \frac{\partial p(x,t)}{\partial x} - D_{\text{F}}(t) \frac{\partial^2 p(x,t)}{\partial x^2} = -\lambda(t)[p(x,t) - p(x,0)], \tag{8}$$

where F_0 is the strength of the applied electric field, and $\mu(t)$, $D_{\text{F}}(t)$ and $\lambda(t)$ are the time-dependent mobility, coefficient of field-assisted diffusion and trapping frequency, respectively. These values are defined as

$$\mu(t) = \mu_0 \theta_1(t), \tag{9a}$$

$$D_{\text{F}}(t) = \tau_0^{-1} (\mu_0 F_0 \tau_0)^2 \theta_1^3(t)/\theta_2(t), \tag{9b}$$

$$\lambda(t) = \theta_1(t)/\tau(t), \tag{9c}$$

where

$$1/\theta_m(t) = \int_{E_d(t)}^{E_{trans}} dE\, g(E)[\tau_0\omega(E)]^{-m}, \qquad m = 1, 2, \tag{10}$$

$$1/\tau(t) = \int_{-\infty}^{E_d(t)} dE\, g(E)/\tau_0, \tag{11}$$

$\omega(E)$ and $E_d(t)$ are defined by (3) and (7), respectively, and the mobility μ_0 in 'conductive' states is introduced as $\mu_0 = (1/6)(e/kT)a^2/\tau_0$, where a is defined by (6). Obviously, $\theta_m(t)$ decreases with time, while $\tau(t)$ increases.

In a typical TOF experiment the condition $eF_0L \gg kT$ is fulfilled, and hence diffusion could be neglected in comparison to drift. However, in a disordered system there is an additional spreading of an initially narrow sheet of charge carriers that gives rise to the diffusion-like term in (8). This kind of spreading was analysed analytically for quasi-equilibrium conditions in [10, 12] and called field-assisted or field diffusion. It appears due to (i) small deviations from equilibrium in the shallow trap population, caused by electric field, and (ii) dispersion of release times of carriers [10–12]. The mean distance of drift in 'conductive states', $\mu_0F_0\tau_0$, is a 'mean free path' in the coefficient D_F, see (9*b*), and hence $D_F \sim F_0^2$. Details of the thermalization of charge carriers and the way to derive equation (8) are given in appendix B. One has to note that a low level of charge carrier generation is considered, and hence filling of deep states is neglected here, as in GDM simulations [1].

Obviously, $E_d(t) = E_{trans}$ at $t = \tau_0$ i.e. all traps are deep and occupation of all traps is off-equilibrium. In the course of thermalization, the lower energetic boundary $E_d(t)$ of shallow states, that are in quasi-equilibrium, moves towards deeper states. Shortly after charge carriers are generated, however, transport is exclusively dominated by deep traps, i.e. it is entirely dispersive. The time duration of this period is defined by the condition $\theta_1(t)^{-1}\, d\tau(t)/dt < 1$ [9]. Under this condition one can neglect the term $\partial p/\partial t$; in addition, the field-diffusion term can be neglected in comparison with the right-hand side of (8). Since equation (8) transforms to the ordinary dispersive transport equation [9, 13],

$$\mu_0\tau(t)F_0\frac{\partial p(x,t)}{\partial x} = -[p(x,t) - p(x,0)]. \tag{12}$$

In contrast, $\lambda(t) \to 0, \mu(t) \to \mu_{eq}$, $D_t(t) \to D_{eq}$ in the limit of long time, and hence equation (8) reduces to the usual Fokker–Planck equation, which describes quasi-equilibrium transport with time-independent mobility μ_{eq} and field-dependent diffusion coefficient D_{Feq} [10, 12]. These constants are defined by (9*a*), (9*b*) and (10) with $E_d(t) \to -\infty$. Thus, the system of equations (8)–(11) provides an analytic description of hopping transport of carriers in the dispersive transport regime and also allows us to analyse subsequent relaxation towards quasi-equilibrium. Coefficients and time dependences from (8) will be analysed extensively in the following section.

