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# Theory to carrier recombination in organic disordered semiconductors

 A. Hofacker,<sup>1</sup> J. O. Oelerich,<sup>1,a)</sup> A. V. Nenashev,<sup>2,3</sup> F. Gebhard,<sup>1</sup> and S. D. Baranovskii<sup>1</sup>
<sup>1</sup>Department of Physics and Material Sciences Center, Philipps-University, D-35032 Marburg, Germany

<sup>2</sup>Institute of Semiconductor Physics, 630090 Novosibirsk, Russia

<sup>3</sup>Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russia

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A theoretical description for recombination kinetics of charge carriers in a disordered system with a broad energy distribution of localized states (DOS) is suggested. This kinetics is governed by the exchange of carriers between transport states and traps. Concentration transients in systems with Gaussian DOS, typical for organic semiconductors, appear much steeper than those obtained for systems with exponential DOS. This difference in recombination kinetics is caused by the difference in thermalization kinetics for these two types of the DOS functions. The comparison of the recombination transients for mobile and trapped carriers in exponential and Gaussian DOS might help to distinguish between these two possible shapes of the DOS using experimental data for transient photoconductivity and photoabsorption. © 2014 AIP Publishing LLC.

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## I. INTRODUCTION

The problem of charge carrier recombination belongs to the central topics in research on semiconductors, particularly organic disordered semiconductors. Recombination efficiency determines the performance of all optoelectronic devices, and therefore, its understanding is of vital importance for device applications of semiconducting materials. Recombination processes in disordered semiconductors demonstrate several peculiar features, which do not appear in ordered crystalline materials and make the appropriate theoretical description of such processes a challenging issue.

The absence of any crystalline structure in disordered materials leads to an energetically broad distribution of localized states (DOS) that can act as traps for charge carriers if the energy scale of the DOS is larger than the thermal energy  $kT$ . In inorganic amorphous semiconductors, such as amorphous silicon and chalcogenide glasses, localized states form the so-called *band tails*, which are separated from the extended states by the mobility edge. At not extremely low temperatures, charge transport takes place via motion of carriers in the extended states, occasionally interrupted by trapping into the localized states with a subsequent release back into the transport states.<sup>1,2</sup> This so-called *multiple trapping* (MT) transport model is illustrated in Fig. 1. The MT model has been suggested in order to describe the time-dependent carrier mobility in the so-called *dispersive transport* regime in inorganic disordered materials, such as chalcogenide glasses and amorphous silicon.<sup>3-5</sup>

The DOS in inorganic amorphous materials is believed to have an exponential shape<sup>1-7</sup>

$$g(\varepsilon) = \frac{N_t}{\varepsilon_0} \exp\left(\frac{\varepsilon}{\varepsilon_0}\right), \quad (1)$$

where  $N_t$  is the total concentration of localized states and  $\varepsilon_0$  is the energy scale of the DOS. The energy of a localized

state  $\varepsilon$  is counted negative into the band gap from the mobility edge as a reference level ( $\varepsilon = 0$ ).

Theoretical description of charge transport and recombination in organic amorphous semiconductors is not yet as well developed as that in inorganic disordered semiconductors. Some researchers suggest that a band structure with mobility edges separating extended and localized states is valid also for organic materials,<sup>8-10</sup> in which case mechanisms for charge transport and recombination should be very similar to those in inorganic disordered materials. Other researchers suggest that all electronic states in organic disordered systems are localized, and charge carriers move via incoherent tunneling (hopping) between spatially and energetically distributed localized states.<sup>11</sup> In any case, the energy spectrum in disordered organic materials has a Gaussian shape<sup>11-14</sup>

$$g(\varepsilon) = \frac{N_t}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right), \quad (2)$$

where  $\sigma$  denotes the energy scale of the DOS. It has been well established<sup>14-18</sup> that also in the case of hopping transport in a system with a steeply energy-dependent DOS, like

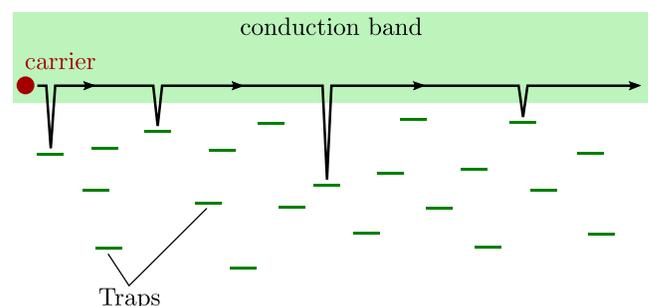


FIG. 1. Schematic view of the MT transport mode. Carrier motion in the conduction band is interrupted by trapping into and subsequent release from localized tail states.

