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Theory of bulk electron-hole recombination in a medium with energetic disorder

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The kinetics of bulk recombination between electrons and holes in semiconductors that have energetic disorder is studied theoretically. The effect of energetic disorder in the medium is taken into account by using a multiple trapping model in which charges repeat trapping into and detrapping from trap sites with different trapping energies. We assume that recombination between an electron and a hole can occur only when at least one of them is detrapped. The distribution of trap sites with different trapping energies E is assumed to be exponential: $\sim\exp(-E/E_0)$. A general theory for the kinetics of bulk recombination between electrons and holes is formulated which is valid for an arbitrary ratio of the recombination rate constant k_r and the trapping rate constant k_t. In the cases of $k_r = k_t$ and $k_r \ll k_t$ the kinetics of bulk recombination is solved analytically. The analytical result for the case of $k_r = k_t$ agrees with the simulation results by Nelson [Phys. Rev. B **67**, 155209 (2003)] for the same case. Our theory predicts that the number density of charges decays as $t^{-\alpha}$ at long times, where $\alpha = k_B T/E_0$ and T is the temperature. This result explains recent experimental observations on bulk recombination between electrons and holes in organic solar cells.

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I. INTRODUCTION

Charge recombination in organic solar cells is a loss factor, whether it is geminate charge recombination or bulk charge recombination.[1–6] Therefore it is important to know how the rate of charge recombination is affected by various physical factors involved in organic solar cells. Two major factors that affect the rate of charge recombination is the transport process of charges in semiconductors and the intrinsic recombination rate at the encounter of an electron and a hole. The effects of the intrinsic recombination rate on geminate and bulk recombination were recently analyzed in Refs. 7 and 8.

Semiconductors used in organic solar cells usually have energetic disorder. It is well known that in the presence of energetic disorder the transport of charges becomes dispersive. There are two models for dispersive transport of charges in semiconductors that have energetic disorder. One is a continuous time random-walk (CTRW) model.[9] In this model charges move between trap sites by nearest-neighbor random walk. The kinetics of CTRW is characterized by a waiting time distribution $\psi(t)$ that is defined as the probability that a random walker will leave the original site for a next one between time t and $t+dt$. For dispersive transport one usually assumes a power-law waiting time distribution. The other model is a multiple trapping (MT) model.[10] In this model a distribution of trap sites with different trapping energies is assumed. Charges are thermally detrapped into the free state with a rate constant that depends on the trapping energy exponentially. They stay in the free state for a while and are then trapped again. The MT model was applied to analyze transport process in amorphous semiconductors by Rudenko and Arkhipov and many other people.[11,12] Both CTRW and MT models were applied to analyze charge recombination process in dye sensitized solar cells.[13–16] The MT model and the CTRW model are mathematically equivalent.[17] However, in our understanding they are physically different. In the MT model the dispersive waiting time distribution arises from the distribution of trap depths while in the CTRW model it arises from the distribution of tunneling distances. In Ref. 18 Nelson also distinguish between them essentially in the same way.

Recently Durrant and other workers[19–21] experimentally studied the kinetics of bulk recombination between photogenerated electrons and holes in organic solar cells. They found that the decay of holes by bulk recombination with electrons is fast at short times but decelerated with time and follows a power law at long times. Nelson[18] did Monte Carlo simulations on the basis of the MT model to explain the results obtained by Durrant.

In this paper we present a theory for the kinetics of bulk recombination between electrons and holes in semiconductors that have energetic disorder. The model we use is similar to the one used by Nelson. However, we solve it analytically. On the basis of the obtained analytical results we analyze recent experimental observations on bulk recombination between photogenerated electrons and holes in organic solar cells.

II. THEORY

A. Kinetic model

Motion of holes is assumed to be described by the MT model.[10,12] In this model holes are trapped in trap sites with different trapping energies and occasionally thermally detrapped to the free state. When they are detrapped into the free state, they are subsequently either retrapped by vacant trap sites or recombine with trapped electrons. We denote the energy distribution of trap sites by $g(E)$ and assume that it decreases exponentially with increasing trapping energy,

$$g(E) = (1/E_0)\exp(-E/E_0), \tag{1}$$

where E_0 is a parameter characterizing the distribution. Although Bässler[22] assumes that the energy distribution of trap sites in polymers is Gaussian, we do not think that this is true for all polymers. If the Gaussian distribution is assumed, it seems impossible to explain the observed power-law kinetics of bulk charge recombination. Nelson assumed the exponential distribution in Ref. 18. We followed her assumption. In addition, our work is intended not only for charge recombination in polymers but also for that in amorphous semiconductors. The rate constant of thermal detrapping depends on the trapping energy E exponentially,

$$k_d(E) = \nu_d \exp(-E/k_B T). \tag{2}$$

We denote the number density of trap sites by N. Hereafter we use dimensionless units $\tau = \nu_d t$ and $\epsilon = E/k_B T$ for time and energy. In dimensionless unit the trapping energy distribution of trap sites and the detrapping rate constant are given by

$$g(\epsilon) = \alpha \exp(-\alpha\epsilon), \tag{3}$$

$$k_d(\epsilon) = \exp(-\epsilon), \tag{4}$$

respectively, where $\alpha = k_B T/E_0$ is the ratio of thermal energy to the parameter characterizing the trapping energy distribution of trap sites. This is a very important quantity in MT model. If α is small compared with unity, E_0 is large compared with thermal energy, which indicates that the trapping energy is distributed up to energies much larger than thermal energy. In this case it takes long times for holes trapped in trap sites with such large trapping energies to be detrapped, so recombination between holes and electrons becomes dispersive, namely, continues up to very long times.

