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Non-equilibrium charge transport in disordered organic films

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1. Introduction

Charge transport in disordered organic layers has been intensively investigated in recent years both experimentally and theoretically. In these investigations, basic studies are needed for practical and technological developments in modern organic electronics and photonics. The concept of Gaussian disorder model (GDM) i. e. the temperature- and field- assisted tunneling (hopping) of charge carriers between localized states (LSs), forms the background for understanding of the physical nature of transport (Bässler, 1993; Novikov et al., 1998). Energetic disorder is described by Gaussian distribution of energies of LSs. 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.

Excess charge carriers are generated in an organic film by light in course of TOF experiments. These carriers are not yet in quasi- equilibrium shortly after their generation, notably if there is an excess energy during excitation (Bässler, 1993). This circumstance together with a strong variance of transition rate of carriers between LSs in disordered materials causes a decrease of the average mobility with time, while the spatial dispersion of carriers relative to their mean position is anomalously large, i.e. the transport occurs in non-equilibrium conditions. Usually this case is referred to dispersive transport (Bässler, 1993; Arkhipov & Bässler, 1993b), whereas at long time transport is characterized by time-independent mobility and diffusion coefficients. The latter transport mode, referred to quasi- equilibrium, or Gaussian transport, is the topic of recent works (Arkhipov et al., 2001a; Schmechel, 2002; Fishchuk et al., 2002; Pasveer et al., 2005). It is often realized in materials with moderate energetic disorder. Indeed, the TOF transients of $\geq 1\mu\text{m}$ thick samples at room temperature bear out a well-developed plateau. This circumstance, however, does not always imply that transport is completely quasi- equilibrium. An unambiguous signature of the deviation is the anomalously large dispersion of formally non- dispersive TOF signals and the concomitant scaling of the tails of TOF signal as a function of sample thickness and electric field strength. Moreover, quasi- equilibrium transport is questionable for the case of thin ($<100\text{ nm}$) organic films, suitable for organic light- emitting diodes (OLEDs), when the transit time is short enough (Blom & Vissenberg, 1998).

Transport of charge carriers from electrodes to the zone of most efficient recombination is an essential part of operation of OLEDs. Transient electroluminescence (TrEL) is the important experimental method of investigations of charge transport in single- layer OLEDs (Pinner et al., 1999), where application of TOF method is difficult. Initial rise of TrEL in single- layer OLEDs based on organic material with strong asymmetry of mobilities is controlled by incoming flux of carriers with higher mobility to the recombination zone. The present methodology of TrEL analyses is usually based, however, on the questionable assumption that transport of charge carriers in OLEDs can be described in terms of time- independent mobility and diffusion coefficients (see, for example, Pinner et al., 1999).

The main computational method in GDM 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 (Bässler 1993). This problem can be overcome by analytic modelling. Theoretical description of hopping transport can be greatly simplified by means of the concept of effective transport energy (see, for example, Monroe, 1985; Baranovskii et al., 2000; Arkhipov et al., 2001a). The effective transport energy is analogous to the mobility edge in the multiple- trapping (MT) model, while deeper LSs can be considered as traps. This concept allows adapting the earlier results of MT model (Arkhipov & Nikitenko, 1989) for the hopping.

In the recent work (Nikitenko et al., 2007) an analytic theory of non- equilibrium hopping charge transport in disordered organic materials, based on the concept of effective transport energy (see section 2 of this chapter), is proposed. Previously this concept has not been applied for the general case of non- equilibrium hopping transport, only the asymptotic regimes of quasi- equilibrium (Arkhipov & Bässler, 1993a) and extremely non- equilibrium (dispersive) (Arkhipov & Bässler, 1993b) hopping (long and short times after generation, respectively) have been considered analytically. In this chapter this theory is described briefly (section 3) with special emphasis on transport in thin samples, e. g. used in OLEDs. Results of the theory are in good agreement with both TOF experiments for molecularly doped polymers and Monte- Carlo simulations of GDM (Bässler, 1993; Borsenberger et al., 1993; Borsenberger & Bässler, 1994), see section 4. In the section 5 the theory applied to the modelling of initial rise of TrEL from a single- layer OLED (Nikitenko & von Seggern, 2007; Nikitenko et al., 2008) both in injection- limited (IL) and space- charge limited (SCL) transport regimes. A method for determination of TrEL mobility is proposed.

2. Effective transport energy

An inherent feature of disordered materials is a broad distribution of LSs in energy and mutual distances. The energy distribution of states (DOS) is described by the distribution function $g(E)$. The appropriate choice for organic materials is the Gaussian DOS,

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

Analyses of transport in disordered materials can be greatly simplified by the concept of transport energy. 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 target state E_{trans} does not depend on the energy of initial state E , if $E \ll E_{trans}$ since $g(E)$ decreases drastically to lower energies. The states around E_{trans} (the latter is usually called 'transport energy'), contributes mostly to the transport process. The deep

states, $E < E_{trans}$, can be considered as traps, while E_{trans} and LSs with $E > E_{trans}$ are mobility edge and 'conductive states', respectively. The method to calculate E_{trans} should be introduced here.

The transition rate of charge carrier from LS of the energy E to the LS of energy E' , which are separated by the distance r , is described in this work in terms of Miller- Abraham expression, i. e. $\nu(r, E, E') = \nu_0 \exp[-\eta(E' - E)(E' - E)/kT - 2\gamma r]$, where $\eta(x)$ 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. If transport is dominated by energetic rather than by positional disorder one can assume that the typical release frequency of a carrier from LS with the energy E , $\omega(E)$, depends only on the energy of this LS, E . This assumption will be justified by comparing of theoretical results with data of experiments and Monte- Carlo simulations in GDM (see below). The steep dependence of the transition rate on energy difference and separation in space together with positional disorder implies that one of neighbor target states is strongly preferable. Following the work (Arkhipov et al., 2001a), one can define the typical release frequency $\omega(E)$ by the condition, that the mean number of neighbors for the LS of energy E , which are available during the time shorter than ω^{-1} , is equal to unity. This number is a sum of 2 terms, $n(E, \omega) = n_{\downarrow} + n_{\uparrow}$, the latter and former accounting for upward and downward (in energy) jumps, respectively. The result is (Nikitenko et al. 2007)

$$\omega(E) = \nu_0 \exp[-(E_{trans} - E)/kT - 2\gamma a], \quad E \ll E_{trans}, \quad (2)$$

where $a = (E_{tr} - E_{trans})/2\gamma kT$ is the typical hopping distance, and the maximal energy of the target state, E_{tr} , is defined by the conditions

$$\omega(E) \rightarrow \nu_0 \exp[-(E_{tr} - E)/kT], \quad E \rightarrow -\infty, \quad (3)$$

and $n \approx n_{\uparrow}(E, \omega) = 1$, if release frequency from deep LSs is described by Eq. (3). One should remember that the energy E_{tr} cannot be considered as the upper energetic limit of sites that can act as traps because Eq. (3) does not contain the tunneling term $2\gamma a$, see Eq. (2).