<sup>a)</sup>Electronic mail: jan.oliver.oelerich@physik.uni-marburg.de

a Gaussian one, motion of charge carriers can be described in the framework of the MT formalism by replacing the mobility edge in the MT model by some particular energy level  $\varepsilon_t$ , called the *transport energy*. Furthermore, it has been shown that  $\varepsilon_t$  for the Gaussian DOS is situated close to the maximum of the DOS at conditions relevant for experimental studies.<sup>14,18</sup> For simplicity, we will therefore exploit the MT formalism below for inorganic and organic systems, assuming the position of the mobility edge (or the transport energy) at  $\varepsilon=0$  for both shapes of the DOS given by Eqs. (1) and (2).

A powerful model of charge carrier recombination accompanied by thermalization of carriers has been suggested by Orenstein and Kastner.<sup>2</sup> In this model, carriers perform the MT process, i.e., they are trapped into localized states with subsequent activation towards the mobility edge. The activation rate from a localized state with energy  $\varepsilon < 0$  toward the mobility edge ( $\varepsilon=0$ ) is given by

$$\nu(\varepsilon) = \nu_0 \exp(\varepsilon/kT), \quad (3)$$

where  $\nu_0$  is the *attempt-to-escape* frequency usually taken of the order of the phonon frequency  $\nu_0 \approx 10^{12} \text{ s}^{-1}$ ,  $k$  is the Boltzmann constant, and  $T$  is temperature. As soon as a carrier appears at the mobility edge, there are two options for this carrier: (i) to be recaptured by a localized state with a capture coefficient  $b_t$  and herewith to continue the MT process, or (ii) to recombine via one of the recombination centers with a recombination coefficient  $b_r$ . The quantities of interest are the total time-dependent concentration of carriers  $N(t)$  and the concentration of free carriers (those at the mobility edge)  $n(t)$  after a pulsed excitation. The former concentration can be measured, for instance, by the transient photoabsorption and the latter one by the transient photoconductivity.<sup>2,6</sup>

Orenstein and Kastner obtained the dependencies  $N(t)$  and  $n(t)$  via an elegant and transparent analytical solution,<sup>2</sup> though valid only for the case  $b_r \geq b_t$ . The model suggested by Orenstein and Kastner<sup>2</sup> has later been exploited<sup>19,20</sup> to describe the transient photoconductivity in bulk homogeneous systems with exponential DOS given by Eq. (1). The assumption of quasiequilibrium allowed Adriaenssens *et al.*<sup>19</sup> to treat a realistic relation  $b_r < b_t$  in contrast to the less realistic condition  $b_r \geq b_t$  considered by Orenstein and Kastner.<sup>2</sup>

Literally, the same model has later been used by Nelson<sup>21</sup> to describe experimental data obtained for transient concentration of charge carriers in organic heterojunction solar cells. Nelson performed a straightforward computer simulation of the energy relaxation and recombination of carriers in a spatially homogeneous system and compared the results with experimental data obtained in heterojunction inhomogeneous materials. No comparison with analytical results obtained in the framework of the same model<sup>2</sup> has been attempted. The model has once more been studied in the framework of a detailed, though rather elaborate, analytical theory by Tachiya and Seki,<sup>22</sup> who were able to reproduce the data obtained numerically by Nelson.<sup>21</sup> In all these studies, the DOS was assumed purely exponential as given by

Eq. (1). In full analogy to Adriaenssens *et al.*,<sup>19</sup> Tachiya and Seki<sup>22</sup> assumed the system of recombining carriers to be in thermal equilibrium. In Sec. III, we will use the result by Tachiya and Seki<sup>22</sup> to check the validity of our approach in the case of thermal equilibrium for exponential DOS given by Eq. (1).

In the current report, we suggest an extension of the transparent approach by Orenstein and Kastner<sup>2</sup> for the realistic case  $b_r < b_t$ . Our approach is free from the assumption of thermal equilibrium necessary for the analytical treatments by Tachiya and Seki<sup>22</sup> and by Adriaenssens *et al.*,<sup>19</sup> i.e., it is valid for the case of thermal equilibrium as well as for the case of non-equilibrium carriers relaxing in energy. Furthermore, we apply the extended approach to describe recombination processes in systems with a Gaussian DOS inherent for organic disordered semiconductors and compare the results with those obtained for systems with exponential DOS. This comparison provides a recipe for how to distinguish between the Gaussian and exponential DOS by experimentally studying the transient phenomena.

In Sec. II, we briefly summarize the original theoretical approach by Orenstein and Kastner<sup>2</sup> valid in the case  $b_r \geq b_t$ . In Section III, we extend this approach for the realistic case  $b_r < b_t$  and, in Sec. IV, check the results for the exponential DOS by comparison with the exact solution by Tachiya and Seki<sup>22</sup> valid in the case of thermal equilibrium. In Sec. V, we compare the results for a Gaussian DOS with those for exponential DOS and suggest a recipe for how to distinguish between these two shapes of the DOS by studying the transient concentrations of free and trapped carriers experimentally. Concluding remarks are gathered in Sec. VI.