B. Recombination kinetics in the case only holes are mobile

We assume that electrons are deeply trapped and immobile. Let $f(\epsilon,\tau)$ denote the number density of holes trapped with trapping energy ϵ at time τ. The kinetic equation for the distribution $f(\epsilon,\tau)$ is given by

$$\frac{\partial f(\epsilon,\tau)}{\partial \tau} = -e^{-\epsilon} f(\epsilon,\tau) + k_t \frac{Ng(\epsilon) - f(\epsilon,\tau)}{k_t N + (k_r - k_t) n(\tau)} \int_0^\infty e^{-\epsilon} f(\epsilon,\tau) d\epsilon, \tag{5}$$

where k_t and k_r are the rate constants for trapping and recombination with a trapped electron, respectively, of a hole in the free state. In our model no extended state is assumed. What we assume is just that after detrapping a hole will be either trapped again by a trap with a rate proportional to the trap density or recombine with an electron with a rate proportional to the electron density. The first term on the right-hand side corresponds to the decrease in the distribution due to detrapping. The second term corresponds to the increase in the distribution due to trapping. It can be derived in the following way. The factor $\int_0^\infty e^{-\epsilon} f(\epsilon,\tau) d\epsilon$ gives the number density of holes detrapped into the free state per unit time. They are subsequently either retrapped into trap sites with trapping energy ϵ or recombine with trapped electrons. The probability that a detrapped hole will be retrapped into a trap site with trapping energy ϵ is proportional to the trapping rate constant k_t and the number density of vacant trap sites with trapping energy ϵ. This number density is given by $Ng(\epsilon) - f(\epsilon,\tau)$, where $Ng(\epsilon)$ is the total number density of trap sites with trapping energy ϵ. The probability that a detrapped hole will recombine with a trapped electron is proportional to the recombination rate constant k_r and the number density of trapped electrons. This number density is equal to the total number density of holes and is given by $\int_0^\infty e^{-\epsilon} f(\epsilon,\tau) d\epsilon$. Therefore, the probability that a detrapped hole will be trapped into a trap site with trapping energy ϵ is given by

$$\frac{k_t[Ng(\epsilon) - f(\epsilon,\tau)]}{k_t \int_0^\infty [Ng(\epsilon) - f(\epsilon,\tau)] d\epsilon + k_r \int_0^\infty f(\epsilon,\tau) d\epsilon} = \frac{k_t[Ng(\epsilon) - f(\epsilon,\tau)]}{k_t N + (k_r - k_t) n(\tau)}, \tag{6}$$

where we have used $\int_0^\infty g(\epsilon) d\epsilon = 1$. $n(\tau)$ is the time-dependent number density of holes and given by

$$n(\tau) = \int_0^\infty f(\epsilon,\tau) d\epsilon. \tag{7}$$

When holes are photogenerated, the probability that they are initially trapped by trap sites with trapping energy ϵ is proportional to $g(\epsilon)$. Therefore, if the initial density of photogenerated electrons is n_0, the initial condition on the distribution is given by

$$f(\epsilon,0) = n_0 g(\epsilon). \tag{8}$$

Integration of both sides of Eq. (5) over ϵ yields

$$\frac{\partial}{\partial \tau} n(\tau) = -\frac{k_r n(\tau) \int_0^\infty \exp(-\epsilon) f(\epsilon,\tau) d\epsilon}{k_t N + (k_r - k_t) n(\tau)}. \tag{9}$$

It is convenient to introduce the normalized distribution function defined by

$$\phi(\epsilon,\tau) = f(\epsilon,\tau)/n(\tau). \tag{10}$$

By use of the above equation Eq. (5) is rewritten as

$$\frac{\partial}{\partial \tau} \phi(\epsilon,\tau) = -\exp(-\epsilon)\phi(\epsilon,\tau) + \frac{k_t N g(\epsilon) + (k_r - k_t) n(\tau) \phi(\epsilon,\tau)}{k_t N + (k_r - k_t) n(\tau)} \Phi(\tau), \tag{11}$$

where

$$\Phi(\tau) = \int_0^\infty \exp(-\epsilon) \phi(\epsilon,\tau) d\epsilon. \tag{12}$$

On the other hand, by use of Eq. (12), Eq. (9) is expressed as

$$\frac{\partial}{\partial \tau} n(\tau) = -\frac{k_r [n(\tau)]^2 \Phi(\tau)}{k_t N + (k_r - k_t) n(\tau)}. \tag{13}$$

One can calculate the decay kinetics of holes by solving Eqs. (11)–(13). These equations can be solved analytically for the cases of $k_r = k_t$ and $k_r \ll k_t$, as shown below. For a general case they cannot be solved analytically, so we have solved them numerically.