Obviously, for $n_{\uparrow} > 1/2$ jumps are preferably upward in energy and, hence, the upper limit of traps, i. e. the transport energy E_{trans} , can be defined by the condition

$$n_{\uparrow}[E_{trans}, \omega(E_{trans})] = 1/2. \quad (4)$$

The calculation of $n_{\uparrow}[E, \omega(E)]$ is described in the works Arkhipov et al., 2001a; Nikitenko et al. 2007. Neighbours from which a carrier preferably returns to the initial state are not included to the number $n_{\uparrow}$ because these roundtrip jumps do not contribute to transport.

Since jumps from the LSs with energies $E \geq E_{trans}$ 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, i. e. in the states with energies above E_{trans} . It should be noted that the condition $2\gamma N^{-1/3} kT/\sigma \gg 1$, where N is the spatial density of LSs, is usually fulfilled in organic materials even at moderately low temperatures. For this case, Eqs. (2), (4) yields $E_{trans} \approx 0$ and $a \approx E_{tr}/2\gamma kT \approx 0.745 N^{-1/3}$ (Nikitenko et al. 2007). This is plausible because the jump rate to the neighbor LS is defined by the spatial distance rather than by the energy difference.

Fig. 1. Temperature dependence of the transport energy level for several values of the energy width of the Gaussian trap distribution, as shown in the figure.

One has to note that transport energy was introduced previously by different ways (see Baranovskii et al., 2000; Schmechel, 2002). The results of the calculation of the temperature dependence of E_{trans} from Eqs. (3) and (4), using for several values of σ are shown in Fig. 1 (solid lines), providing that $2\gamma N^{-1/3}=10$. For comparison, Fig. 1 shows the temperature dependences of the transport energy, obtained using the method of Baranovskii et al., 2000 (dash-dotted lines), and the results of the calculations under the assumption that returns to the initial states are absent, as in the cited work (dashed lines). The difference between the two latter results at not too high temperatures, $T < 200$ K, does not exceed kT . The same conclusion (Nikitenko et al., 2007) results from the comparison with results of Schmechel, 2002 (in that work the transport energy defined as the maximum of energy dependent "differential conductivity", that describes the contribution of states with given energy E to the total conductivity). This supports the notion that the definition of E_{trans} by Eq. (4) 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 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 Eq. (2), and by energy-independent capture time $\tau_0 = \exp(-2\gamma a)$, respectively, can be described in complete analogy with MT model, $E < E_{\text{trans}}$ being the mobility edge. The states with energies $E < E_{\text{trans}}$ are referred below as traps.

3. Analytic theory of non-equilibrium transport

3.1 Equation of non- equilibrium transport

One has to remember, that in a TOF experiment, charge carriers are generated in the upper portion of the DOS, relative to quasi- equilibrium state. That implies subsequent energetic relaxation (thermalization) of charge carriers. It occurs simultaneously with transport, and should be considered as a two- step process (Monroe, 1995; Arkhipov & Bäessler, 1993b; Nikitenko, 1992). The first step is a sequence of fast jumps downwards in energy right after a carrier was started at $t=0$. The characteristic time of this process cannot exceed

considerably the time τ_0 under the presumed condition $2\gamma N^{-1/3} kT/\sigma > 1$, because (i) it is the time of the slowest jump in this sequence and (ii) the number of downward jumps is small. Upward 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 $t = \tau_0$ will be referred as $t = 0$ below, because τ_0 is much shorter than all other characteristic times.

One has to remind also the approximation of demarcation energy, which simplifies greatly the analytic modeling of energetic relaxation of charge carriers [Arkhipov & Rudenko 1982b; Arkhipov & Nikitenko 1992; Arkhipov & Bäessler 1993b]. In this approximation all the traps (i.e. LSs with energies $E < E_{trans}$) are considered as being either currently deep or either currently shallow. The trap is currently deep, if release of a previously captured carrier is not probable up to time t , and vice versa. The demarcation energy $E_d(t)$ is defined from the condition $\omega[E_d(t)]t = 1$ and Eq. (2) as

$$E_d(t) = E_{tr} - kT \ln(\nu_0 t) = E_{trans} - kT \ln(t/\tau_0), \quad t > \tau_0. \quad (5)$$

In the simplest approximation, all traps are deep, if $E < E_d(t)$, and vice versa.

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 MT model (Arkhipov & Nikitenko, 1989),

$$\frac{\partial p(x, t)}{\partial t} + \mu(t) F_0 \frac{\partial p(x, t)}{\partial x} - D_F(t) \frac{\partial^2 p(x, t)}{\partial x^2} = -\lambda(t) [p(x, t) - p(x, 0)], \quad (6)$$

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

$$\mu(t) = \mu_0 \theta_1(t), \quad \lambda(t) = \theta_1(t)/\tau(t), \quad D_F(t) = \tau_0^{-1} (\mu_0 F_0 \tau_0)^2 \theta_1^3(t)/\theta_2(t), \quad (7)$$

where the mobility in «conductive» states is introduced as $\mu_0 = (1/6)(e/kT)a^2/\tau_0$, and

$$1/\theta_m(t) = \int_{E_d(t)}^{E_{trans}} dE g(E) [\tau_0 \omega(E)]^{-m}, \quad m = 1, 2, \quad (8)$$

$$1/\tau(t) = \int_{-\infty}^{E_d(t)} dE g(E) / \tau_0. \quad (9)$$

Obviously, $\theta_m(t)$ decreases with time, while $\tau(t)$ increases.

In a typical TOF experiment the condition $eF_0 L \gg kT$ 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 Eq. (6). This kind of spreading was analyzed analytically for quasi-equilibrium conditions (Arkhipov & Bäessler, 1993a) and called as 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. The mean distance of drift in «conductive

states», $\mu_0 F_0 \tau_0$, is a «mean free path» in coefficient D_F , see Eq. (7), and hence $D_F \sim F_0^2$. Details of thermalization of charge carriers and the way of derivation of Eq. (6) are described in the paper Nikitenko et al. 2007.

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 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 Eq. (6) in the infinite sample

$$p(x, t) = G(x, t, 0) + \int_0^t dt' \lambda(t') G(x, t, t'), \quad (10a)$$

$$G(x, t, t') = A_0 \exp \left\{ -\Lambda(t, t') - \left[x - F_0 M(t, t') \right]^2 / 4 S_F(t, t') \right\} / \sqrt{4 \pi S_F(t, t')} \quad (10b)$$

where $S_F(t, t') = \int_{t'}^t d\tau D_F(\tau)$, $\Lambda(t, t') = \int_{t'}^t d\tau \lambda(\tau)$, $M(t, t') = \int_{t'}^t d\tau \mu(\tau)$. Remember that conventional diffusion is neglected and hence charge carriers cannot penetrate to the region $x < 0$, i.e. $p(x, t) \sim \eta(x)$. Disagreement of this statement with Eq. (10) is, however, not principal. One should remember that diffusion-like term in Eq. (8) is only an approximate way to describe field-assisted dispersion of a carrier packet, and this approximation is not valid at short time domain. The condition of applicability of field-diffusion approximation, namely $t\theta_2(t)/\theta_1(t) \gg 1$ (Arkhipov & Rudenko 1982a), is fulfilled, however, in all calculations that are performed in this work. It means that shift of the mean position of charge carriers exceeds their dispersion considerably, and unphysical «tail» of $p(x, t)$ at $x < 0$, is unimportant.