## II. DESCRIPTION OF RECOMBINATION VIA THE DEMARCATION ENERGY AT $b_r \geq b_t$

The key quantity determining recombination kinetics in the model by Orenstein and Kastner<sup>2</sup> is the so-called *demarcation energy*

$$\varepsilon_d(t) = -kT \ln(\nu_0 t), \quad (4)$$

determined by the condition<sup>2,15</sup>

$$\nu[\varepsilon_d(t)]t \approx 1. \quad (5)$$

In Eqs. (4) and (5),  $t$  is the time passed since the pulsed photoexcitation. For Eq. (5), one simply requires, according to Eq. (3), that within this time approximately one activation event to  $\varepsilon=0$  occurs. Hence, activation to the mobility edge  $\varepsilon=0$  is possible within time  $t$  from states with energies above  $\varepsilon_d(t)$  and improbable from states below  $\varepsilon_d(t)$ . The states *above*  $\varepsilon_d(t)$  can therefore be considered in thermal equilibrium, while states *below*  $\varepsilon_d(t)$  are not able to thermalize within time  $t$  and are therefore occupied in accord with the DOS. Because the equilibrium distribution decays upwards above  $\varepsilon_d(t)$  within scale  $kT$  and the DOS decays downwards within scale  $\varepsilon_0$ , the maximum of the carrier distribution corresponds to the vicinity of  $\varepsilon_d(t)$ .

Under these circumstances, the ratio between the concentration  $n$  of free carriers (those at the mobility edge) and

the concentration  $N$  of trapped carriers (those with energies around  $\varepsilon_d(t)$ ) is

$$\frac{n}{N} = \frac{g(0)}{g(\varepsilon_d(t))} \exp\left[\frac{\varepsilon_d(t)}{kT}\right], \quad (6)$$

assuming the equilibrium Boltzmann distribution for carriers above  $\varepsilon_d(t)$ . Because of the low concentration of intrinsic carriers, recombination in disordered materials is usually of a bimolecular character, i.e., photoinduced electrons recombine with photoinduced holes.<sup>23</sup> In this case, the recombination process is governed by the following dynamics:<sup>2,23</sup>

$$\frac{dN(t)}{dt} = -b_r N(t)n(t). \quad (7)$$

This equation takes into account that mobile electrons (holes) with concentration  $n$  recombine with all holes (electrons) characterized by the concentration  $N(t)$ .

The concentration of trapped carriers,  $N(t)$ , is equal to the integral of the product of the density of states  $g(\varepsilon)$  and the time-dependent energy distribution of carriers  $f(\varepsilon, t)$ . Because  $f(\varepsilon, t)$  cuts off abruptly above  $\varepsilon_d(t)$ , the following assumption was used by Orenstein and Kastner:<sup>2</sup>

$$N(t) \simeq \int_{-\infty}^0 f(\varepsilon, t)g(\varepsilon)d\varepsilon \simeq F(t) \int_{-\infty}^{\varepsilon_d} g(\varepsilon)d\varepsilon, \quad (8)$$

where  $F(t)$  is defined as the mean occupation number for  $\varepsilon < \varepsilon_d$ . Since  $F(t)$  describes the occupation of states below  $\varepsilon_d$ , i.e., states with not yet released carriers, this quantity is determined by the equation<sup>2</sup>

$$\frac{dF(t)}{dt} \simeq b_t[1 - F(t)]n(t). \quad (9)$$

Equations (7)–(9) determine the kinetics of both  $N(t)$  and  $n(t)$  self-consistently.<sup>2</sup> In this approach by Orenstein and Kastner, it is, however, assumed that  $1 - F(t) \simeq 1$ , i.e., that the average filling of states  $F$  is very low at all times  $t$ . This assumption is only valid when recombination is significantly more efficient than trapping ( $b_r \gg b_t$ ) and no saturation of the carrier distribution can be established. Assuming the more realistic condition of  $b_r \ll b_t$ , at which carrier distribution saturates and  $F(t)$  approaches unity, one comes to the clear difficulty of diverging concentrations using the above equations by Orenstein and Kastner.