2.2. Non-equilibrium hopping mobility and field diffusion coefficient

Using (1), (3) and (10) one obtains the following expressions for the functions that define the time dependences of the mobility and field-assisted diffusion coefficient via (9*a*) and (9*b*),

$$\frac{\theta_m(t)^{-1}}{(\nu_0\tau_0)^m} = \frac{1}{2}\exp\left[\frac{m}{2}\left(\frac{\sigma}{kT}\right)^2 + \frac{mE_{tr}}{kT}\right]\left\{\mathrm{erfc}\left[\frac{m\sigma}{\sqrt{2}kT} + \frac{E_d(t)}{\sqrt{2}\sigma}\right] - \mathrm{erfc}\left[\frac{m\sigma}{\sqrt{2}kT} + \frac{E_{trans}}{\sqrt{2}\sigma}\right]\right\}, \tag{13}$$

where $m = 1, 2$, and $\mathrm{erfc}(x) = (2/\sqrt{\pi}) \int_x^\infty \mathrm{d}t \exp(-t^2)$ is the complementary error function. Equations (3), (9) and (13) for the limit $t \to \infty$ yield

$$\mu(t) \approx \mu_{\mathrm{eq}} = \frac{e}{kT} \chi_\mu(E_{\mathrm{trans}}) \frac{\nu_0 a^2}{6} \exp\left[-\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2 - \frac{E_{\mathrm{tr}}}{kT}\right], \qquad t \geqslant t_{\mathrm{eq\_}\mu}, \tag{14}$$

$$D_{\mathrm{F}}(t) \approx D_{\mathrm{Feq}} = \chi_D(E_{\mathrm{trans}})(\nu_0 a^2) \left(\frac{eF_0 a}{6kT}\right)^2 \exp\left[\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2 - \frac{E_{\mathrm{tr}}}{kT}\right], \qquad t \geqslant t_{\mathrm{eq\_}D}, \tag{15}$$

where a is defined from (6), $\chi_\mu(E_{\mathrm{trans}}) = 2/\mathrm{erfc}[-\sigma/\sqrt{2}kT - E_{\mathrm{trans}}/\sqrt{2}\sigma]$, $\chi_D(E_{\mathrm{trans}}) = \chi_\mu^3 \,\mathrm{erfc}[-\sqrt{2}\sigma/kT - E_{\mathrm{trans}}/\sqrt{2}\sigma]$. Both factors χ_μ, χ_D are nearly 1 for the practically relevant case $\sigma/kT \gg 1$. The equilibrium mobility μ_{eq}, see (14), is the same as in [6], since here E_{tr} is taken from [6], except for the numerical factor $\approx 1/6$.

The factor $\exp[-E_{\mathrm{tr}}/kT]$ in (14), (15) determines the dependence of μ and D_{F} on the density of the LS, N. For the limit of dilute systems, $2\gamma N^{-1/3} kT/\sigma \gg 1$, one obtains $E_{\mathrm{tr}}/kT \approx 1.2(6\gamma^3/\pi N)^{1/3} = 2\gamma a$. Thus, $\mu_{\mathrm{eq}} \sim \exp(-C2\gamma N^{-1/3})$, and the value $C = 0.745$ is close to the well-known result of percolation theory [24], i.e. $C_{\mathrm{perc}} = 0.865$.

One has to note that the field dependence of mobility has not been analysed in this paper because it is restricted to the low-field limit, i.e. $eF_0 a/kT < 1$. Therefore the effect of field strength on the mobility and on the field diffusion, see (9*b*), is of minor importance. On the other hand, at room temperature and $a \approx 0.6$ nm, one obtains $F_0 < 4 \times 10^5$ V cm^{-1}, that is strong enough to neglect conventional diffusion.

Analysing equation (13) yields the following relaxation times $t_{\mathrm{eq\_}\mu}$ and $t_{\mathrm{eq\_}D}$ of mobility and field diffusion, respectively:

$$\nu_0 t_{\mathrm{eq\_}\mu} = \exp[(\sigma/kT)^2 + E_{\mathrm{tr}}/kT], \qquad \nu_0 t_{\mathrm{eq\_}D} = \exp[2(\sigma/kT)^2 + E_{\mathrm{tr}}/kT]. \tag{16}$$

2.3. Transient current for the conditions of the time-of-flight experiment

The initial condition for conducting a TOF experiment is to generate a narrow sheet of carriers at $x = 0$; hence $p(x, 0) = A_0 \delta(x)$ is proportional to the Dirac delta function, and A_0 is the area density of generated carriers. Fourier transformation with respect to the variable x yields the following solution of equation (8) in the infinite sample:

$$p(x, t) = G(x, t, 0) + \int_0^t \mathrm{d}t' \lambda(t') G(x, t, t'), \tag{17a}$$

$$G(x, t, t') = A_0 \exp\{-\Lambda(t, t') - [x - F_0 M(t, t')]^2/4S_{\mathrm{F}}(t, t')\}/\sqrt{4\pi S_{\mathrm{F}}(t, t')} \tag{17b}$$

where

$$S_{\mathrm{F}}(t, t') = \int_{t'}^t \mathrm{d}\tau D_{\mathrm{F}}(\tau), \qquad \Lambda(t, t') = \int_{t'}^t \mathrm{d}\tau \lambda(\tau), \qquad M(t, t') = \int_{t'}^t \mathrm{d}\tau \mu(\tau).$$