The transit time t_{tr} is defined by the condition that the mean position of charge carriers is equal to the film thickness L . Eq. (6) yields

$$F_0 \int_0^{t_{tr}} dt' \exp[-\Lambda(t, 0)] \mu(t') = L. \quad (11)$$

Obviously, $E_d(t) = E_{traps}$ at $t = \tau_0$ i.e. all traps are deep and occupation of all traps is off-equilibrium. In 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 were generated, however, transport is exclusively dominated by deep traps i.e. it is entirely dispersive. Time duration of this period is defined by the condition $\theta_1(t)^{-1} d\tau(t)/dt < 1$ (Arkhipov & Rudenko 1982b). Under this condition one can neglect the term $\partial p / \partial t$ as well as field-diffusion term can be neglected in comparison with right-hand side of Eq. (6). Since eq. (6) transforms to the ordinary dispersive transport equation (Arkhipov & Bäessler 1993b),

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

The solution of Eq. (12) is

$$p_{disp}(x, t) = A_0 \eta(x) \exp[-x / \mu_0 F_0 \tau(t)] / \mu_0 F_0 \tau(t). \quad (13)$$

Spatial profiles of charge carrier density, as calculated from Eqs. (10), are shown in the Fig. 2

Fig. 2. Spatial profiles of the charge carrier density $p(x,t)$ (solid lines). Dashed lines shows the respective Gaussians. Dash- dotted lines shows $p(x,t)$ under the assumption that transport is dispersive, see Eq. (13). $E_0 = 2 \cdot 10^5 \text{ V/cm}$, $\sigma/kT = 3.5$, $2\gamma N^{-1/3} = 10$, $L = 5 \mu\text{m}$.

for $t = 0.5t_{tr}$ and $t = t_{tr}$ (see solid lines) considering $t_{eq-\mu} \ll t_{tr}$. Obviously, maximum of a carrier distribution is practically in the position $x = L$ at $t = t_{tr}$. The front of $p(x,t)$ profile is practically Gaussian while the carrier density near $x = 0$ greatly exceed the values that are expected from Gaussian function. Consequently, the mean position of carriers is slightly behind the maximum, see arrows in the figure, while both values increases practically linear with time. A non- Gaussian tail of the distribution appears due to capture of carriers on deep traps with release times greater than transit time. Meanwhile these spatial profiles differ significantly from an exponential function $p_{disp}(x,t)$, see Eq. (13).

Vice versa, $\lambda(t) \rightarrow 0$, $\mu(t) \rightarrow \mu_{eq}$, $D_t(t) \rightarrow D_{eq}$ in the limit of long time and hence Eq. (6) reduces to the usual drift- diffusion equation, which describes quasi- equilibrium transport with time- independent mobility μ_{eq} and field- dependent diffusion coefficient D_{Feq} . These constants are defined by Eqs. (7), (8) with $E_d(t) \rightarrow -\infty$.

Thus, the system of Eqs. (6)- (9) provide an analytic description of hopping transport of charge carriers in dispersive transport regime and allow also to analyze subsequent relaxation towards quasi- equilibrium. Coefficients and time dependencies from Eq. (8) will be analyzed extensively in the following section.

3.2 Non- equilibrium drift and field- stimulated diffusion

Using Eqs. (1), (2) and (8) one obtains

$$\frac{\theta_m(t)^{-1}}{(\nu_0 \tau_0)^m} = \frac{1}{2} \exp \left[\frac{m}{2} \left(\frac{\sigma}{kT} \right)^2 + \frac{mE_{tr}}{kT} \right] \left\{ \operatorname{erfc} \left[\frac{m\sigma}{\sqrt{2}kT} + \frac{E_d(t)}{\sqrt{2}\sigma} \right] - \operatorname{erfc} \left[\frac{m\sigma}{\sqrt{2}kT} + \frac{E_{trans}}{\sqrt{2}\sigma} \right] \right\}, \quad (14)$$

where $m = 1, 2$, and $\operatorname{erfc}(x) = \left(2/\sqrt{\pi}\right) \int_x^\infty dt \exp(-t^2)$ is the complementary error function. Eqs. (2), (7) and (14) for the limit $t \rightarrow \infty$ yields

$$\mu(t) \approx \mu_{eq} = \frac{e}{kT} \chi_\mu \frac{\nu_0 a^2}{6} \exp \left[-\frac{1}{2} \left(\frac{\sigma}{kT} \right)^2 - \frac{E_{trans}}{kT} - 2\gamma a \right], \quad t \geq t_{eq-\mu}, \quad (15)$$

$$D_F(t) \approx D_{Feq} = \chi_D \nu_0 a^2 \left(\frac{eF_0 a}{6kT} \right)^2 \exp \left[\frac{1}{2} \left(\frac{\sigma}{kT} \right)^2 - \frac{E_{trans}}{kT} - 2\gamma a \right], \quad t \geq t_{eq-D}, \quad (16)$$

where $\chi_\mu = 2 / \operatorname{erfc} \left[-\sigma / \sqrt{2kT} - E_{trans} / \sqrt{2}\sigma \right]$, $\chi_D = \chi_\mu^3 \operatorname{erfc} \left[-\sqrt{2}\sigma / kT - E_{trans} / \sqrt{2}\sigma \right]$. Both factors χ_μ , χ_D are nearly 1 for the practically relevant case $\sigma/kT \gg 1$. For the limit of dilute systems, $2\gamma N^{-1/3} kT / \sigma \gg 1$, one obtains $E_{trans} \approx 0$ and $a \approx 0.745 N^{-1/3}$. Thus, $\mu_{eq} \sim \exp(-C2\gamma N^{-1/3})$, and the value $C = 0.745$ is close to the well-known result of percolation theory, $C_{perc} = 0.865$ (Shklovskii & Efros, 1984).

In general, the temperature dependence of D_{Feq} is determined by the factor $\exp \left[0.5(\sigma/kT)^2 \right]$, as in the work Arkhipov & Bäessler, 1993a. However, value of D_{Feq} , see eq. (16), exceeds considerably the respective result of this work, although the latter does not include the exponential dependence of hopping distance. Comparable values of D_{Feq} can be obtained only for the case of relative „dense“ systems, $2\gamma a \leq 5$. This is not surprising because only in this limit the method of the work Arkhipov & Bäessler, 1993a, i. e. the method of configurational averaging of hopping rates in respect to hopping distances and energies of starting and target states, is applicable.

One has to note that the field dependence of $\mu(t)$, has not been analyzed 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 mobility is of minor importance. On the other hand, at room temperature and $a \approx 0.6 \text{ nm}$, one obtains $F_0 < 4 \cdot 10^5 \text{ V/cm}$, that is strong enough to neglect conventional diffusion.

