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Geminate-pair dissociation yield in systems with exponential energetic disorder — a Monte Carlo study

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Abstract

Geminate electron-hole recombination in systems with exponential energetic disorder is studied by Monte Carlo method. The field and temperature dependencies of geminate-pair dissociation probability are calculated. It is established that the dissociation yield of carrier pairs depends mainly on the extent of carrier thermalization, which influences the Einstein relationship. The approximate limiting temperature is given by $T_e = \varepsilon_0/2k_B$, where ε_0 determines the decay rate of exponential distribution of localized states. For systems in approximate thermal equilibrium, at $T > T_e$, the yield of free carriers is almost independent of disorder degree and its temperature dependence at zero field has an Arrhenius form. These simulation results are well described by classical Onsager theory. For non-equilibrium systems, at $T < T_e$, the free-carrier yield significantly increases with growing disorder and temperature dependence of zero-field carrier yield is sub-Arrhenius one. At sufficiently low temperatures the carrier yield approaches constant value. These results are described with good accuracy by modified Onsager theory, with T replaced by T_e. It is concluded that experimental investigations of geminate-carrier dissociation yield in disordered materials may be valuable tool for verifying the Einstein relation and determining the energy distribution of localized states.

Keywords:
charge photogeneration, Onsager model, geminate recombination, hopping

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transport, exponential energetic disorder, Monte Carlo simulation

1. Introduction

It is now commonly accepted that the carrier photogeneration in organic solids and in some inorganic ones, like chalcogenide glasses, is governed at low light intensities by the geminate carrier recombination. This means that the generated carrier recombine with its parent carrier of opposite charge. The geminate recombination plays essential role in many photoelectronic devices, such as electrophotographic photoreceptors and solar cells [1–4]. Therefore, detailed understanding of this process is of significant practical importance.

The classical treatment of geminate recombination of charge carriers in continuous medium was developed by Onsager [5] and further ameliored by other authors [6–8]. They calculated the dissociation yield of charged carrier pairs by solving the equation of carrier Brownian motion under the influence of their Coulombic attraction and external electric field. The initial orientation of electron-hole pairs is assumed to be isotropic. Whereas Onsager assumed that the carrier recombination proceeds instantly at infinitesimally small distance, the latter authors considered the more general case of finite distance and finite rate of carrier recombination.

According to Onsager theory, the average escape probability of geminate-carrier pair is given by the formula [9]

$$\eta = 1 - \frac{1}{2}\int_0^2 \exp\left(-Cy\right) \mathrm{d}y \int_0^{r_C/r_0} \exp\left(-x\right) \mathrm{I}_0\left(2\sqrt{Cxy}\right) \mathrm{d}x. \tag{1}$$

Here, $\mathrm{I}_0\left(\ldots\right)$ is the zeroth-order Bessel function of imaginary argument, r_0 is the initial distance of geminate pair, r_C denotes the Coulomb radius,

$$r_C = \frac{e^2}{4\pi\kappa_r\kappa_0 k_B T}, \tag{2}$$

and the factor

$$C = \frac{eFr_0}{2k_B T}, \tag{3}$$

with e being the elementary charge, $\kappa_r\kappa_0$ — the electric permittivity, k_BT — the Boltzmann factor, F — the electric field strength. In the zero-field limit (1) simplifies to

$$\eta = \exp\left(-r_C/r_0\right). \tag{4}$$

As follows from (2) and (4), the zero-field free-carrier yield is a thermally activated quantity, with activation energy corresponding to the initial Coulombic energy of an electron-hole pair.

The efficiency of geminate carrier recombination in solids might deviate from the predictions of Onsager theory for several reasons. The initial distances of photogenerated carrier pairs may be only few times larger than the interatomic distances. The carrier transport frequently proceeds via hopping motion between close atoms or molecules, particularly in disordered solids, in which the electronic levels are distributed in energy. According to general view, the organic and inorganic solids are characterized, respectively, by Gaussian and exponential distributions of energy levels (see, e.g., [10], ch. 2 and 6). Some investigators suggested also the existence of exponential disorder in some specific organic materials [11], but this assumption is controversial [12].