1. Case of $k_r = k_t$

When the recombination rate constant k_r is equal to the trapping rate constant k_t, Eqs. (11) and (13) reduce to

$$\frac{\partial}{\partial \tau}\phi(\epsilon,\tau) = -\exp(-\epsilon)\phi(\epsilon,\tau) + g(\epsilon)\Phi(\tau), \tag{14}$$

$$\frac{1}{n^2}\frac{\partial}{\partial \tau}n(\tau) = -\frac{1}{N}\Phi(\tau). \tag{15}$$

Equation (15) is a generalization of second-order reaction kinetics and $(1/N)\Phi(\tau)$ represents a generalized rate constant. It indicates that the rate of bulk recombination is proportional to the number density of trapped electrons and that of holes but the rate constant is time dependent. The time dependence of the rate constant arises because the distribution of holes among trap sites with different trapping energies changes with time. If $(1/N)\Phi(\tau)$ is time independent, Eq. (14) reduces to well-known normal second-order reaction kinetics. The decay kinetics of holes is given by the solution of Eq. (15),

$$1/n(\tau) - 1/n_0 = (1/N)R(\tau), \tag{16}$$

where

$$R(\tau) = \int_0^\tau \Phi(\tau_1)d\tau_1. \tag{17}$$

Equation (16) is alternatively expressed as

$$n(\tau)/N = 1/[1/(n_0/N) + R(\tau)]. \tag{18}$$

Now our task is to calculate $R(\tau)$. The Laplace transform of $R(\tau)$ is given by

$$\hat{R}(s) = (1/s)\hat{\Phi}(s), \tag{19}$$

where $\hat{\Phi}(s)$ is the Laplace transform of $\Phi(\tau)$. $\hat{\Phi}(s)$ can be calculated in the following way. Laplace transformation of Eq. (14) followed by rearrangement yields

$$\hat{\phi}(\epsilon,s) = [1 + \hat{\Phi}(s)]g(\epsilon)/[s + \exp(-\epsilon)], \tag{20}$$

where $\hat{\phi}(\epsilon,s)$ is the Laplace transform of $\phi(\epsilon,\tau)$. Multiplication of both sides by $\exp(-\epsilon)$ followed by integration over ϵ yields

$$\hat{\Phi}(s) = [1 + \hat{\Phi}(s)]\int_0^\infty \frac{g(\epsilon)\exp(-\epsilon)}{s + \exp(-\epsilon)}d\epsilon. \tag{21}$$

Solving the above equation for $\Phi(s)$, we have

$$\hat{\Phi}(s) = 1/\hat{h}(s) - 1, \tag{22}$$

where

$$\hat{h}(s) = s\int_0^\infty \frac{g(\epsilon)}{s + \exp(-\epsilon)}d\epsilon. \tag{23}$$

$\hat{h}(s)$ can be expressed in terms of the hypergeometric function,[23]

$$\hat{h}(s) = {}_2F_1(1,\alpha;1+\alpha;-1/s). \tag{24}$$

Finally $\hat{R}(s)$ is obtained by substituting Eq. (22) in Eq. (19),

$$\hat{R}(s) = (1/s)[1/\hat{h}(s) - 1]. \tag{25}$$

Inverse Laplace transformation of $\hat{R}(s)$ can be readily evaluated numerically. Once $R(\tau)$ is obtained, the decay kinetics of holes can be calculated from Eq. (16) or Eq. (18). In the long-time limit which corresponds to $s \to 0$ $\hat{h}(s)$ is approximated as[23]

$$\hat{h}(s) = s^\alpha \pi\alpha \csc(\pi\alpha). \tag{26}$$

So $R(\tau)$ is obtained as

$$R(\tau) = b_\alpha \tau^\alpha, \tag{27}$$

where $b_\alpha = \sin(\pi\alpha)/[\pi\alpha\Gamma(1+\alpha)]$ and $\Gamma(x)$ is the gamma function. Therefore, in the long-time limit Eqs. (16) and (18) reduce to

$$1/n(\tau) - 1/n_0 = (b_\alpha/N)\tau^\alpha, \tag{28}$$

$$n(\tau)/N = 1/[1/(n_0/N) + b_\alpha\tau^\alpha], \tag{29}$$

respectively. Note that the recombination kinetics is described in terms of α. At very long times $n(\tau)$ is further simplified to

$$n(\tau)/N = (1/b_\alpha)\tau^{-\alpha}. \tag{30}$$

Nelson suggested that $n(\tau)$ decays as $\tau^{-\alpha}$ at long times.[13] However, her reasoning is valid only in the limit of $k_t/k_r \to 0$ as shown in Sec. II B 3. In normal second-order reaction kinetics $n(\tau)$ decays as τ^{-1} at long times. However, when α is smaller than unity, Eq. (30) predicts the decay kinetics that is more dispersive than τ^{-1}. The kinetics described by Eq. (30) may be called fractional second-order reaction kinetics. Figure 1 shows the decay kinetics of holes by bulk recombination with electrons calculated by use of Eq. (18) together with $R(\tau)$ obtained by numerical inverse Laplace transformation of Eq. (25) in the case of $k_r = k_t$ and $\alpha = 0.4$ for different values of n_0/N. Figure 2 shows the decay kinetics in the case of $k_r = k_t$ and $n_0/N = 0.01$ for different values of α.

The energy distribution of hole sites given by Eq. (3) contains a contribution of zero trapping energy. In the simulations of Nelson the following distribution was used by including additional contribution of zero trapping energy:

$$g(\epsilon) = p\alpha\exp(-\alpha\epsilon) + (1-p)\delta(\epsilon). \tag{31}$$

In order to compare our analytical theory with her simulations we calculated the decay kinetics of holes for the distribution given by Eq. (31). In this case Eq. (24) is modified as

$$\hat{h}(s) = p\,{}_2F_1(1,\alpha;1+\alpha;-1/s) + (1-p)s/(s+1). \tag{32}$$

In Fig. 3 our analytical theory is compared with the simulation results of Nelson. In Nelson's plots time is expressed in terms of an arbitrary unit. We assume that time in her plots is proportional to our normalized time and the proportionality coefficient was determined such that the best agreement between the two results is obtained. Agreement between our