Analyzing Eq. (14) yields the following relaxation times $t_{eq-\mu}$ and t_{eq-D} of mobility and field diffusion, respectively

$$\nu_0 t_{eq-\mu} = \exp \left[(\sigma/kT)^2 + E_{tr}/kT \right], \quad \nu_0 t_{eq-D} = \exp \left[2(\sigma/kT)^2 + E_{tr}/kT \right]. \quad (17)$$

From eqs. (7) and (14) one obtains the following analogue of the Einstein relation of time dependent mobility and field diffusion coefficient,

$$\frac{e}{kT} \frac{D_F(t)}{\mu(t)} \approx \frac{1}{12} \left(\frac{eF_0 a}{kT} \right)^2 \operatorname{erfc} \left[\frac{\sqrt{2}\sigma}{kT} + \frac{E_d(t)}{\sqrt{2}\sigma} \right] \exp \left[\left(\frac{\sigma}{kT} \right)^2 \right]. \quad (18)$$

In the long time limit, $t \gg t_{eq-D}$, this ratio reaches a maximal value,

$\approx (1/6)(eF_0 a / kT)^2 \exp[(\sigma/kT)^2] \gg 1$, $\sigma/kT \gg 1$. In Fig. 4 time dependencies $eD_F(t) / \mu_{eq} kT$ and $\mu(t) / \mu_{eq}$ are calculated from Eqs. (7), (14), and plotted vs normalized time $t / t_{eq-\mu}$ for several values of energetic disorder parameter σ/kT . It demonstrates enhanced field-

assisted diffusion in the time domain $t_{eq-\mu} \ll t < t_{eq-D}$, if $\sigma/kT \geq 2.5$. Obviously, the FAD coefficient increases at long time domain, although mobility remains practically constant, see Eq. (17).

Fig. 3. Time dependences of the field- assisted diffusion coefficient, normalized by equilibrium value of the coefficient of usual diffusion, $\mu_{eq}kT/e$, parametric in σ/kT values. Respective dependences $\mu(t)/\mu_{eq}$ are also shown in the figure. Arrows mark relaxation time t_{eq-D} . Full circles show the values of $eD_F(t_{tr})/\mu_{eq}kT$ at $t = t_{tr}$, providing that $L = 5\mu m$. Other parameters: $F_0 = 2 \cdot 10^5 V/cm$, $N = 4.6 \cdot 10^{21} cm^{-3}$, $\gamma^{-1} = 0.12 nm$, $T = 295 K$.

Simulation data in the work Pautmeier et al., 1991 on a system with pure energy disorder ($\sigma/kT = 3.0$) also delineated the different time scales for relaxation of mobility and diffusivity. Time dependence of the diffusivity is taken from Fig. 1 of the work Pautmeier et al., 1991 and compared with the function $D_F(t)$ in the Fig. 4. The latter is calculated from Eqs. (7), (14) and is normalized by the minimal value of GDM diffusivity. The time is normalized by the typical hopping time $t_0 = (1/6)\exp(2\gamma N^{-1/3})$ (Bässler, 1993). Both dependences are in good agreement. They bear out a minimum at $t \cong t_{eq-\mu}$. For GDM data the latter is defined by the condition $\mu(t_{eq-\mu})/\mu_{eq} \approx 2$, in accordance with Fig. 3. At shorter times the transport is dispersive. Meanwhile the time $t_{eq-\mu}$ is practically the same as the time when the averaged energy of localized carrier approaches to the equilibrium when the averaged energy of localized carrier approaches to the equilibrium value σ^2/kT , i. e. the difference becomes less than kT , while both the maximum of distribution of occupied states (DOOS) and demarcation energy $E_d(t)$ reaches σ^2/kT (see inset to the Fig. 4). The time t_{eq-D} is of the same order of magnitude as the time when the dispersion of energies approaches to the equilibrium value σ (Pautmeier et al., 1991). Slow relaxation of the latter reflects slow relaxation of carriers towards the very tail states. This is shown in the inset to the Fig. 4, where time evolution of spatially averaged DOOS, is calculated, see details in the

Fig. 4. Comparison of time dependences $D_F(t)$ from this work (solid line) and from GDM (points, see the work Pautmeier et al., 1991). Relaxation times of μ and D_F as defined from GDM and this model are marked by solid and dashed arrows, respectively. Inset shows the time evolution of the density of occupied states. Ratios $t/t_{eq-\mu}$ are shown in the figure, respective positions of demarcation energy $E_d(t)$ are shown by arrows. Steady-state distribution is denoted by dotted line.

work Nikitenko et al., 2007. The coefficient of FAD is controlled by 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.

4. Transient current in time- of- flight experiment

Time-of-flight is the conventional technique for studies of electron-hole transport behaviors in materials with long dielectric relaxation times. By this method, one measures the time required for a sheet of carriers generated by a short flash of radiation to transit a sample of known thickness. A polymer layer, typically 1-30 μm in thickness is placed between two blocking electrodes, at least one of which must be semitransparent. The sample is used as a capacitor in an RC circuit. The applied voltage charges the capacitor to a potential V and then sample is illuminated by a highly absorbed flash of radiation. The duration of the light impulse is short compared to the transit time. The flash generates a sheet of carriers that then drift across the sample. R is selected such that RC is much less than the transit time. This arrangement is described as the small current mode. Under these conditions, the voltage across R is proportional to the current flowing in the sample, $j(t)$. When the carriers exit the sample, a sharp decrease in the current is observed. The time corresponding to the decrease in current is usually defined as the transit time, the time required for the sheet of charge to transit a thickness L . If transport is quasi-equilibrium, the transit time is related to the mobility μ as

$$t_{tr} = L/\mu F_0 = L^2/\mu V \quad (19)$$

For polymers, it can usually be assumed that prior to charge injection, the field in the sample is uniform and given as V/L . In order that the field in the sample is not perturbed by the

injected charge, the experiments are performed so that the injected charge is small compared to the charge on the electrodes. The analysis of non- equilibrium transport is highly complicated, see below.

Eqs. (10) together with the following equation (Arkhipov & Rudenko, 1982b)

$$j(t) = (e/L) \partial / \partial t \int_0^L dx (x-L) p(x,t) \quad (20)$$

solve the problem to calculate the transient current under TOF conditions. Accounting the condition $t\theta_2(t) / \theta_1(t) \gg 1$, Eqs. (10), (20) yield

$$j(t) \approx j_{drift}(t) = (eA_0F_0/L) \left[\mu(t) - \lambda(t) \int_0^t dt' \mu(t') \exp[-\Lambda(t,t')] \right], \quad t \ll t_{tr}, \quad (21)$$

Obviously, $j_{drift}(t)$ is also the asymptotic solution of Eqs. (10), (20) for the limit of pure drift, i. e. $D_F \rightarrow 0$, $t < t_{tr}$ (Arkhipov & Rudenko, 1982b).