Remember that conventional diffusion is neglected and hence charge carriers cannot penetrate to the region $x < 0$. Disagreement of this statement with (17) is, however, not principal. One should remember that the diffusion-like term in (8) is only an approximate way to describe field-assisted dispersion of a carrier packet, and this approximation is not valid in the short time domain. The condition of applicability of the field-diffusion approximation, namely $t\theta_2(t)/\theta_1(t) \gg 1$ [10], is fulfilled, however, in all calculations that are performed in this work. Namely, the integral $\int_0^\infty \mathrm{d}x\, p(x, t)/A_0$ was no less than 0.95 for the shortest times involved in calculations. This means that dispersive drift contributes generally to the dispersion of charge carriers, and the unphysical 'tail' of $p(x, t)$ at $x < 0$ is unimportant, even at short

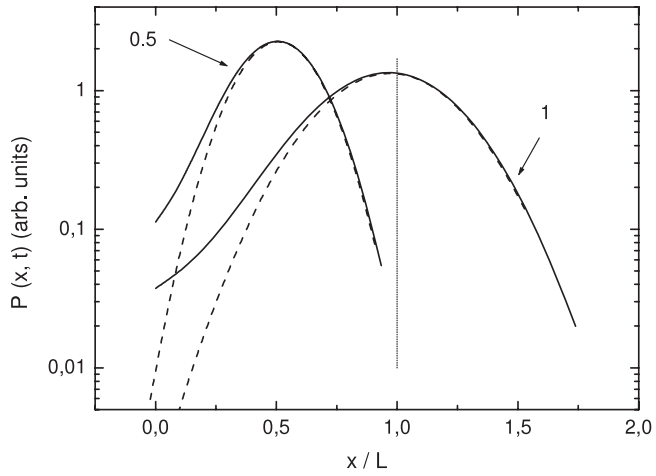

Figure 2. Spatial profiles of the charge carrier density $p(x, t)$ are calculated from equations (17) for the times $t = 0.5t_{\rm tr}$ and $t = t_{\rm tr}$ (solid lines). The dashed lines show the respective Gaussians. $F_0 = 2 \times 10^5$ V cm^{-1}, $\sigma/kT = 3.5$, $2\gamma N^{-1/3} = 10$, $L = 5$ μm.

times. Thus, equations (17) together with the following equation [9, 10]

$$j(t) = (e/L)\partial/\partial t \int_0^L {\rm d}x(x - L)p(x, t) \tag{18}$$

solve the problem of calculating the transient current under TOF conditions. Neglecting field-stimulated diffusion, the transit time of charge carriers can be determined from the following equation [10]:

$$F_0 \int_0^{t_{\rm tr}} {\rm d}t' \mu(t') \exp[-\Lambda(t_{\rm tr}, t')] = L. \tag{19}$$

One can simplify the highly complicated time dependence $j(t)$ as defined by (17), (18) for the relevant case of moderately non-equilibrium transport, $t \geqslant t_{\rm eq\_\mu}$, or $t\lambda(t) < 1$. Estimating integrals in (17), (18) for this case yields $p(x, t) \approx G(x, t, 0)$ and

$$j(t) \approx (1/2)(eA_0F_0/L)\mu(t) \exp[-t\lambda(t)]{\rm erfc}[(F_0M(t, 0) - L)/2\sqrt{S_{\rm F}(t, 0)}]. \tag{20}$$

3. Discussion

Spatial profiles of charge carrier density, as calculated from equations (17), are shown in figure 2 for $t = 0.5t_{\rm tr}$ and $t = t_{\rm tr}$ (see solid lines) considering $t_{\rm eq\_\mu} \ll t_{\rm tr}$.

Dashed lines shows Gaussian profiles with widths that are identical to the front of $p(x, t)$. Obviously, the maximum of a carrier distribution is practically in the position $x = L$ at $t = t_{\rm tr}$. The front of the $p(x, t)$ profile is practically Gaussian while the carrier density near $x = 0$ greatly exceeds the values that are expected from the Gaussian function. Consequently, the mean position of carriers is slightly behind the maximum, see the arrows in the figure, while both values increase practically linearly with time. A non-Gaussian tail of the distribution appears due to the capture of carriers on deep traps with release times greater than the transit time.