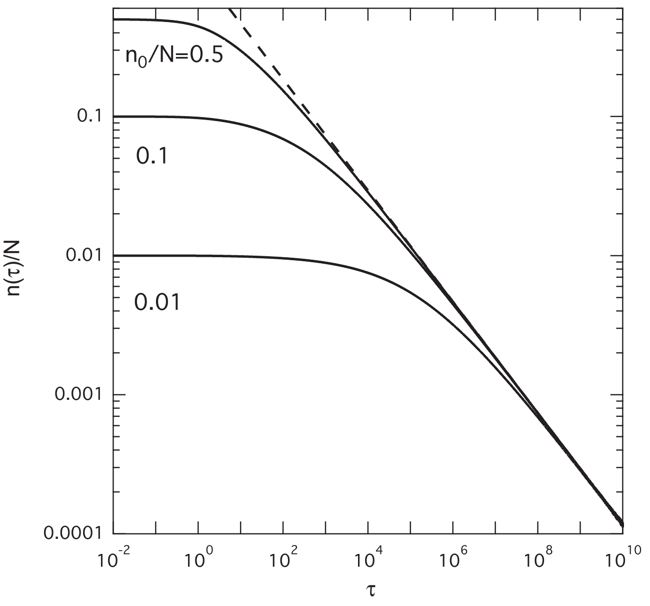

FIG. 1. $n(\tau)/N$ against τ in the case of $k_r = k_t$ and $\alpha = 0.4$. Solid lines represent Eq. (18) together with $R(\tau)$ obtained by numerical inverse Laplace transformation of Eq. (25). $n_0/N = 0.5$, 0.1, and 0.01 from top to bottom. The dashed line is obtained from Eq. (30).

analytical theory and the simulation results of Nelson is good except for the case of $n_0/N = 0.001$. The reason for the significant discrepancy in the case of $n_0/N = 0.001$ is not clear. Some minor discrepancy in the cases of $n_0/N = 0.04$ and 0.06 may be due to a slight difference between the models used in the two approaches. In the model used by Nelson a detrapped hole is allowed to move only to the nearest-neighbor sites while we used a general MT model in which this restriction is not imposed.

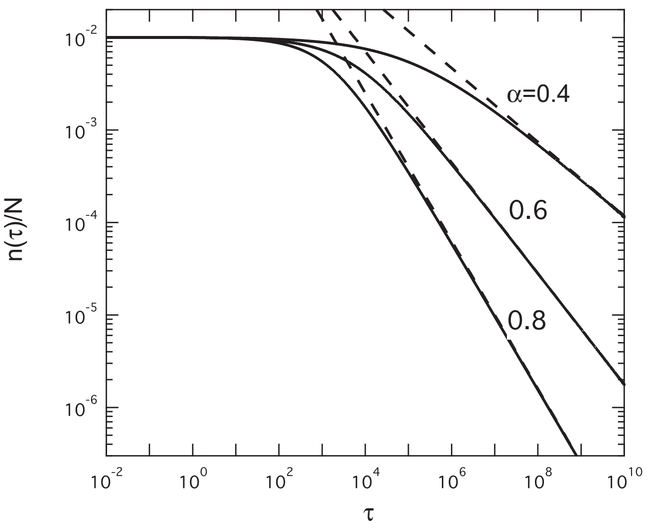

FIG. 2. $n(\tau)/N$ against τ in the case of $k_r = k_t$ and $n_0/N = 0.01$. Solid lines represent Eq. (18) together with $R(\tau)$ obtained by numerical inverse Laplace transformation of Eq. (25). The dashed lines are obtained from Eq. (30). $\alpha = 0.4$, 0.6, and 0.8 from top to bottom.

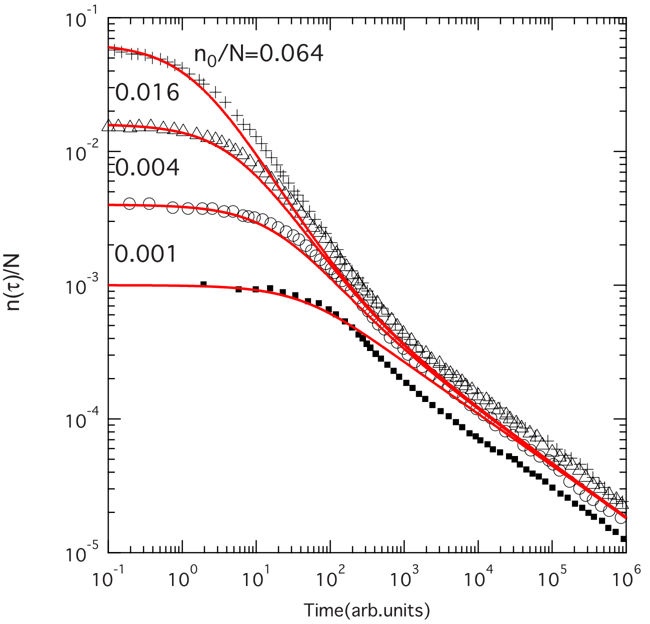

FIG. 3. (Color online) Hole density against time for different initial number of holes. Solid lines represent Eq. (18) together with $R(\tau)$ obtained by numerical inverse Laplace transformation of Eq. (25) with Eq. (32). $p = 0.01$. $\alpha = 0.4$. $n_0/N = 0.064$, 0.016, 0.004, and 0.001 from top to bottom. Symbols denote the results of Fig. 2(a) of Ref. 11.