In the next section, we introduce an extension of the model that does not depend on the assumption of low carrier occupancy and therefore covers more realistic parameter ranges than the original model.<sup>2</sup>

### III. EXTENSION OF THE MODEL FOR THE CASE $b_r < b_t$

The key to the simplicity of the approach by Orenstein and Kastner is the approximation that carriers have a step-like distribution in energy, i.e., states below  $\varepsilon_d$  are uniformly occupied and states above  $\varepsilon_d$  are empty. We suggest to keep this approximation, which is reflected in Eq. (8), but to

replace the demarcation energy  $\varepsilon_d$  (see Eq. (4)) by some effective energy  $\varepsilon^*$ , which is calculated in consistence with the carrier concentration dynamics (see below). Eq. (8) then reads

$$N(t) \simeq F(t) \int_{-\infty}^{\varepsilon^*(t)} g(\varepsilon)d\varepsilon, \quad (10)$$

where  $F(t)$  is the mean occupation number for  $\varepsilon < \varepsilon^*$ , in full analogy to the original approach by Orenstein and Kastner.<sup>2</sup> With  $\varepsilon_d$  replaced by  $\varepsilon^*$ , Eq. (9) means that detrapping is considered as inefficient for states with  $\varepsilon \leq \varepsilon^*$ .

In addition to Eqs. (7), (9), and (10), one more equation is needed in order to determine the dynamics of  $F(t)$ ,  $N(t)$ ,  $n(t)$ , and the new quantity  $\varepsilon^*(t)$  self-consistently. For that purpose, we can use Eq. (6), which connects  $n(t)$  and  $N(t)$ , replacing  $\varepsilon_d$  with  $\varepsilon^*$ ,

$$\gamma(\varepsilon^*) = \frac{n}{N} = \frac{g(0)}{g[\varepsilon^*(t)]} \exp[\varepsilon^*(t)/kT]. \quad (11)$$

By doing so, we assume that the concentration of free carriers is given by the Boltzmann tail of the trapped carrier concentration, which resembles thermal equilibrium above  $\varepsilon^*$ .

In order to obtain the carrier concentration dynamics, we now have to solve the system of ordinary differential equations: Eqs. (7) and (9) to (11). Straightforward calculations yield two coupled differential equations for  $N(t)$  and  $\varepsilon^*(t)$ ,

$$\frac{dN}{dt} = -b_r N^2(t)\gamma(\varepsilon^*), \quad (12)$$

$$\frac{d\varepsilon^*}{dt} = -\frac{\gamma(\varepsilon^*)}{g(\varepsilon^*)} G(\varepsilon^*)N(t) \left[ b_r - b_t + b_t \frac{G(\varepsilon^*)}{N(t)} \right], \quad (13)$$

with

$$G(\varepsilon^*) = \int_{-\infty}^{\varepsilon^*} g(\varepsilon)d\varepsilon. \quad (14)$$

To check the validity of the suggested approach, let us consider how  $\varepsilon^*(t)$  behaves for  $F(t) \ll 1$ , where we would expect that  $\varepsilon^* \simeq \varepsilon_d$ . The condition  $F(t) \ll 1$  is equal to the condition  $N(t) \ll G(\varepsilon^*)$ . If we assume the latter, Eq. (13) yields

$$\frac{d\varepsilon^*}{dt} = -b_t \frac{\gamma(\varepsilon^*)}{g(\varepsilon^*)} G^2(\varepsilon^*). \quad (15)$$

Equation (15) can be separated and integrated over  $t$  and  $\varepsilon^*$ . Estimating  $G(\varepsilon^*) \simeq Cg(\varepsilon^*)$  with some constant  $C$ , we arrive at

$$\varepsilon^*(t) = -kT \ln\left(\frac{b_t g(0) C^2}{kT} (t - t_0) + 1\right), \quad (16)$$

where  $t_0$  is the time, at which  $\varepsilon^* = 0$ . This time  $t_0$  should be equal to  $\nu_0^{-1}$  in the multiple-trapping description. If we

compare Eq. (16) with Eq. (4), we notice that the logarithmic time-dependence of  $\varepsilon_d(t)$  is reproduced.

In the long-time limit,  $\varepsilon^*$  should approach the Fermi level  $\varepsilon_F$ , when  $F(t)$  approaches unity. Indeed, setting  $F(t) = 1$  in Eq. (10) makes  $\varepsilon^*$  equal to the Fermi level in the limit  $T = 0$  K. At finite temperatures, the position of  $\varepsilon^*$  appears very close to  $\varepsilon_F$ , as clearly seen in Fig. 2(a). The difference between  $\varepsilon^*$  and  $\varepsilon_F$  is small as compared to the energy scale of the DOS.