Figure 3 shows good quantitative agreement with the TOF signal as calculated from the approximate equation (20) and from (17), (18), see dashed and solid lines, respectively, and qualitative agreement both with experimental, see line with circles, and simulated

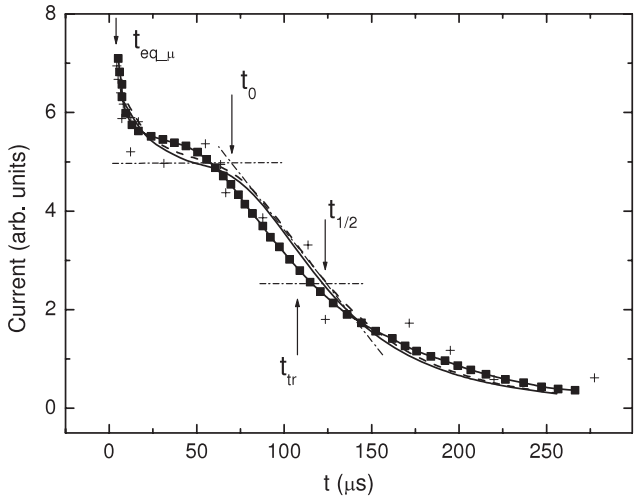

Figure 3. Time dependence of the TOF current. Solid and dashed lines are the results of calculations from equations (17), (18) and (20), respectively. Results of the TOF experiment (line with squares) and Monte Carlo simulations of the GDM (crosses) are taken from figure 22 of [1]. Arrows indicate the characteristic times; see text. $T = 312$ K, $\sigma/kT = 3.5$, $N = 4.6 \times 10^{21}$ cm^{-3}, $\gamma^{-1} = 0.12$ nm.

results in GDM data, see full circles. Data for polycarbonate (PC), doped by 1,1-bis(di-4-tolylaminophenyl) cyclohexane (TAPC), are taken from figure 22 of [1].

Although $t_{\mathrm{eq\_}\mu}$ is much less than the transit time, see arrows on the figure, the current is not strictly constant at any time, because of the moderate decrease of $\mu(t)$ and strong spatial dispersion of carriers. The 'plateau' level j_0 is defined operationally by the time of the minimal tangent, and then characteristic values $j_{1/2} = j_0/2 = j(t_{1/2})$, t_0 and $t_{1/2}$ are defined by the dot–dashed lines in figure 3. Obviously, the transit time t_{tr} from (22) is good approximation to the time $t_{1/2}$.

Equation (16) predicts that in the course of field-assisted carrier diffusion, their relaxation to quasi-equilibrium is not at all completed when the current reached its asymptotic value, i.e. $t_{\mathrm{eq\_}D} \gg t_{\mathrm{eq\_}\mu}$ for $\sigma/kT \gg 1$. In figure 4, the time dependences $eD_{\mathrm{F}}(t)\mu_{\mathrm{eq}}kT$ and $\mu(t)/\mu_{\mathrm{eq}}$, see (9*a*), (9*b*), (13), are plotted versus normalized time $t/t_{\mathrm{eq\_}\mu}$ for several values of the energetic disorder parameter σ/kT. It demonstrates enhanced field-assisted diffusion in the time domain $t_{\mathrm{eq\_}\mu} \ll t < t_{\mathrm{eq\_}D}$, if $\sigma/kT \geqslant 2.5$, although the mobility remains practically constant. This explains why in TOF experiments the dispersion of the carrier arrival times, $W = (t_{1/2} - t_0)/t_{1/2}$ [1, 21], exceeds the value predicted by conventional diffusion. Using equation (20), one obtains

$$W \approx L^{-1}\left[\pi \int_0^{t_{\mathrm{tr}}} \mathrm{d}t\, D_{\mathrm{F}}(t)\right]^{1/2}. \tag{21}$$

In the limit $t_{\mathrm{tr}} > t_{\mathrm{eq\_}D}$, one can reduce (21) to the well-known form [1]

$$W \approx \sqrt{\pi\, D_{\mathrm{F}}(t_{\mathrm{tr}})/\mu_{\mathrm{eq}} F_0 L}, \tag{22}$$

implying $t_{\mathrm{tr}} \approx L/\mu_{\mathrm{eq}}F_0$ and $D_{\mathrm{F}}(t) \approx D_{\mathrm{F}}(t_{\mathrm{tr}})$. The ratio $f \approx eD_{\mathrm{F}}(t_{\mathrm{tr}})/kT\mu_{\mathrm{eq}}$, that can be derived from the measured dispersion W differs considerably from that predicted under the premise of the quasi-equilibrium limit $f(t \to \infty) = eD_{\mathrm{Feq}}/kT\mu_{\mathrm{eq}}$, if $t_{\mathrm{tr}} < t_{\mathrm{eq\_}D}$ (figure 4).