2. Case of $k_r \ll k_t$

The case in which the recombination rate constant is much slower than the trapping rate constant is also practically important, especially in organic solar cells. The kinetic equation for the number density $n(\tau)$ of holes is given by Eq. (9). If the intrinsic recombination rate constant k_r is much smaller than the trapping rate constant k_t, the distribution of holes among trap sites with different trapping energies is equilibrated before recombination with trapped electrons effectively starts. In other words, the distribution $f(\epsilon,\tau)$ in Eq. (9) is well approximated by a Fermi distribution with a Fermi energy $\epsilon_F(n)$ which depends on the number density $n(\tau)$ of holes,

$$f(\epsilon,\tau) = \frac{Ng(\epsilon)}{\exp\{-[\epsilon - \epsilon_F(n)]\} + 1}. \tag{33}$$

By use of the above equation, the factor $\int_0^\infty \exp(-\epsilon) f(\epsilon,\tau) d\epsilon$ in Eq. (9) is calculated as

$$\int_0^\infty \exp[-\epsilon f(\epsilon,\tau)]d\epsilon$$

$$= \int_0^\infty \exp(-\epsilon)\frac{Ng(\epsilon)}{\exp\{-[\epsilon - \epsilon_F(n)]\} + 1} d\epsilon$$

$$= \exp[-\epsilon_F(n)] \int_0^\infty Ng(\epsilon)\left[1 - \frac{1}{\exp\{-[\epsilon - \epsilon_F(n)]\} + 1}\right] d\epsilon$$

$$=\exp[-\epsilon_F(n)](N-n). \tag{34}$$

Substitution of the above equation in Eq. (9) yields

$$\frac{d}{d\tau}n(\tau)=-k_r\exp[-\epsilon_F(n)]\frac{n(N-n)}{k_t(N-n)+k_rn}. \tag{35}$$

If k_r is much smaller than k_t and if $N-n$ is not smaller than n, the above equation is approximated as

$$\frac{d}{d\tau}n(\tau)\approx -k(n)n, \tag{36}$$

where n is the number density of trapped electrons and the apparent rate constant $k(n)$ is given by

$$k(n)=(k_r/k_t)\exp[-\epsilon_F(n)]. \tag{37}$$

The apparent rate constant $k(n)$ depends on the number density of holes through the Fermi energy. The relation between the Fermi energy and the number density of holes is given by

$$\int_0^\infty \frac{Ng(\epsilon)}{\exp\{-[\epsilon-\epsilon_F(n)]\}+1}d\epsilon=n. \tag{38}$$

The left-hand side of the above equation can be expressed in terms of the hypergeometric function[23] and approximated as

$$N[\pi\alpha/\sin(\pi\alpha)]\exp[-\alpha\epsilon_F(n)]=n \tag{39}$$

from which we obtain

$$\exp[-\alpha\epsilon_F(n)]=c_\alpha(n/N)^{1/\alpha} \tag{40}$$

with $c_\alpha=[\sin(\pi\alpha)/(\pi\alpha)]^{1/\alpha}$. Substitution of the above equation in Eq. (37) yields

$$k(n)=(k_r/k_t)c_\alpha(n/N)^{1/\alpha}. \tag{41}$$

According to Eq. (41), the apparent rate constant is proportional to the $(1/\alpha)$th power of the number density of holes. The strange dependence of the apparent rate constant on the number density of holes arises because the detrapping rate depends on the Fermi energy which in turn changes with the number density of holes. The solution of Eq. (36) with Eq. (41) is obtained as

$$n^{-1/\alpha}-n_0^{-1/\alpha}=(c_\alpha/\alpha)N^{-1/\alpha}(k_r/k_t)\tau. \tag{42}$$

It is alternatively expressed as

$$n/N=(n_0/N)[1+(c_\alpha/\alpha)(n0/N)^{1/\alpha}(k_r/k_t)\tau]^{-\alpha}. \tag{43}$$

At long times $n(\tau)$ is further simplified to

$$n/N=[(c_\alpha/\alpha)(k_r/k_t)]^{-\alpha}\tau^{-\alpha}. \tag{44}$$

The recombination kinetics in this case also exhibits dispersive kinetics. Figure 4 shows the decay kinetics of holes by bulk recombination with electrons calculated by use of Eq. (43) in the case of $k_r/k_t=0.1$ and $\alpha=0.4$ for different values of n_0/N. The decay kinetics calculated by solving Eqs. (11)–(13) numerically is also included in the figure. Agreement between Eq. (43) and the exact numerical results is very good. Figure 5 shows the decay kinetics in the case of $k_r/k_t=0.1$ and $n_0/N=0.01$ for different values of α.

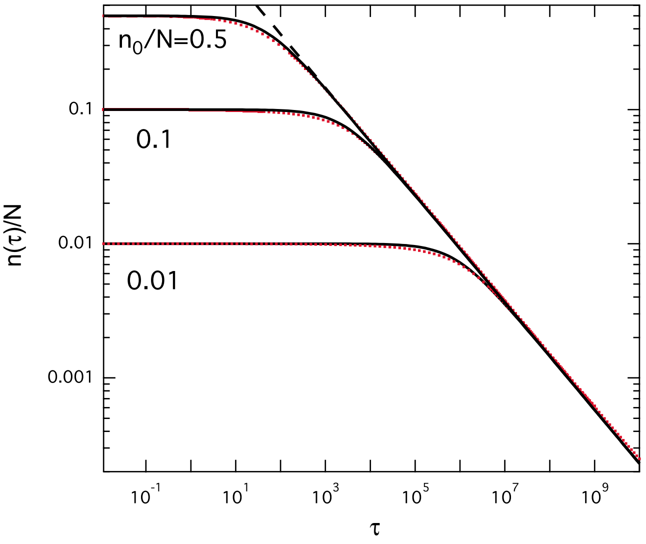

FIG. 4. (Color online) $n(\tau)/N$ against τ in the case of $k_r/k_t=0.1$ and $\alpha=0.4$. $n_0/N=0.5$, 0.1, and 0.01 from top to bottom. The red dots show the exact numerical results. The solid lines represent Eq. (43). The dashed line is obtained from Eq. (44).