#### IV. RESULTS FOR THE EXPONENTIAL DOS

Let us check the approach suggested in Sec. III by comparison with the exact, though elaborate solution by Tachiya and Seki<sup>22</sup> obtained for the exponential DOS. Inserting Eq. (1) into Eqs. (11)–(14), one obtains

$$\frac{dN}{dt} = -b_r N^2(t) \exp\left(\frac{\varepsilon^* - \varepsilon_0}{kT}\right), \quad (17)$$

$$\frac{d\varepsilon^*}{dt} = N(t) \varepsilon_0 \exp\left(\frac{\varepsilon^* - \varepsilon_0}{kT}\right) \times \left[ b_t - b_r - b_t \frac{N_t}{N(t)} \exp\left(\frac{\varepsilon^*}{\varepsilon_0}\right) \right]. \quad (18)$$

Equation (17) allows a direct comparison with the results in Ref. 22. The system of ordinary differential equations in Eq. (17) was solved numerically for different initial carrier concentrations  $N_0$  and temperatures  $T$ . The value of the ratio

$b_r/b_t$  was fixed at  $b_r = 0.1b_t$ . The results are compared with the solution of Eq. (43) in Ref. 22. In order to perform the comparison, we assume that  $\nu_0 = b_t N_t$ . The results of Eq. (17) are plotted in Fig. 3 along with those from Ref. 22.

It is clearly visible from the figure that the approach from Eq. (17) agrees well with the results of the much more elaborate theory by Tachiya and Seki.<sup>22</sup> This good agreement confirms the validity of the approach suggested in Sec. III. Parameters for the comparison were chosen to justify that the thermal equilibrium is established before the launch of recombination, which is necessary for the approach in Ref. 22. For long times  $t$ , the typical power-law behavior<sup>2,22</sup> is observed, i.e.,  $N(t) \propto t^{-\alpha}$ , where  $\alpha = kT/\varepsilon_0$ .

In Fig. 2(b), the time dependence of the free-carrier concentration  $n(t)$  is plotted together with the dynamics of  $\varepsilon^*$ , showing a plateau for the case of very slow recombination  $b_r = 0.001b_t$ . These results can be interpreted as follows. At some time,  $\tau_s$  saturation is established, i.e.,  $\varepsilon^*$  arrives at the Fermi level  $\varepsilon_F$ . At this point,  $n(t)$  attains a stable value and does not decay further until recombination starts. When recombination comes in play at some time  $\tau_r > \tau_s$ ,  $n(t)$  starts to decay again because  $\varepsilon^*$  follows  $\varepsilon_F$  into the bandgap. Such behavior has been predicted by Orenstein and Kastner, though only qualitatively.<sup>2</sup> However, if recombination is fast enough,  $b_r = 0.1b_t$  in Fig. 2, this saturation behavior vanishes and the dynamics of  $\varepsilon^* \approx \varepsilon_d$ , as studied by Orenstein, and Kastner is recovered.

#### V. RESULTS FOR THE GAUSSIAN DOS

The extended approach suggested in Sec. III allows one to theoretically treat the charge carrier recombination

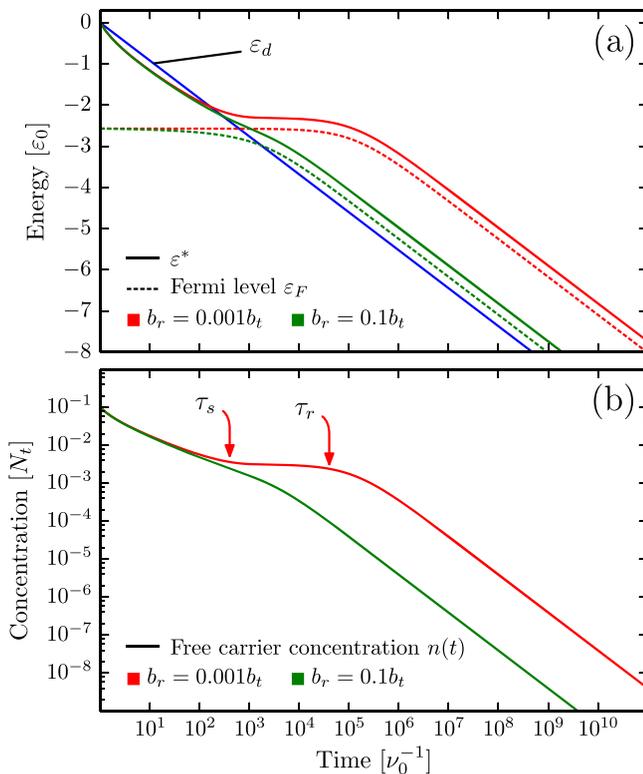


FIG. 2. Dynamics of  $\varepsilon^*$  and  $\varepsilon_F$  (a) and of the free carrier concentration (b) in the exponential DOS for two different recombination rates  $b_r$ . The beginnings of saturation at  $\tau_s$  and of recombination at  $\tau_r$  for the case  $b_r = 0.001b_t$  are marked by arrows. The demarcation energy  $\varepsilon_d$  from Eq. (4) is shown in (a) for comparison.