Variation of $D_{\mathrm{F}}(t_{\mathrm{tr}})$ with the t_{tr} parametric of σ/kT, F_0 and L should cause substantial deviations from the predictions of equations (9*a*), (9*b*), (14), (15), and (22), i.e. $W \sim F_0^{0.5}$,

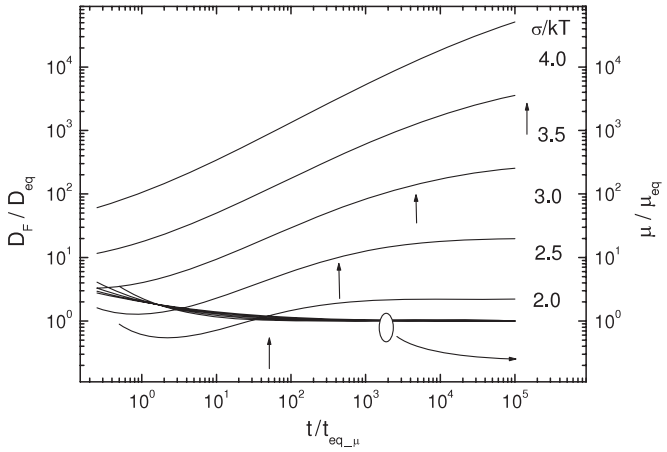

Figure 4. Time dependences of the field-assisted diffusion coefficient, normalized by the equilibrium value of the coefficient of usual diffusion, $D_{\rm eq} = \mu_{\rm eq} kT/e$, parametric in σ/kT values. Respective dependences $\mu(t)/\mu_{\rm eq}$ are also shown in the figure. Time is normalized by the relaxation time of mobility $t_{\rm eq\_\mu}$, see equation (16). The arrows mark the relaxation times $t_{\rm eq\_D}$. Other parameters: $F_0 = 2 \times 10^5$ V cm^{-1}, $N = 4.6 \times 10^{21}$ cm^{-3}, $\gamma^{-1} = 0.12$ nm, $T = 295$ K.

$W \sim L^{-0.5}$, $W \sim \exp[0.5(\sigma/kT)^2]$, if the transit time is sufficiently large to achieve quasi-equilibrium. This is in agreement with GDM simulations and TOF experiments [1, 19–22] for large sample thickness or weak field. On the other hand, the $W(L, F_0)$ dependence becomes weak as L and F_0^{-1} decreases [1, 21, 22]. In the sense of the current model, the power-like increase of field diffusion coefficient in a long-time domain such as $D_{\rm F} \sim t^{0.6}$ for $\sigma/kT = 4$ (see figure 4) causes $W \sim (F_0/L)^{0.2}$; see (21). In view of the statistical scatter of experimental or GDM data, the latter is difficult to distinguish from $W = \text{const}$ [20]. GDM simulations on a sample with positional disorder and intermediate thickness yield power-law dependences $W \sim L^{-n}$, $0 < n < 0.5$ [21]. In figure 5, calculated $W(L)$ dependences are compared with experimental data at several values of σ/kT. Data on TAPC-doped polystyrene are taken from the [22]. A $W \sim L^{-0.5}$ law is indicated by dashed straight lines. This is confirmed by the $W(L)$ dependence for $\sigma/kT = 2.6$. For $\sigma/kT = 3.0$ $W(L)$ become weaker ($L < 3$ μm), and for $\sigma/kT = 4.4$ the dispersion is practically independent of sample thickness. Values of W, as calculated from (21) and (22), are in qualitative agreement with experimental data (see solid and dash–dotted lines). The peculiarities of the $W(L, F_0, \sigma/kT)$ dependences, mentioned above, are a signature of transport being not completely in quasi-equilibrium although the mobility has equilibrated already. The coefficient of field-assisted diffusion continues to increase during several orders of magnitude in time even at moderate energy disorder, i.e. $\sigma/kT = 3.0$ (figure 4). This transport regime will therefore be referred to as quasi-dispersive.

Simulation data in [19] on a system with pure energy disorder and $\sigma/kT = 3.0$ delineated the different timescales for relaxation of mobility and diffusivity. The time dependence of the diffusivity is taken from figure 1 of [19] and compared with the function $D_{\rm F}(t)$ in figure 6. The latter is calculated from (9*b*), (13) and is normalized by the minimal value of GDM diffusivity. The time is normalized by the typical hopping time $t_0 = (1/6)\exp(2\gamma N^{-1/3})$ [1]. Both dependences are in good agreement. They show a minimum at $t \cong t_{\rm eq\_\mu}$. For the GDM data, the latter is defined by the condition $\mu(t_{\rm eq\_\mu})/\mu_{\rm eq} \approx 2$, in accordance with figure 4.