According to above statements, in the calculations of free-carrier yield in solids their discrete structure and the hopping mode of carrier transport has to be taken into account. For homogenous organic solids such studies were performed by Bässler and coworkers with the aid of Monte Carlo method. They established that in the case of ordered isotropic systems the predictions of Onsager theory are fulfilled with good accuracy, provided that the lattice constant is sufficiently small [13]. On the other hand, in the case of systems with energetic Gaussian disorder the calculated carrier yield is much larger than that following from Onsager theory and the temperature dependence of zero-field yield has a sub-Arrhenius character [14, 15]. These features were verified experimentally in [15]. Later on, Monte Carlo simulations of geminate recombination process have been extended to spatialy non-uniform systems — organic heterojunctions and blends [16–20].

In this paper we perform the Monte Carlo investigations of geminate-carrier recombination in homogenous systems with exponential energetic distribution of localized states, being characteristic for disordered inorganic solids. Such a study seems desirable because of different character of carrier relaxation in solids with Gaussian and exponential disorder, as described below.

2. Einstein relationship for disordered solids

The features of carrier hopping transport in a system with disordered energy levels are determined mainly by the extent of carrier thermalization.

In particular, the Einstein relationship between mobility μ and diffusion coefficient D of hopping carriers,

$$\frac{\mu}{D} = \frac{e}{k_B T}, \tag{5}$$

is fulfilled solely in the case of thermal equilibrium. Since the above relation is used in Onsager description of geminate recombination, for the non-equilibrium case one can expect meaningful deviations from predictions of Onsager theory.

Theoretically, for a Gaussian distribution of localized states the thermal equilibrium should always be reached, although the equilibration rate strongly decreases with growing distribution width [21]. However, in Monte Carlo simulations the maximum hopping distance is limited. The criterion of thermal equilibration has then the form of $\sigma < dk_B T$ [22], where the parameter σ determines the width of distribution and the constant d increases with the number of available neighboring sites. Since in the above-mentioned simulations [14, 15] of geminate-pair dissociation the criterion was not fulfilled, they concerned the non-equilibrium case.

For an exponential distribution of localized states the condition of thermal equilibration is $\varepsilon_0 < k_B T$ ([10], ch. 2.5) where the energy ε_0 characterizes the distribution decay rate. With decreasing temperature the relation between μ and D evolves from Einstein's law (5) to its zero-temperature form [23, 24]

$$\frac{\mu}{D} = \frac{2e}{\varepsilon_0}. \tag{6}$$

Here, the numerical coefficient '2' concerns the case of carrier transport in discrete lattice between neighboring sites and should be replaced by '2.3' in the case of continuous medium.

The above-mentioned results concern nondegenerated systems and low-field regime. Otherwise, there occur another deviations from Einstein relationship [25, 26].

From the comparison of (5) and (6) it follows that the dissociation yield of carrier pairs in systems with exponential disorder at low temperatures could be described by Onsager formulas (1) - (4), in which the temperature T of solid is replaced by the characteristic temperature

$$T_e = \frac{\varepsilon_0}{2k_B} \tag{7}$$

of exponential distribution. The free-carrier yield should be then independent of temperature. It is easy to show that at the temperature $T = T_e$ the total numbers of non-equilibrium and equilibrium carriers are nearly equal each other. Thus, one can assume that (5) and (6) are approximately valid for $T > T_e$ and $T < T_e$, respectively.

3. Simulation procedure

As in the previous papers on the subject, calculation method consists of simulation of carrier hopping motion on regular cubic lattice with the constant a. Only the carrier of one sign (for definiteness, electron) is assumed to be mobile, the carrier of opposite sign (for definiteness, hole) is fixed at the lattice center, corresponding to the origin of coordinate system. The electron position at site i is indicated by the vector $\vec{r}_i$. The external electric field $\vec{F}$ is directed along the z-axis.