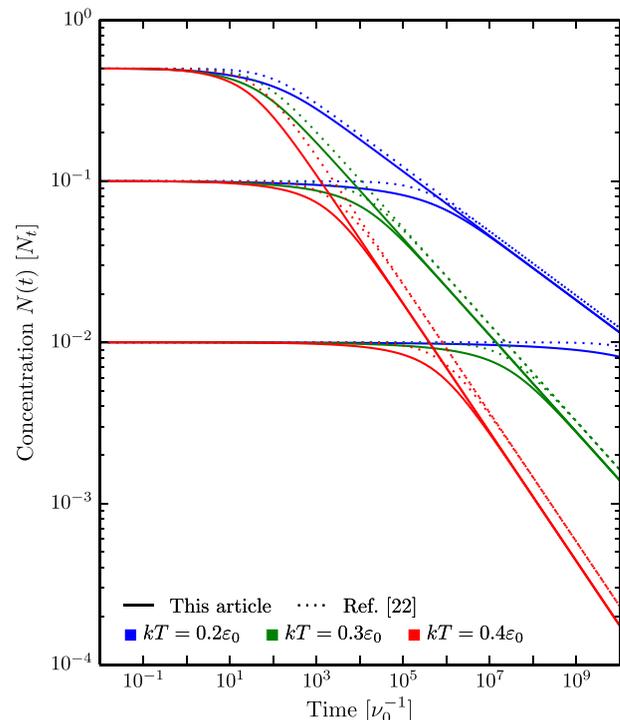


FIG. 3. Concentration of the carriers  $N(t)$  given by Eq. (17) at  $b_r = 0.1b_t$  for different initial carrier concentrations and different temperatures compared to the results of Ref. 22.

accompanied by the energy relaxation of carriers not only in the case of exponential DOS, as described in Sec. IV, but also for other shapes of the energy spectrum, in particular, for the Gaussian DOS given by Eq. (2), inherent for disordered organic semiconductors.<sup>11–14</sup> Treating systems with the DOS steeper than the exponential one given by Eq. (1), one should, however, take into account the principal difference in the way of carrier thermalization in systems with the exponential DOS and those with steeper DOS functions.

In the exponential DOS, carriers dive in energy until no more unoccupied states with deeper energy are available, i.e., the system is saturated. In thermal equilibrium, the carrier distribution  $g(\varepsilon)f(\varepsilon, \varepsilon_F)$  has a maximum at the Fermi level  $\varepsilon_F$ , decaying downwards in accord with the DOS and upwards in accord with the Boltzmann tail of the Fermi function. Hence, the equilibrium carrier distribution is determined by the position of the Fermi level, rendering all electronic processes in the exponential DOS concentration-dependent.

In the Gaussian DOS, the equilibration behavior appears essentially different to that in the exponential DOS. At low carrier concentrations and in thermal equilibrium, the carrier energy distribution  $g(\varepsilon)f(\varepsilon, \varepsilon_F)$  has its maximum not at the Fermi level, but rather at some energy  $\varepsilon_\infty$  independent of the concentration of charge carriers.<sup>11,14</sup> This happens because the DOS decays downwards in energy more steeply than  $f(\varepsilon, \varepsilon_F)$  increases. The energy  $\varepsilon_\infty$  is called *equilibration energy* and is calculated as<sup>11</sup>

$$\varepsilon_\infty = \frac{\int_{-\infty}^{\infty} \varepsilon g(\varepsilon) \exp(-\varepsilon/kT) d\varepsilon}{\int_{-\infty}^{\infty} g(\varepsilon) \exp(-\varepsilon/kT) d\varepsilon} = -\frac{\sigma^2}{kT}. \quad (19)$$

In the Gaussian DOS, a charge carrier relaxes from high-energy states downwards in energy only until it arrives at the equilibration energy  $\varepsilon_\infty$ , even in an empty system without any interaction between relaxing carriers.<sup>11,14</sup> These relaxation dynamics have been studied in detail by analytical theories<sup>24</sup> and computer simulations.<sup>11</sup> In the simulations, noninteracting carriers were initially distributed uniformly over states in the Gaussian DOS, and their energy relaxation was traced. In course of time, the distribution moves downwards until its maximum arrives at the equilibration energy  $\varepsilon_\infty$ . Besides other consequences, this observation means that our picture of carrier energy relaxation, described by the time-dependent energy  $\varepsilon^*(t)$  in Sec. III, should be replaced by the time-independent equilibrium energy distribution of carriers (governed by  $\varepsilon_\infty$ ), as soon as  $\varepsilon^*(t)$  arrives at  $\varepsilon_\infty$  at a time  $\tau_{rel}$  determined by the condition  $\varepsilon^*(\tau_{rel}) = \varepsilon_\infty$ . This picture of carrier relaxation with the decisive role of  $\varepsilon_\infty$  is valid if the concentration of carriers is not too large and the condition  $\varepsilon_\infty > \varepsilon_F$  holds, which we assume throughout the following analysis. Because of the role of the equilibration energy  $\varepsilon_\infty$ , one should separately consider the time intervals  $t < \tau_{rel}$  and  $t \geq \tau_{rel}$ .