At shorter times the transport is dispersive. Values of $t_{\rm eq\_\mu}$ and $t_{\rm eq\_D}$, as defined from the data of [19] and from (16), are shown by solid and dashed arrows, respectively. Meanwhile the

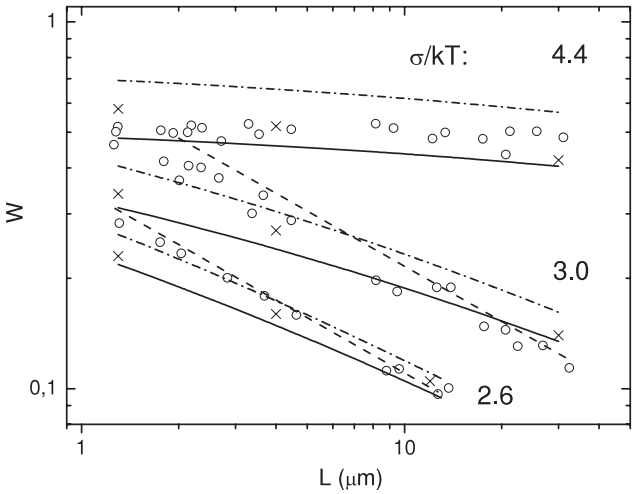

Figure 5. Dependences of the relative dispersion of the transient current W on the sample thickness L for several values of σ/kT (shown in the figure). Other parameters are: $F_0 = 2 \times 10^5$ V cm^{-1}, $N = 4.6 \times 10^{21}$ cm^{-3}, $\gamma^{-1} = 0.15$ nm. Experimental data (circles) are from [22]. Solid and dash–dotted lines are calculated from approximate equations (21) and (22), respectively. The dashed lines are the dependences $W \sim L^{-1/2}$. Crosses are the results of straightforward determination of $W = (t_{1/2} - t_0)/t_{1/2}$ from $j(t)$ curves.

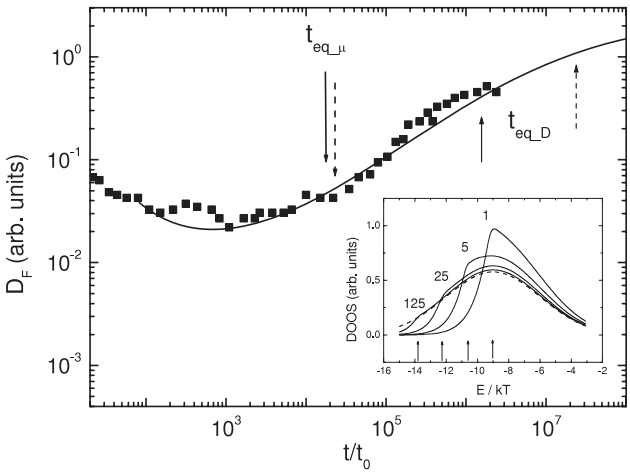

Figure 6. Comparison of time dependences $D_F(t)$ from this work (solid line) and from GDM (points, see figure 1 of [19]), $\sigma/kT = 3$. Time is normalized to $t_0 = (1/6)\exp(2\gamma N^{-1/3})$. Relaxation times of μ and D_F as defined from the GDM and this model are marked by solid and dashed arrows, respectively. The inset shows the time evolution of the density of occupied states, as calculated from equations (B.1) and (3). Ratios t/t_{eq_μ} are shown in the figure, and respective positions of the demarcation energy $E_d(t)$ are shown by arrows. The steady-state distribution is denoted by the dotted line.

former time is practically the same as the time when the averaged energy of localized carrier approaches the equilibrium value σ^2/kT, i.e. the difference becomes less than kT, while both the maximum of the distribution of occupied states (DOOS) and the demarcation energy $E_d(t)$ reach σ^2/kT (see the inset to figure 6). The time t_{eq_D} is of the same order of magnitude