3. Case of $k_r \gg k_t$

We have also calculated the decay kinetics of holes by solving Eqs. (11)–(13) numerically for an arbitrary ratio of k_r and k_t. The exact solution can be obtained in the limit of $k_t=0$. In the limit, Eq. (5) simplifies into

$$\frac{\partial f(\epsilon,\tau)}{\partial\tau}=-e^{-\epsilon}f(\epsilon,\tau). \tag{45}$$

Following Ref. 24, the decay kinetics of holes and the asymptotic decay are given by

$$n(\tau)=n_0\alpha\gamma(\alpha,\tau)/\tau^\alpha \tag{46}$$

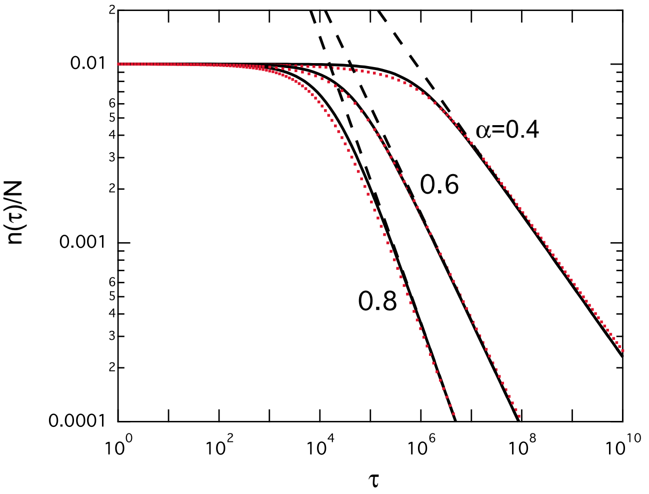

FIG. 5. (Color online) $n(\tau)/N$ against τ in the case of $k_r/k_t=0.1$ and $n_0/N=0.01$. $\alpha=0.4$, 0.6, and 0.8 from top to bottom. The red dots show the exact numerical results. The solid lines represent Eq. (43). The dashed line is obtained from Eq. (44).

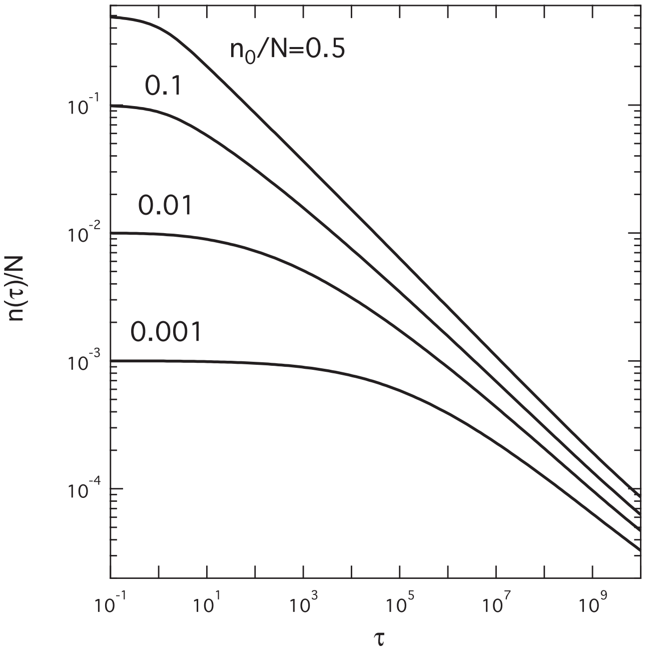

FIG. 6. $n(\tau)/N$ against τ in the case of k_r/k_t=10 and α=0.4. n_0/N=0.5, 0.1, 0.01, and 0.001 from top to bottom. The solid lines represent the exact numerical results.

$$\approx n_0\Gamma(\alpha+1)/\tau^{\alpha}, \tag{47}$$

where $\gamma(z,p)\equiv\int_0^p e^{-t}t^{z-1}dt$ for (Re $z>0$) is the incomplete gamma function.[23] Figure 6 shows the decay kinetics in the case of k_r/k_t=10 and α=0.4 for different values of n_0/N. In Fig. 7, the decay kinetics in the case of α=0.4 and n_0/N =0.1 is shown for different values of k_r/k_t. As shown in the Appendix, it is possible to derive the asymptotic decay for a general value of k_r/k_t. The result is given by

$$\frac{n(\tau)}{N}\approx\frac{\pi\alpha}{\sin(\pi\alpha)}\frac{\Gamma(1+\alpha k_t/k_r)}{\Gamma[1+\alpha(k_t/k_r-1)]}\frac{1}{\tau^{\alpha}}. \tag{48}$$

It indicates that $n(\tau)$ decays as $\tau^{-\alpha}$ at long times for any values of k_r/k_t. In Fig. 7, asymptotic power law with the exponent α is observed in the cases of k_r/k_t=0.1 and 1 but not yet for larger values of k_r/k_t.