Fig. 5. Time dependence of the TOF current. Solid and dashed lines are the results of calculations from Eqs. (10), (20) and (22), respectively. Results of TOF experiment (line with circles) and Monte- Carlo simulations of GDM (full circles). $T = 312K$, $\sigma/kT = 3.5$, $N = 4.6 \cdot 10^{21} cm^{-3}$, $\gamma^{-1} = 0.12 nm$.

One can simplify the highly complicated time dependence $j(t)$ as defined by Eqs. (10), (20) for the relevant case of moderately non- equilibrium transport, $t \geq t_{eq-\mu}$, or $t\lambda(t) < 1$. Estimating integrals in Eqs. (10), (20) for this case yields $p(x,t) \approx G(x,t,0)$ and

$$j(t) \approx (1/2)(eA_0F_0/L) \mu(t) \exp[-t\lambda(t)] \operatorname{erfc} \left[(F_0M(t,0) - L) / 2\sqrt{S_F(t,0)} \right]. \quad (22)$$

Fig. 5 shows good quantitative agreement with the TOF signal as calculated from the approximate Eq. (22) and from Eqs. (10), (20), see dashed and solid lines, respectively, and qualitative agreement both with experimental, see line with circles, and simulated in GDM data, see full circles. Data for polycarbonate (PC), doped by 1,1-bis(di-4-tolylaminophenyl) cyclohexane (TAPC) are taken from Fig. 22 of the paper Bässler, 1993. Although $t_{eq-\mu}$ is

much less than transit time, see arrows on the figure, the current is not strictly constant at any time, because of strong spatial dispersion of carriers. The „plateau“ level j_0 is defined operationally by the time of 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 dot- dashed lines in Fig. 5. Obviously, the transit time t_{tr} from Eq. (11) is good approximation to the experimentally determined time $t_{1/2}$. Eq. (18) explains why in TOF experiments the dispersion of the carrier arrival times, $W = (t_{1/2} - t_0)/t_{1/2}$, greatly exceeds the value predicted by conventional diffusion (Bässler, 1993; Borsenberger et al., 1993b). Using Eq. (22) one obtains

$$W \approx L^{-1} \left[\pi \int_0^{t_{tr}} dt D_F(t) \right]^{1/2} \quad (23)$$

In the limit $t_{tr} > t_{eq_D}$, one can reduce Eq. (23) to the well- known form (Bässler 1993)

$$W \approx \sqrt{\pi D_F(t_{tr}) / \mu_{eq} F_0 L}, \quad (24)$$

implying $t_{tr} \approx L / \mu_{eq} F_0$, see Eq. (19), and $D_F(t) \approx D_F(t_{tr})$. The ratio $eD_F(t_{tr}) / kT \mu_{eq}$, that can be derived from the measured dispersion W , differs considerably from that predicted under premise of quasi- equilibrium, $eD_{Feq} / kT \mu_{eq}$, if $t_{tr} < t_{eq_D}$ (Fig. 3).

Fig. 6. Normalized field- assisted diffusion coefficient as a function of σ/kT . The values of $eD_F(t_{tr}) / \mu(t_{tr})kT$ are shown by circles (the variable is σ) and by squares (the variable is kT). Data of GDM at $\Sigma = 0$ (diamonds), $\Sigma = 3.25$ (triangles), and experimental results (full circles) are shown for comparison.

The dependences of the ratio $eD_F(t_{tr}) / \mu(t_{tr})kT$ on the energy disorder parameter σ/kT are shown on the Fig. 6, providing that $F_0 = 3.6 \cdot 10^5 \text{ V/cm}$, $L = 6.75 \mu\text{m}$, $N = 4.6 \cdot 10^{21} \text{ cm}^{-3}$, $\gamma^{-1} = 0.12 \text{ nm}$. Experimental and simulation data are taken from Fig. 8 of the paper (Borsenberger et al., 1993a). Experimental TOF data for TAPC, doped by bisphenol-A-polycarbonate (BPPC), are indicated by full circles on the Fig. 6. Diamonds and triangles are

show results of GDM simulations for the case of vanishing and large positional disorder, respectively. Results of the present theory, as calculated from Eqs. (14)-(16), (11), are denoted on Fig. 6 by squares (variation of σ , $T = 295K$) and open circles (variations of T , $\sigma = 0.075eV$). These results are in qualitative agreement with experiment for the system with large positional disorder, if $\sigma/kT \geq 3$, that means $\sigma/kT \geq \Sigma$, where $\Sigma = 3.25$ is the parameter of positional disorder in GDM (Bässler, 1993). This confirms the validity of the present approach to the materials with predominance of energetic disorder. In Fig. 7 calculated $W(L)$ dependences are compared with experimental data at several values of σ/kT , providing that $F_0 = 2 \cdot 10^5 V/cm$, $N = 4.6 \cdot 10^{21} cm^{-3}$, $\gamma^{-1} = 0.15 nm$. Data on TAPC-doped polystyrene are taken from the work Borsenberger & Bässler, 1994. A $W \sim L^{-0.5}$ law is indicated by dashed straights. This is confirmed by the $W(L)$ dependence for $\sigma/kT = 2.6$. For $\sigma/kT = 3.0$ $W(L)$ become weaker ($L < 3 \mu m$), and for $\sigma/kT = 4.4$ the dispersion is practically independent of sample thickness. Values of W , as calculated from Eqs. (23) and (24), are in qualitative agreement with experimental data (see solid and dash- dotted lines).

Fig. 7. Dependences of the relative dispersion of the transient current W on the sample thickness L for several values of σ/kT . Experimental data are shown by circles. Solid and dash- dotted lines are calculated from approximate Eqs. (23) and (24), respectively. The dashed lines are the dependences $W \sim L^{-1/2}$. Crosses are results of straightforward determination of $W = (t_{1/2} - t_0)/t_{1/2}$ from calculated $j(t)$ curves.

The peculiarities of $W(L, F_0, \sigma/kT)$ 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. $\sigma/kT = 3.0$ (Fig. 4). This transport regime will therefore be referred to as quasi-dispersive.

One should expect that in the quasi- dispersive regime the normalized time dependences $j(t/t_{tr})/j_0$ for different L and F_0 are universal, since W does not depend on these parameters. This kind of scaling is a well- known signature of dispersive transport. However, in

accordance with previous GDM results (Bässler, 1993; Pautmeier et al., 1991), this work indicates, that there is also scaling in non- dispersive TOF transients provided that there is

Fig. 8. Time dependences of transient current at several values of F_0 and L , $\sigma/kT = 3.5$ (a) and $\sigma/kT = 2.0$ (b). Other parameters are: $N = 4.6 \cdot 10^{21} cm^{-3}$, $\gamma^{-1} = 0.12nm$, $T = 295K$.

also scaling in non- dispersive TOF transients provided that disorder is sufficiently strong ($t_{eq_D} > t_{tr}$) but below the critical value at which transit time dispersion commences ($t_{eq_D} < t_{tr}$). Figs. 8a and 8b illustrate both occurrence and violation of scaling in TOF signals.