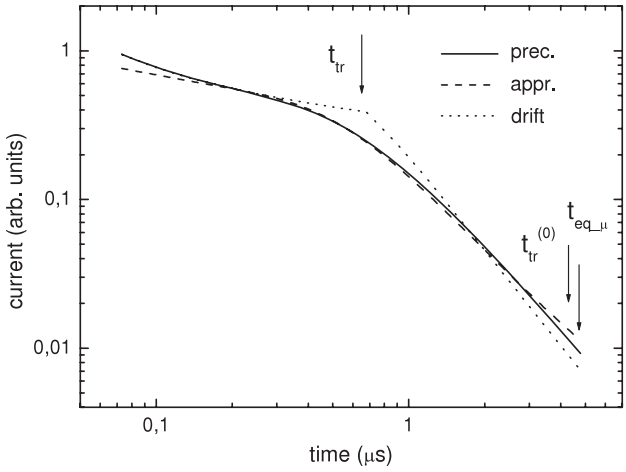

Figure 7. TOF current in thin film, $L = 100$ nm. Other parameters are the same as for figure 3. The solid line is the calculation based upon equations (17) and (18) while the dotted line is the same, but field diffusion is neglected. The dashed line is calculated from the approximate equation (20). Arrows indicate the characteristic times; see text.

as the time when the dispersion of energies approaches the equilibrium value σ [19]. Slow relaxation of the latter reflects slow relaxation of carriers towards the very tail states; see details in appendix B. This is shown in the inset to figure 6, where time evolution of spatially averaged DOOS $\langle\rho\rangle(t)$ is calculated from equations (B.1) and (3). The coefficient of field diffusion is controlled by the entire DOOS because it determines the variance of dwell times for carriers. On the other hand, shallow LSs contribute preferably to the current, and their equilibration takes much less time.

Obviously, charge transport must become dispersive in thin samples when the transit time is short enough [1, 18]. Figure 7 shows the calculated occurrence of dispersive transport in a thin film, $L = 100$ nm. The other parameters are the same as for figure 3. Neglecting the field diffusion, one obtains the break of TOF current at $t = t_{\rm tr}$ (see dotted line). Obviously, $t_{\rm tr} \ll t_{\rm tr}^{(0)}$, where $t_{\rm tr}^{(0)} = L/\mu_{\rm eq}F$ is the time of flight of carriers calculated under the (violated) assumption that the mobility has reached its quasi-equilibrium value already. Therefore the apparent mobility, defined as $\mu_{\rm app} = L/F_0 t_{\rm tr}$, increases considerably at low temperatures or strong energy disorder upon decreasing the sample thickness. One should remember that $L \leqslant 100$ nm are typical values for organic light-emitting diodes.

In single-layer diodes the transit time of charge carriers determines the characteristic time of onset of electroluminescence, $t_{\rm EL}$ [25]. It is obvious that the temperature and field dependences of mobility as defined from $t_{\rm EL}$ should differ from values derived from TOF experiments at $L \gg 1$ μm if the dispersive character of transport is disregarded.

4. Concluding remarks

It has been shown that in energetically and spatially random hopping systems there is a time domain in which the transport is neither fully dispersive nor quasi-equilibrated. It is referred to as a quasi-dispersive regime. It is the time domain in which the charge carriers in the top portion of the density of states distribution that contribute most to the current are already equilibrated while the entire ensemble of photoexited carriers still relaxes towards the bottom

states. Previous Monte Carlo simulations delineated that field-assisted diffusion increases in the long-time domain although the carrier mobility has saturated already [19, 21]. The present analytic theory is able to account for the quasi-dispersive features, i.e. scaling of normalized transient currents with anomalously large tails at different values of sample thickness and field strength as well as almost equilibrated transport borne out by the plateau in the $j(t)$ dependence. It also provides a quantitative explanation for the experimentally observed and simulated spread of the transit times, quantified by the dispersion parameter $W(L, \sigma/kT, F_0)$ as a function of sample thickness, energy disorder parameter and electric field strength [20, 21]. The theory applies to the case of moderate electric field, and the field dependence of mobility is not considered here.

Acknowledgment

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Appendix A

Assuming strong positional disorder, i.e. a large variation of hopping distances r, the average number of neighbours above the energy E of the initial state, whose hopping parameters are not larger than u_0, can be calculated as [6]

$$n_{\uparrow}(E, u_0) = 4\pi N \int_0^{u_0/2\gamma} \mathrm{d}r\, r^2 \int_E^{E+kT(u_0-2\gamma r)} \mathrm{d}E'\, g(E') W_{nr}(E', r), \qquad \text{(A.1)}$$

where $W_{nr}(E', r)$ is the probability of a carrier for not returning to the initial state after having jumped to the state of energy E', $E' > E$. After an upwards jump over the distance r, a carrier will, most probably, not return to the initial state if there is at least one additional hopping neighbour, which is separated from the target site by a distance smaller than r, outside the sphere of radius r centred at the initial state [6]. In accord with a Poisson distribution, $W_{nr}(E', r) = 1 - \exp[-n_b(E', r)]$, where $n_b(E', r)$ is the average number of neighbours, specified above,