C. Recombination kinetics in the case both electrons and holes are mobile

We extend the above treatments to the case in which both electrons and holes are mobile. First we consider the case in which the recombination rate constant k_r is equal to the trapping rate constant k_t. In this case, if motions of electrons and holes are both described by the MT model, Eq. (15) is extended to

$$(1/n_2)\frac{d}{d\tau}n=-(1/N_1)\Phi_1(\tau)+(1/N_2)(\nu_{d2}/\nu_{d1})\Phi_2[(\nu_{d2}/\nu_{d1})\tau], \tag{49}$$

where ν_{d1} and ν_{d2} are the frequency factors of the hole and electron detrapping rate constants, $\tau=\nu_{d1}t$, N_1 and N_2 are the number densities of hole and electron trap sites, and $\Phi_1(\tau)$ and $\Phi_2(\tau)$ are $\Phi(\tau)$ functions for holes and electrons, respectively. The Laplace transforms of $\Phi_i(\tau)$ functions are given by

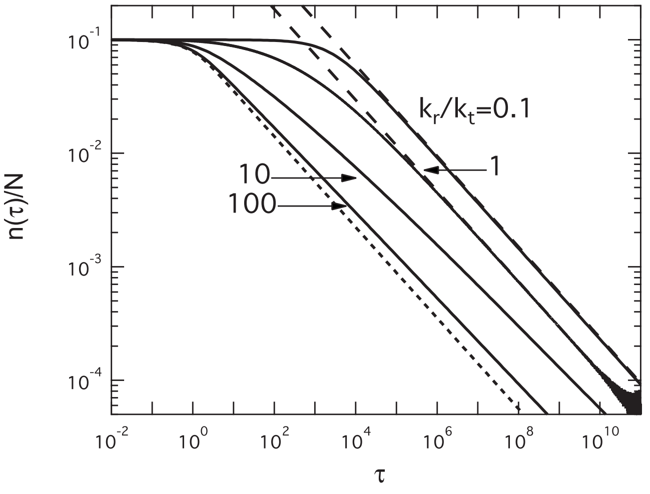

FIG. 7. $n(\tau)/N$ against τ for α=0.4 and n_0/N=0.1. k_r/k_t=0.1, 1, 10, and 100 from top to bottom. The solid lines represent the exact numerical results. The short-dashed line represents the exact solution for k_t=0 given by Eq. (46). The long-dashed lines represent Eq. (48) with k_r/k_t=0.1 and 1.

$$\hat{\Phi}_i(s)=1/h_i(s)-1 \tag{50}$$

with $\hat{h}_i(s)=s\int_0^\infty[g_i(\epsilon)/(s+e^{-\epsilon})]d\epsilon$, where $g_i(\epsilon)$ is given by $g_i(\epsilon)=\alpha_i\exp(-\alpha_i\epsilon)$ and α_1 and α_2 are α values for holes and electrons, respectively. The decay kinetics of holes is described by

$$1/n(\tau)-1/n_0=(1/N_1)R_1(\tau)+(1/N_2)R_2(\tau), \tag{51}$$

where

$$R_1(\tau)=\int_0^{\tau}\Phi_1(\tau_1)d\tau_1, \tag{52}$$

$$R_2(\tau)=\int_0^{(\nu_{d2}/\nu_{d1})\tau}\Phi_2(\tau_1)d\tau_1. \tag{53}$$

At long times the decay kinetics is described by

$$1/n(\tau)-1/n_0=(b_{\alpha1}/N_1)\tau\alpha_1+(b_{\alpha2}/N_2)[(\nu_{d2}/\nu_{d1})\tau]\alpha_2. \tag{54}$$

Next we consider the case in which the recombination rate constant k_r is much smaller than the trapping rate constant k_t. In this case, if motions of electrons and holes are both described by the MT model, $k(n)$ in Eq. (37) is extended to

$$k(n)=(k_{r1}/k_{t1})\exp[-\epsilon_{F1}(n)]+(k_{r2}/k_{t2})\exp[-\epsilon_{F2}(n)], \tag{55}$$

where k_{r1} and k_{t1}, and k_{r2} and k_{t2} are the recombination and trapping rate constants of holes and electrons, and $\epsilon_{F1}(n)$ and $\epsilon_{F2}(n)$ are the Fermi energies of holes and electrons, respectively. The factors $\exp[-\epsilon_{Fi}(n)]$ $(i=1,2)$ are given by

$$\exp[-\epsilon_{Fi}(n)] = c_{\alpha i}(n/N_i)^{1/\alpha i}. \tag{56}$$

Therefore, the rate equation is given by

$$\frac{d}{dt}n \approx -[(k_{r1}/k_{t1})c_{\alpha 1}n(n/N_1)^{1/\alpha 1} + (k_{r2}/k_{t2})c_{\alpha 2}n(n/N_2)^{1/\alpha 2}]. \tag{57}$$

The above equation can be solved numerically.

III. DISCUSSION

The model we used is essentially the same as the one used by Nelson. However, there are two major differences between her work and ours. First she analyzed the model by using Monte Carlo simulations while we analyzed it analytically. Second her conclusion is that the slow decay kinetics of bulk charge recombination is due to the trap filling effect while our conclusion is that the slow decay kinetics is due to a delayed detrapping of trapped charges from a continuous distribution of trap states. Similar explanations to ours were proposed by Zaban *et al.* and Foertig *et al.*,[25,26] although in our opinion they are less clear and less quantitative compared with ours.