At  $t < \tau_{rel}$ , one can evaluate Eqs. (11)–(14) using the DOS from Eq. (2), obtaining

$$\frac{dN}{dt} = -b_r N^2(t) \exp\left[\left(\frac{\varepsilon^*}{\sqrt{2}\sigma} + \frac{\sigma}{\sqrt{2}kT}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2\right], \quad (20)$$

$$\begin{aligned} \frac{d\varepsilon^*}{dt} = & N(t) \sigma \sqrt{\frac{\pi}{2}} \exp\left[\left(\frac{\varepsilon^*}{\sigma} + \frac{\sigma}{2kT}\right)^2\right] \exp\left[-\frac{1}{4}\left(\frac{\sigma}{kT}\right)^2\right] \\ & \times \left[1 + \operatorname{erf}\left(\frac{\varepsilon^*}{\sqrt{2}\sigma}\right)\right] \\ & \times \left[b_t - b_r - b_t \frac{N_t}{N(t)} \left(1 + \operatorname{erf}\left(\frac{\varepsilon^*}{\sqrt{2}\sigma}\right)\right)\right]. \end{aligned} \quad (21)$$

Equations (20) and (21) describe the dynamics of  $\varepsilon^*$  and  $N(t)$  in the case of a Gaussian DOS before the carrier distribution has relaxed to  $\varepsilon_\infty$ .

At  $t = \tau_{rel}$ , i.e., as soon as  $\varepsilon^*(t)$ , obtained from Eq. (21) arrives at  $\varepsilon_\infty$ , the recombination becomes controlled by the conventional equation for bimolecular recombination with the time-independent recombination coefficient

$$\frac{dN}{dt} = -b_r N^2(t) \exp\left[-\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2\right]. \quad (22)$$

Equation (22) is the result of Eqs. (7) and (11) with  $\varepsilon^*(t)$  replaced by  $\varepsilon_\infty$ . It has the solution

$$N(t) = \frac{N(\tau_{rel})}{1 + (t - \tau_{rel})N(\tau_{rel})b_r \exp\left[-\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2\right]}. \quad (23)$$

Results for the concentration of trapped carriers  $N(t)$  obtained at  $\varepsilon^*(t) > \varepsilon_\infty$  via solution of Eqs. (20) and (21) and at  $\varepsilon^*(t) < \varepsilon_\infty$  via Eq. (23) are shown by solid lines in Fig. 4.

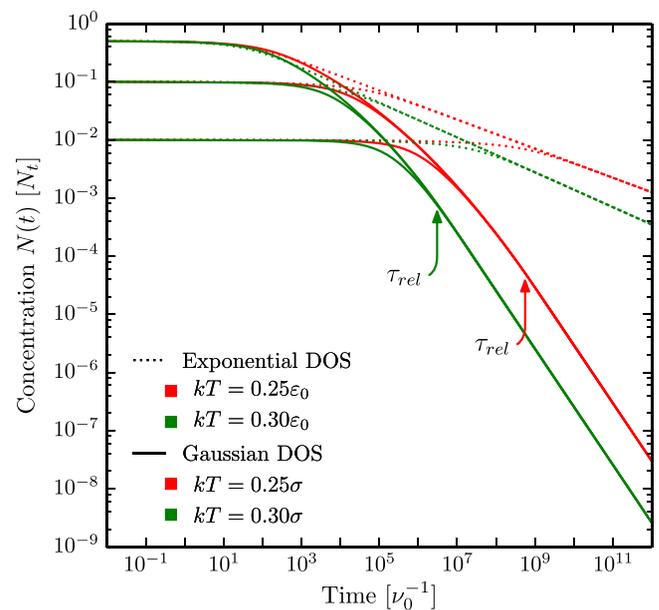


FIG. 4. Comparison of the dynamics of  $N(t)$  for the Gaussian and exponential DOS, shown at  $b_r = 0.1b_t$  for different temperatures  $T$  and different initial concentrations  $N(0)$ . The values of the relaxation time  $\tau_{rel}$  determined by the condition  $\varepsilon^*(\tau_{rel}) = \varepsilon_\infty$  are marked by arrows.