$$n_b(E', u) = 4\pi \int_0^r \mathrm{d}r' r'^2 \int_{\arccos(r'/2r)}^{\pi} \mathrm{d}\vartheta\, \sin\vartheta \int_{-\infty}^{E'+2\gamma kT(r-r')} \mathrm{d}E'' g(E''), \qquad \text{(A.2)}$$

where ϑ is the angle between the directions of jumps to the initial state and to another neighbour in the vicinity of the target site at distance r' [6]. Neighbours from which a carrier preferably returns to the initial state are not included in the number $n_{\uparrow}(E, u_0)$ because these round trip jumps do not contribute to transport.

Appendix B

By analogy with the MT model, one can use the following kinetic equation for the distribution of occupied states (DOOS) $\rho(x, t, E)$, $E < E_{\mathrm{trans}}$, which is the product of a density of states $g(E)$ and occupation probability,

$$\frac{\partial \rho(x, t, E)}{\partial t} = g(E) p_{\mathrm{c}}(x, t)/\tau_0 - \rho(x, t, E)\omega(E), \qquad \text{(B.1)}$$

where $p_{\mathrm{c}}(x, t)$ is the density of carriers occupying 'conductive states' with energies $E > E_{\mathrm{trans}}$. Since these states carry most of the current, one can introduce the continuity equation as

$$\frac{\partial p(x, t)}{\partial t} + \mu_0 F_0 \frac{\partial p_{\mathrm{c}}(x, t)}{\partial x} = 0. \qquad \text{(B.2)}$$

Integration with respect to time yields $p(x,t) - p(x,0) + \mu_0 F_0 \partial \tilde{p}_c(x,t)/\partial x = 0$, where $\tilde{p}_c(x,t) = \int_0^t dt' p_c(x,t')$. Since most of the carriers are localized on traps, if $\sigma/kT \gg 1$, one can consider $p(x,t) \approx \int_{-\infty}^{E_{trans}} dE\rho(x,t,E)$. Considering shallow traps, one can obtain from (B.1)

$$\rho_{sh}(x,t,E) \approx \rho_{sh}^{(1)}(x,t,E) = g(E)p_c(x,t)[\tau_0\omega(E)]^{-1}, \qquad E_d(t) < E < E_{trans}, \tag{B.3}$$

as a first approximation, assuming $\partial\rho(x,t)/\partial t \approx 0$ in (B.1). Obviously, $\rho_{sh}^{(1)}(x,t,E) \sim \exp(-E/kT)$, see equation (3), i.e. in this approximation it follows the Boltzmann function. The second (release) term in the right-hand side of (B.1) could be neglected if deep traps are considered. Integration of the DOOS with respect to energy yields [9]

$$p_c(x,t) \approx p(x,t)\theta_1(t) - \lambda(t)\tilde{p}_c(x,t). \tag{B.4}$$

The left-hand side is negligible under the condition $\theta_1(t)^{-1}\, d\tau(t)/dt < 1$ [9], i.e. at short times, implying that transport is entirely dispersive. Integrating (B.2) with respect to time and combining the resulting equation with (B.4), one obtains equation (8), except for the field-diffusion term. In order to obtain the latter, one should consider the second-order approximation in (B.1), substituting the first-order result, see (B.3), into the time derivative in (B.1) [11]. As a result, the additional term $[\theta_1(t)/\theta_2(t)]\partial p_c(x,t)/\partial t$ appears in the right-hand side of equation (B.4) as a manifestation of small deviations from a Boltzmann distribution in the population of shallow states. This term can be considered as a small perturbation under the condition [9, 11]

$$t\theta_2(t)/\theta_1(t) \gg 1, \tag{B.5}$$

that limits applicability of the field-diffusion approximation at short times. The first-order equation (B.4) can be substituted into the time derivative $\partial p_c(x,t)/\partial t$ in an additional term, because it is small. Inserting the modified right-hand side of equation (B.4) into (B.2), combining the result with time-integrated equation (B.2) and neglecting numerous smaller perturbations, including contributions from deep traps (that is possible under the conditions $d[\theta_1(t)/\theta_2(t)]/dt \ll 1$, $\lambda(t)\theta_1(t)/\theta_2(t) \ll 1$, which are practically equivalent to (B.5), implying the almost power-law-like time dependences $\theta_1(t)$, $\theta_2(t)$ and $\tau(t)$), one obtains equation (8), including the field-diffusing term.

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