Fig. 9. TOF current in thin film, $L = 100nm$. Solid line is the calculation from Eqs. (10), (20) while the dotted line is the same but field diffusion is neglected. Dashed line is calculated from the approximate Eq. (22).

Current and time are normalized by the plateau value $j_0 = e\mu_{eq}A_0F_0/L$ and by the transit time t_{tr} . Obviously, charge transport must become dispersive in thin samples when the transit time is short enough (Bässler, 1993; Pautmeier et al., 1991). Fig. 9 shows the calculated occurrence of dispersive transport in a thin film, $L = 100nm$. Other parameters are the same

as for Fig. 5. Neglecting the field diffusion one obtains the break of TOF current at $t = t_{tr}$ (see dotted line). Fig. 9 shows that the time t_{tr} , see Eq. (11), is a good estimate of the transient time even for dispersive regime. Obviously, $t_{tr} \ll t_{tr}^{(0)}$, where $t_{tr}^{(0)} = L/\mu_{eq}F$ 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 $\mu_{app} = L/F_0 t_{tr}$, increases considerably at low temperatures or strong energy disorder upon decreasing the sample thickness. Fig 10 shows the calculated dependence of the ratio μ_{app}/μ_{eq} on L at several temperatures, providing that $N = 4.6 \cdot 10^{21} \text{ cm}^{-3}$, $\gamma^{-1} = 0.12 \text{ nm}$, $F_0 = 2 \cdot 10^5 \text{ V/cm}$, $\sigma = 0.075 \text{ eV}$. One should remember that $L \leq 100 \text{ nm}$ are typical values for organic light-emitting diodes. In single-layer diodes (Pinner et al., 1999) the transit time of charge carriers determine the characteristic time of onset of electroluminescence.

Fig. 10. Ratio μ_{app}/μ_{eq} is calculated as a function of film thickness L for several temperatures. Arrows show the values of L , which satisfy the condition $t_{tr} = t_{eq-\mu}$.

It is obvious that the temperature and field dependences of mobility as defined from the latter time, see the next section, should differ from values derived from TOF experiments at $L \gg 1 \mu\text{m}$ if dispersive character of transport is disregarded.

5. Transient electroluminescence from light-emitting diodes

Transient electroluminescence (TrEL) is widely considered as a general technique for determination of charge carrier mobility in thin organic films ($L \leq 100 \text{ nm}$). A typical single-layer OLED is similar to a sample for TOF measurements. TrEL measurements have the advantage that they provide information directly from the light emitting device. The delay time, i.e., the time lag between applying a rectangular voltage pulse to the device and the first appearance of electroluminescence (EL), is identified as the time until the two leading fronts of injected carriers—holes and electrons—meet in the device. Zone of the most intensive EL is typically a narrow sheet (several nanometers in thickness) in proximity to

one of the electrodes because of strong asymmetry of hole and electron mobilities (Crone et al., 1999; Friend et al., 1999). Consequently, the transport of the fast carriers across almost whole layer is the key process for the EL onset.

5.1 The injection- limited regime

Injection of holes is limited by a sufficiently high energetic barrier in this regime. Space charge density of holes is small, hence electric field is approximately uniform, except of a thin layer near the cathode. It is instructive to examine the possibility of non- equilibrium transport for this case. At the first glance, initial energy distribution of injected carriers should be rather “cold” in order to preclude their subsequent energetic relaxation. However, one has to remember that (i) the DOS is shifted to lower energies in the proximity of the electrode by the image- force Coulomb potential and (ii) energetic disorder provide the possibility of downward jumps. One can estimate the initial density of occupied states (DOOS) as a product of the DOS and the rate of initial jumps (Gartstein & Conwell, 1996), namely $\rho_1(E) \propto g(E) \exp[-\eta(E+U(a))(E+U(a))/kT]$ (the zero point of energy is the peak of Gaussian DOS), where $U(a) = H_h - e^2/16\pi\epsilon\epsilon_0 a - eF_0 a$, H_h is the injection barrier. Thus, the energetic dependence of initial DOOS resembles the quasi- equilibrium (“cold”) distribution, namely $\rho_{eq}(E) \propto \exp(-(E-E_{eq})^2/2\sigma^2)$, $E_{eq} = -\sigma^2/kT$, if $E > -U(a)$. Otherwise, the energetic dependence of DOOS is “hot”, $\rho_1(E) \propto g(E)$. Considerable energetic relaxation (and therefore the dispersive transport) is possible in course of subsequent motion, if $E_{eq} < -U(a)$, i.e. $H_h < H_*$, where $H_* = \sigma^2/kT + e^2/16\pi\epsilon\epsilon_0 a + eF_0 a$. Indeed, the simple calculation yield for the average energy of initial DOOS $\langle E \rangle \geq E_{eq} + kT$, if $H_h \leq H_*$ (the same result is obtained by the use of the method of the work (Arkhipov et al., 1999), i.e. including dispersion of lengths of initial jumps). One obtains $H_* = 0.5$ eV ($\sigma = 0.075$ eV) and $H_* = 0.7$ eV ($\sigma = 0.1$ eV), providing that $a = 0.6$ nm, $\epsilon = 2.5$, and $F_0 = 3 \cdot 10^5$ V/cm (Nikitenko & von Seggern, 2007). One has to note that the equality $\langle E \rangle \geq E_{eq} + kT$ is equivalent to $t \leq t_{eq-\mu}$ (Nikitenko et al., 2007), providing that the DOOS is “hot” at $t = 0$, as in the previous section (respectively, $t \leq t_{eq-D}$, if $H_h \leq H_* + \sigma^2/kT$). Therefore the *quasi-dispersive* (although not *dispersive*) regime of charge transport can be realized, even if $H_h \geq H_*$. The difference in initial conditions, mentioned above, should be unimportant, if the time interval $t \gg t_{eq-\mu}$ is considered.

One has to remember that the injection is a multi- step hopping motion of a charge carrier (Gartstein & Conwell, 1996; Arkhipov et al., 1999). It include two competitive processes: (i) “cooling” by energetic relaxation and (ii) “heating” in course of their motion across the energetic barrier, which is formed by the potential energy $U(x)$, because the probability to overcome this barrier is smaller for a carrier with lower energy. One obtains practically the same DOOS of *eventually* injected carriers, as $\rho_1(E)$, following the ref. (Arkhipov et al., 1999). The arguments mentioned above approve the application of the simple model of this section to the description (at least qualitative) of the initial TrEL.