The electron hopping rate from site i to site j is determined from the Miller-Abrahams formula [27],

$$w_{ij} = \nu_0 \exp\left(-2\gamma r_{ij}\right) \begin{cases} \exp\left(-\Delta U_{ij}/k_B T\right), & \Delta U_{ij} \geq 0, \\ 1, & \Delta U_{ij} < 0. \end{cases} \tag{8}$$

Here, ν_0 is the frequency factor, γ is the parameter characterizing the overlap of localized state wavefunctions, $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and ΔU_{ij} is the difference of total electron energies in sites i and j. These energies are given by

$$U_{i(j)} = -\frac{e^2}{4\pi\kappa_r\kappa_0 r_{i(j)}} - e\vec{F}\cdot\vec{r}_{i(j)} + \varepsilon_{i(j)}, \tag{9}$$

where $\varepsilon_{i(j)}$ are the random energies of initial (final) localized state. According to (8), the electron hops to site containing hole and to other sites are governed by the same tunneling rate.

The exponential energetic disorder is characterized by the following deviate of the energies of localized states:

$$\rho\left(\varepsilon\right) = \begin{cases} \frac{1}{\varepsilon_0}\exp\left(\frac{\varepsilon}{\varepsilon_0}\right), & \varepsilon \leq 0, \\ 0, & \varepsilon > 0. \end{cases} \tag{10}$$

It is assumed here that the mobility edge is situated at $\varepsilon = 0$ and the energy of localized states is measured negative.

In the program, the electron hops from a given site to all sites within the sphere of radius R_{hop} are allowed. Using the random numbers generator, the program calculates the site energies ε_j and then finds the site to which electron hop occurs. After the electron transfer the energies of available neighboring sites are recalculated. Such approach has been already used, e.g., in [22, 24]. It makes possible to avoid the time-consuming simulation of multiple carrier jumps between the close sites with nearly identical energies, as well as to reduce the occupancy of computer memory.

With a given initial distance r_0 of the electron-hole pair, the results of simulation depend somewhat on the initial electron positions [13]. In the program it is assumed that electrons occupy initially the cube corners (with hole in the cube center). Because of system symmetry it is sufficient to select two initial electron positions, $\vec{r}_0 = (+na, +na, \pm na)$ with equal multiplicities (n — an integer number).

The simulation of hopping motion of individual electron is continued until either electron-hole recombination or electron collection on the sample boundary take place. In the program these events correspond, respectively, to the conditions $r_j = 0$ and $r_j \geq R_{esc}$, where R_{esc} is the radius of spherical sample surface. Thus, the electron hop into the site carrying hole is treated as irreversible process and the site acts as infinite sink, in accordance with assumption of the Onsager theory. By repeating the simulation for large number L of electron-hole pairs and counting the number L_{esc} of dissociation events one obtains the average probability, $\eta = L_{esc}/L$, of pair dissociation.

The majority of calculation parameters was common in all simulations. These are: $a = 3.5 \cdot 10^{-8}$ cm, $\gamma = 3/a$, $r_0 = 4\sqrt{3}a$, $R_{hop} = 2a$, $R_{esc} = 400a$, $\kappa_r = 6$. The values of a and κ_r correspond approximately to interchain distance and dielectric constant of a-Se. The chosen value of overlap parameter γ is relatively large. For ordered system the probability of carrier hopping at distance $r_{ij} > 2a$, estimated from (8), do not exceeds 0.3%. One has to notice that the simulation results depend solely on the relative values of carrier hopping rates (8) and thus are independent of the value of frequency factor ν_0.

4. Results and discussion

With the aid of Monte-Carlo method, we have computed the dependencies of geminate-pair dissociation yield on the external electric field strength and the sample temperature in systems with exponential disorder and in ordered

system. The results are portrayed on the plots of η *versus* F for $T = 100$ K and $T = 300$ K, and on the plots of η *versus* $1000/T$ for $F = 0$. The results referring to disordered and ordered systems are denoted by points and crosses, respectively. The statistical errors, estimated from the comparison of results for several simulation series, are smaller than the dimension of symbols.

We have also calculated the corresponding dependencies of free-carrier yield from the Onsager formulas (1) – (4), either at the temperature T of solid (for $T > T_e$) or at the characteristic temperature T_e of exponential distribution of localized states (for $T < T_e$). These results are denoted, respectively, by solid or dashed lines.