The physical model used by Adriaenssens and Baranovskii seems to be essentially the same as the one we used.[12] However, the quantities calculated in the two papers are different. In our paper the sample is excited with a short pulse. Just after the pulse the distribution of charges among various states is given by Eq. (8). We calculate the decay of charges as a function of time under this initial condition. On the other hand, in their paper the sample is excited with a continuous light and the steady state of the distribution of charges among various states is established. Then the continuous light is turned off. Just after the turnoff of the light the distribution of charges among various states is given by the steady-state distribution. They calculate the decay of charges as a function of time under this initial condition. Furthermore, as they themselves admit, in their treatment charge recombination process is taken into account only empirically.

A detrapped hole will be either trapped again by a trap with the rate constant k_t or recombine with an electron with the rate constant k_r. These rate constants are important parameters. Since the magnitudes of these rate constants are not known, we calculated the kinetics of bulk charge recombination for different ratios of the two rate constants. By comparing the observed kinetics with the calculated ones, one can get information on the magnitudes of the rate constants.

Several groups[19–21,27,28] have observed that the kinetics of bulk recombination between photogenerated electrons and holes in organic solar cells follows a power law,

$$n(t) \sim t^{-\alpha}, \tag{58}$$

where $n(t)$ is the concentration of holes or electrons. Some people[19–21] argue that Eq. (58) indicates that the rate of recombination is proportional to the $(1+1/\alpha)$th order of reactant concentrations

$$\frac{d}{dt}n = -kn^{1+1/\alpha}. \tag{59}$$

It is true that if the rate equation is described by Eq. (59), the decay kinetics follows Eq. (58). However, the reverse is not necessarily true. In Case 1 discussed in Sec. II B the recombination rate is proportional to the second order of reactant concentrations. Nevertheless the decay of reactants follows Eq. (58). This is because the rate constant changes with time, as already pointed out in Sec. II B 1. In Case 2 discussed in Sec. II B the recombination rate is apparently proportional to the $(1+1/\alpha)$th order of reactant concentrations. This is because the recombination rate is proportional to the concentration of trapped electrons [see Eq. (36)] and the apparent rate constant $k(n)$ is proportional to $1/\alpha$th power of the hole concentration [see Eq. (41)].

As already mentioned, Durrant observed that the decay of holes is fast at short times but decelerated with time.[19–21] This result was explained by the trap filling effect.[18,20,21] Here we propose a different explanation. When photogenerated holes are initially trapped, they are trapped into traps with different trapping energies, in accordance with Eq. (8). If $g(\epsilon)$ is described by an exponential distribution, most holes are initially trapped into shallow traps because in this distribution the fraction of shallow traps is much larger than that of deep traps. Holes trapped in shallow traps are quickly detrapped and are subsequently either retrapped or recombine with electrons. When they are retrapped, some of them are retrapped into deeper traps. Holes trapped in deeper traps are more difficult to be detrapped, so remain in the same traps. As a result, as time proceeds, the distribution of holes among traps shifts toward larger trapping energy side. This induces the decrease in the detrapping rate and therefore the decrease in the recombination rate.

The effect of dispersive transport on reaction kinetics is also treated by using a fractional diffusion equation. We studied the effect of subdiffusive motion of reactants on the kinetics of geminate recombination by using a fractional diffusion equation.[29,30] Its extension to bulk recombination will be published in a later publication.

APPENDIX: DERIVATION OF EQ. (48)

In order to find the asymptotic decay of the number density, it is convenient to introduce transformations, $\phi(\epsilon,\tau) \equiv f(\epsilon,\tau)/n^{k_t/k_r}$ and $w(\tau) \equiv q(\tau) - v(\tau)$, where $q(\tau) \equiv n^{-k_t/k_r}$ and $v(\tau) \equiv n^{1-k_t/k_r}/N$. The time evolution equation for $w(\tau)$ and $q(\tau)$ can be written as

$$\frac{d}{d\tau}w(\tau) = \frac{1}{N}\int_0^\infty \phi(\epsilon,\tau)d\epsilon, \tag{A1}$$

$$\frac{d}{d\tau}q(\tau) = \frac{k_t}{k_t N + (k_r - k_t)n}\int_0^\infty \phi(\epsilon,\tau)d\epsilon. \tag{A2}$$

The Laplace transform of $q(\tau)$ and $v(\tau)$ satisfy the exact relation,

$$\hat{q}(s) = [\hat{v}(s)/h(s)] + [q(0) - v(0)]/s, \tag{A3}$$

where $\hat{h}(s)$ is given by Eq. (23) and is approximated as Eq. (26). We assume that the asymptotic form of $n(\tau)$ is given by

$$n(\tau) \approx A\tau^{-\beta}, \tag{A4}$$

where A and β are constants to be determined such that Eq. (A4) satisfies Eq. (A3) asymptotically. By using Eq. (A4), $\hat{q}(s)$ and $\hat{v}(s)$ can be expressed as

$$\hat{q}(s) \approx A^{-k_t/k_r}\Gamma(1+\beta k_t/k_r)/s^{1+\beta k_t/k_r}, \tag{A5}$$

$$\hat{v}(s) \approx A^{1-k_t/k_r}\Gamma[1+\beta(k_t/k_r-1)]/s^{1+\beta(k_t/k_r-1)}. \tag{A6}$$

By introducing Eqs. (A5) and (A6) into Eq. (A3), Eq. (48) is obtained.

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