TrEL is considered here providing that holes moves much faster than electrons, hence the recombination zone is located next to the cathode at the initial (after the switching of voltage pulse at $t=0$) time period. The anode and the cathode are located at $x=0$ and $x=L$, respectively, L is the film thickness. The recombination current density, $J_R(t)$, which is proportional to TrEL intensity, is the product of the conduction current density of holes, $J(L,t)$, incoming to the recombination zone, and the probability of radiative recombination, $\phi(t)$,

$$J_R(t) = J(L,t) \phi(t). \quad (25)$$

The latter function increases with time (adiabatically slow relative to the first one) due to (i) slow increase of electron density and (ii) slow increase of mean lifetime of singlet excitons because of slow (dispersive) transport of electrons apart from the cathode. Therefore, the function $\phi(t)$ is determined by rather complicated physical processes. It can be introduced, however, in a simple phenomenological way in order to reduce the number of model parameters. It is known that TrEL kinetics shows often two different rise times, which are connected with transport of electrons and holes, respectively (Pinner et al., 1999). Thus, one can write the function $\phi(t)$ in this case as follows:

$$\phi(t) \approx J_R(t)/J_R^{st} = 1 - (1 - \phi_0) \exp(-t/\tau_e), \quad t \gg t_{tr}, \quad (26)$$

where t_{tr} is the transit time of holes, J_R^{st} is the long- time limit of $J_R(t)$, and $\phi(t)$ is normalized by the condition $\phi(\infty)=1$, providing that long-time TrEL kinetics can be described by time τ_e , $\tau_e \gg t_{tr}$. One can obtain the parameter $\phi_0 = \phi(0) < 1$ by extrapolation of Eq. (26) to the zero time.

The time dependence of $J(L,t)$ is discussed at first, providing rather high energy barrier for injection of holes, hence the electric field is uniform. One obtains [Nikitenko & von Seggern, 2007]

$$J(L,t) = J_h \left(1 - \int_0^L dx p(x,t) \right), \quad (27)$$

where J_h is the injection current density of holes and $p(x,t)$ is the distribution function of holes, being injected by short pulse at $t=0$ see Eq. (10). It can be approximated by the Gaussian function, if $t \gg t_{eq-\mu}$:

$$p(x,t) \approx \exp \left\{ - \left(x - \mu_{eq} F_0 t \right)^2 / 4 S_F(t, F_0) \right\} / \sqrt{4 \pi S_F(t, F_0)}. \quad (28)$$

This function is characterized by time- dependent coefficients of FAD, $D_F(t, F_0)$, and mobility $\mu(t) \approx \mu_{eq}$, $F_0 = (V - V_{bi})/L$ is the strength of applied electric field, V and V_{bi} are applied and built-in voltages, respectively. Eqs. (27) and (28) yields

$$J(L,t) \approx J_h (1/2) \operatorname{erfc} \left[\left(L - \mu_{eq} F_0 t \right) / 2 \sqrt{S_F(t, F_0)} \right], \quad t \gg t_{eq-\mu}. \quad (29)$$

Quasi-equilibrium transport regime is established at the long- time limit, $t \gg t_{eq-D}$: $D_F(t, F_0) \approx D_{Feq}(F_0)$ and $S_F(t) \approx D_{Feq} t$, although $D_{Feq}/\mu_{eq} \gg kT/e$ ($\sigma/kT \gg 1$). The transit time of holes can be estimated as $t_{tr} \approx L/\mu_{eq} F_0$ in quasi-equilibrium or quasi-dispersive

regime. Obviously, $J(L, L/\mu_{eq}F_0)=0.5J_h$, see Eq. (29). Therefore, $t_{tr} \approx t_{1/2}$, where the half-rise time of TrEL, $t_{1/2}$, is defined as $J_R(t_{1/2})=0.5J_R(\infty)$.

5.2 The space charge- limited regime

If the space- charge limited (SCL) regime of hole's transport is realized, an electric field strength, $F(x,t)$, is determined by space charge of holes (except of several nanometers next to the cathode, where electron's charge is important), in accord with the Poisson's equation. If the dispersive transport is finished, $t > t_{eq-\mu}$, one can connect the current with the density of holes, $p_h(x,t)$:

$$J(x,t) \approx \mu(t) \exp[-\lambda(t)t] F(x,t) p_h(x,t). \quad (30)$$

Following to the work Many & Rakavy, 1962, hence neglecting any diffusion, the density of holes next to the cathode can be written as the step- like function,

$$p_h^{(0)}(x,t) = [\varepsilon\varepsilon_0/eM(t)] \int_0^{x_1(t)} dx_* \delta(x-x_*), \quad (31)$$

Fig. 11. Time dependencies of the initial rise of recombination current, calculated in SCL regime (solid lines) and in IL regime (dashed lines). Dotted lines show how the delay time t_d is defined. The values of applied voltage are shown in the figure.

where, ε is the relative dielectric constant, and $x_1(t) = 2L \ln\{1/[1 - M(t)F_0/2L]\}$ is the leading front position. One can include approximately the field- stimulated broadening of step- like leading front of the distribution (31), replacing the Dirak delta- function in this equation by Gaussian function (28), with x_* and $S_F[t, F(x_*, t)]$ instead of $\mu_{eq}F_0t$ and $S_F(t, F_0)$, respectively. By the use of Eq. (30), one obtains

$$J(L, t) \approx \frac{\varepsilon \varepsilon_0 \mu(t)}{2eM(t)} F(L, t) \exp[-\lambda(t)t] \operatorname{erfc} \left[\frac{L - x_1(t)}{2\sqrt{S_F[t, F(L, t)]}} \right], \quad t < t_1, \quad (32)$$

$$F(L, t) = F^{(0)}(L, t) - (e/\varepsilon \varepsilon_0) \int_L^\infty [p_h(x, t) - p_h^{(0)}(x, t)] dx, \text{ where } F^{(0)}(L, t) = F_0/[1 - M(t)F_0/2L].$$

The time t_1 is the transit time of holes, it is defined as $x_1(t_1) = L$, i.e.

$$F_0 M(t_1)/L \approx 0.787. \quad (33)$$

Obviously, $t_1 \approx 0.787L/\mu_{eq}F_0$ (Many & Rakavy, 1962), because $\mu(t) \approx \mu_{eq}$, if $t_1 \gg t_{eq-\mu}$. Eqs. (25), (26) and (32) (or Eq. (29), in the injection-limited regime), yields approximate analytic description of initial rise of TrEL. One has to note, that the effects of filling of deep states and field dependence of non-equilibrium mobility of holes are not considered here. Indeed, calculations of the refs. [Pasveer et al., 2005, Arkhipov et al., 2001b] yield the weak dependence of mobility on hole's density and field strength, if $p_h/N \leq 10^{-4}$, $F_0 \leq 5 \cdot 10^5$ V/sm, $T > 250$ K, $\sigma/kT \leq 3$.

Fig. 12. Normalized electroluminescence transients, obtained for the structure ITO:PANI/co-PPV (100 nm)/Ca:Al. Dashed lines show how the delay and transit times are defined.