The time evolution of the concentration of trapped carriers  $N(t)$  can be traced experimentally by measuring the intensity of the transient photoabsorption, which is linearly proportional to  $N(t)$ . A question arises herewith on whether it is possible to distinguish between systems with exponential DOS and those with Gaussian DOS by viewing experimental transients. In order to answer this question, in Fig. 4, we compare the results for the Gaussian DOS with those obtained for  $N(t)$  in the case of the exponential DOS, discussed in Sec. IV, for the same set of parameters. In the calculation, the recombination coefficient was  $b_r = 0.1b_i$  and, for simplicity, we chose the same values of  $\varepsilon_0$  and  $\sigma$  for the exponential and Gaussian DOS, respectively. The difference in the magnitudes of the time-dependent decrease of  $N(t)$  for the two different shapes of the DOS seen in Fig. 4 is very pronounced. While the exponential DOS leads to a change in  $N(t)$  by just a couple of orders of magnitude for the given time interval, the decrease of  $N(t)$  in the case of the Gaussian DOS corresponds to more than six orders of magnitude in the same time interval. In the case of the Gaussian DOS, Eq. (23) predicts the dependence  $N(t) \propto 1/t$  at large  $t$ , whereas in the case of the exponential DOS the recombination appears much less efficient than in the case of the Gaussian DOS. This happens because the recombination rate  $dN(t)/dt$ , in accord with Eq. (7), is proportional to the concentration of free carriers  $n(t)$ , which decays in course of time for the exponential DOS not only because of the recombination process, but also due to the energy relaxation of carriers into deeper states. In the Gaussian DOS, this energy relaxation is stopped at  $t \simeq \tau_{rel}$ . Concomitantly,  $n(t)$  becomes linearly proportional to  $N(t)$  at  $t \geq \tau_{rel}$ , meaning that  $n(t)/N(t) = \text{const}$  in the Gaussian DOS whereas  $n(t)/N(t)$  decreases with time in the exponential DOS. Since a larger proportion of the carriers is present above the mobility edge, this effect enhances the recombination rate in systems with Gaussian DOS as compared to those with exponential DOS.

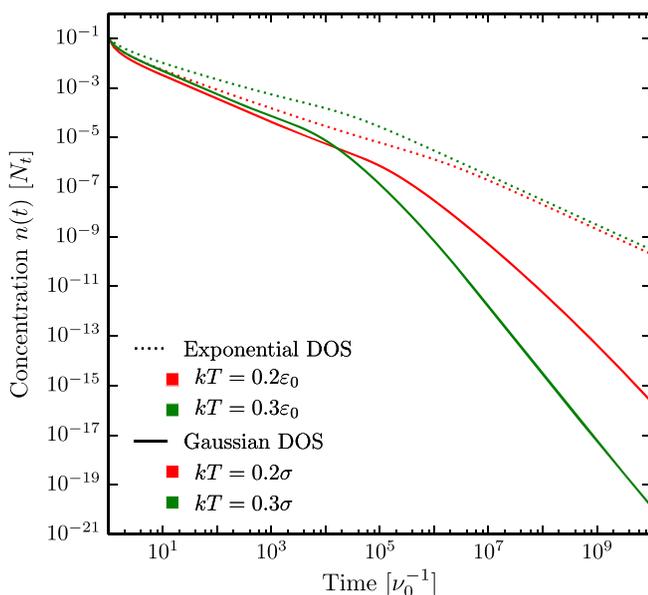


FIG. 5. Dynamics of the free carrier concentration  $n(t)$  at  $b_r = 0.1b_i$  for both shapes of the DOS given by Eqs. (1) and (2) at  $\varepsilon_0 = \sigma$ .

The concentration of mobile carriers  $n(t)$  can be measured, for instance, by tracing the transients of the photoconductivity after terminating the generation of carriers. Theoretical transients of  $n(t)$  for two different types of the DOS are plotted in Fig. 5, for equal values of  $\varepsilon_0$  and  $\sigma$ . The decays of  $n(t)$  for Gaussian DOS are apparently steeper than those for exponential DOS.

## VI. CONCLUSIONS

A theoretical description for recombination of charge carriers accompanied by their energy relaxation through localized states is provided. For systems with exponential DOS, the description by Orenstein and Kastner,<sup>2</sup> initially suggested only for fast recombination, is extended to the realistic case of slow recombination as compared to trapping of carriers into localized states. The theory is further extended for applications to systems with Gaussian DOS inherent for disordered organic semiconductors. In the latter case, thermal equilibration of carriers at the equilibration energy leads to a much more pronounced recombination than in the case of an exponential DOS. This more pronounced recombination in the case of the Gaussian DOS is reflected in the time-dependent transients of the concentrations of trapped ( $N(t)$ ) and mobile ( $n(t)$ ) carriers that appear steeper by several orders of magnitude than those in the exponential DOS. Since the dependences  $N(t)$  and  $n(t)$  can be checked experimentally by measuring the transient photoabsorption and the transient photoconductivity, respectively, the theory may help to experimentally distinguish between different DOS functions.

## ACKNOWLEDGMENTS

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