Normalized TrEL signals calculated for injection-limited (IL) and SCL regimes of hole transport are shown in the Fig. 11 as dashed and solid curves, respectively. Calculations are carried out for two values of applied voltage, 8 and 16 V, and film thickness 100 nm, providing that $\tau_e = 3t_1$, where t_1 is calculated from Eq. (33); $\phi(t) = \phi_0 = 0.3$ (SCL regime); $\sigma = 0.075$ eV, $T = 295$ K, $N = 4.6 \cdot 10^{21}$ cm $^{-3}$, $2\gamma N^{-1/3} = 10$. Time is normalized by the half-rise time, $t_{1/2}$. The simplest case, $\phi = \text{const}$, is assumed for the IL regime. Built-in voltage $V_{bi} = 2$ V is taken in account, so the field lies in the range from $6 \cdot 10^5$ to $14 \cdot 10^5$ V/cm. Fig. 11 shows an approximate universality in both regimes. As field increases, the dispersion

parameter $W_R = (t_{1/2} - t_d)/t_{1/2}$ (Nikitenko & von Seggern, 2007), varies from 0.64 to 0.76 and from 0.52 to 0.58 for IL and SCL regimes, respectively. Obviously, TrEL raises steeper in SCL regime. The delay times, t_d , are defined as it is shown in Fig.11. Both these variations are much less than it is predicted by the formula, $W_R = \sqrt{\pi D/\mu F_0 L}$, which can be derived in analogy with the TOF by the use of Eq. (28), providing the time- independent FAD coefficient $D_{Feq} \propto F_0^2$. A reason of the universality is the non- stationary FAD coefficient, in analogy with TOF experiments. If the Einstein's relation, $D/\mu = kT/e$, is the case, then one obtains variation of W_R from 0.11 to 0.07 contrary to both the calculated and experimental (see below) results.

The results of the calculations are compared with experimental data. Single-layer OLEDs were fabricated on ITO glass substrates covered with polyaniline (PANI) as a hole injecting layer followed by a 100-nm- thick co-PPV layer as active material where co-PPV is poly[(p-phenylenevinylene)-alt-(2-methoxy-5(2-ethylhexyloxy)-p-phenylenevinylene)] from Sigma-Aldrich. A Ca cathode and Al protecting layer were thermal deposited in vacuum. TrEL measurements were performed using a Keithley source-measure unit and photomultiplier tube (Nikitenko et al., 2008).

The built-in voltage for this structure is $V_{bi} = 2$ V and holes are the fastest charge carriers (Scott et al., 1999). Fig. 12 shows the semi logarithmic plot of experimental TrEL intensities, $J_{EL}(t)$, subtracted from its long- time value, $J_{EL}(\infty) = J_{EL}^{max}$, and normalized by the J_{EL}^{max} . Obviously, the transit time can be determined by the method of the work (Pinner et al., 1999), see dashed lines, and this time is very close to the half- rise time of TrEL, $t_{1/2}$ (see also Fig. 13 of the cited work).

Fig 13. Normalized experimental TrEL signals (solid lines), compared with results of calculations (dashed lines). Recombination current calculated for IL regime (left panel, applied voltages are 8, 10, 16 volts) and for SCL regime (right panel, 10 and 16 volts). On the right panel, $t_{tr}=t_{1/2}$ and $t_{tr}=t_1$, see Eq. (33), for experimental and calculated curves, respectively. Increase of voltage is shown by arrows.

One can obtain parameters of $\phi(t)$, see Eq. (26), from the long- time exponential asymptotic, namely $\phi_0 \approx 0.3$ and $\tau_e(V=10) = 2.2 t_{1/2}$, $\tau_e(V=16) = 2.7 t_{1/2}$.

Fig. 13 shows the universality of normalized experimental TrEL intensities. The results are in good agreement with calculations in the IL regime (left panel), see the dashed lines, although initial rise of experimental curves is somewhat steeper. Both calculated and experimental data are normalized to the steady-state level, time is normalized to the theoretical transit time of holes and half-rise time, respectively. Both times coincide practically. Again, one can identify the latter with the transit time of holes, while the delay time of TrEL is much smaller than the transit time.

The difference of the workfunction of ITO and HOMO level of co-PPV yield the energy barrier 0.5 eV. The assumption about IL- regime of hole transport is questionable, however, especially at highest voltage. TrEL is calculated in SCL regime for the same set of parameters and compared with experiment in the right panel of Fig. 13. Obviously, the initial slope of the 16V- curve is reproduced by calculations better, than in the left panel of Fig. 13. One can conclude that the transition from IL to SCL regime of hole's transport occurs with the increase of applied voltage from 10 V to 16 V. Subsequent rise of calculated curves is unreasonably steep, however, suggesting that the accuracy of the approximate Eq. (32) is insufficient at $t \geq t_{tr}$. The steepness of the initial rise of TrEL in SCL regime increases together with the electric field. Rise of TrEL is moderated, on the other hand, by the increase of $\phi(t)$, which reflects an electron's kinetics, hence the calculated $t_{1/2}$ underestimates the transit time at low voltages not considerably.

6. Conclusion

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- *equilibrium*. 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 photoexcited carriers still relaxed towards the bottom states. Previous Monte- Carlo simulations delineated that field- assisted diffusion increases at long time domain although the carrier mobility has saturated already (Pautmeier et al., 1991; Borsenberger et al., 1993b). 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 borned 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 (Borsenberger et al., 1993a,b). The theory applies to the case of moderate electric field and field dependence of mobility is not considered here.

Hirao et al., 1995; 1999 attempt to interpret experimental data on the field dependence of carrier mobility under weak field, based on the assumption that the transport is quasi-equilibrium at all times. Simple analytic expression for $j(t)$ in these works is a consequence of Eq. (20), assuming that the charge density $p(x, t)$ is a Gaussian function characterized by time- independent mobility and diffusion coefficient of charge carriers. These values defined by fitting of experimental $j(t)$ dependencies. This procedure, in spite of its success to

explain the temperature dependence of the charge carrier mobility, cannot reproduce the spatial spread of TOF transients at variable sample thickness for large and small values of σ/kT , see the Fig. 6 of the work (Hirao et al., 1999). It implies $W \sim L^{-1/2}$ for the both cases, at variance with experiment on systems with moderately strong energetic disorder, i. e. $\sigma/kT \geq 3$.

Effects of anomalous field-assisted dispersion on initial TrEL kinetics cannot be ignored, basing on arguments following from both theoretical and experimental data. Transit time of fastest charge carriers (holes) can be identified rather with half- rise time of TrEL (in analogy with half- decay time of TOF signal (Bässler, 1993), than with the delay time. The latter is a measure of a time of flight of fastest fraction of holes which hopping paths include only the states with energies shallower than the mean energy of occupied states in quasi-equilibrium regime, $-\sigma^2/kT$. One can overestimate the mobility (in the case of our experimental device, by a factor 4) if the delay time is taken as a transit time. The same conclusion was made in the work Pinner et al., 1999. The method of this work is appropriate in our case as well (see Fig. 12). In general, the method of half- rise time seems to be more appropriate if the long-time TrEL kinetics is not pure exponential and the steady- state level can be observed clearly.

Most of recent studies of charge transport are focused on behaviour of carrier mobility; this chapter is focused on less studied problem of dispersion of charge carriers in space. The objective was to emphasize that a carrier's non-equilibrium manifestations are much wider than effects of dispersive transport. Results of this chapter provide options for analytic modeling and correct determination of material's parameters from data of time- of- flight and transient electroluminescence measurements.

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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