In figures 1 – 3 the plots of $\eta\,(F)$ dependencies, simulated for systems with exponential disorder at several values of parameter ε_0, are given. For the sake of comparison, the plots of $\eta\,(F)$, simulated for ordered solid as well as calculated from Onsager formulas, are also shown.

Figure 1 presents the field dependencies of free-carrier yield obtained for relatively small disorder parameter, $\varepsilon_0 = 0.01$ eV, which corresponds to the characteristic temperature $T_e = 58$ K. Then, the majority of carriers is in thermal equilibrium at both temperatures, $T = 100$ K and 300 K. It is apparent that computed free-carrier yields are almost equal to those in ordered system and their field dependencies may be described with reasonable accuracy by the Onsager theory.

Figures 2 and 3 show the analogous results for larger disorder parameters, $\varepsilon_0 = 0.03$ eV and 0.05 eV, for which the characteristic temperatures equal to $T_e = 174$ K and 290 K, respectively. Therefore, the approximate carrier equilibrium may be reached solely at higher temperature, $T = 300$ K. One can recognize that carrier yields calculated at this temperature increase only slightly with rising disorder parameter. On the other hand, carrier yields from figures 2 and 3 at $T = 100$ K and low fields are, respectively, about two and three orders of magnitude larger than those from figure 1. Field dependencies of the free-carrier yield at lower temperature are well described by modified Onsager formula, in which temperature T is replaced by higher characteristic temperature T_e of exponential distribution.

In figure 4 the plots of $\eta\,(T)$ dependencies at zero field, obtained for systems with exponential energetic disorder and for ordered system, as well as computed from the Onsager formulas (2) and (4), are shown. The calculations are performed for the same values of disorder parameter ε_0 as in figures 1 – 3. It is seen that the plots concerning disordered system with $\varepsilon_0 = 0.01$ eV and ordered system have an Arrhenius form. The simulated yields of free car-

riers are nearly equal each other and somewhat larger than those calculated from the Onsager theory. In contrast, the plots corresponding to disordered systems with $\varepsilon_0 = 0.03$ eV and 0.05 eV have sub-Arrhenius form. With the temperature decrease the free-carrier yields exhibit gradual transition in the vicinity of T_e from thermally activated behavior to temperature-independent one. The low-temperature carrier yields are close to those calculated from Onsager formulas, with T_e instead of T.

The qualitative features of calculated $\eta(F)$ and $\eta(T)$ dependencies for systems with Gaussian disorder [14, 15] are similar to those presented here, although the increase of free-carrier yield at low temperatures with rising disorder parameter is somewhat weaker. Albrecht and Bässler [14] established that the enhancement of carrier yield by disorder can formally be attributed either to the increase of electron-hole initial distance r_0 or to the decrease of Coulomb radius r_C via rising temperature. One can note that latter interpretation is again consistent with violation of the Einstein relationship (5) at non-equilibrium conditions. In general, the ratio of carrier mobility to diffusivity may be expressed as

$$\frac{\mu}{D} = \frac{e}{k_B T_{eff}}, \tag{11}$$

where the effective temperature T_{eff} depends on the temperature T of solid. According to the Monte Carlo results [22], in low-temperature interval the ratio $\mu/D < e/k_B T$ which implies that $T_{eff} > T$. Thus, the lack of carrier equilibrium translates again into apparent increase of the temperature of disordered system.

In principle, the measurements of free-carrier yields enable us to determine the dependence of the effective temperature T_{eff} on the temperature T of investigated material. This dependence may provide some information about the energy distribution of localized states. In the case of exponential disorder the low-field carrier yield becomes temperature-independent for $T < T_e$. Then, the effective temperature approaches constant value, $T_{eff} = T_e$. It was conjectured in [14] that in the case of Gaussian disorder the carrier yield at low field monotonically decreases with temperature lowering and is thermally activated quantity with small activation energy. This would imply that the effective temperature T_{eff} tends then gradually to zero. However, the low-temperature behavior of T_{eff} for Gaussian disorder needs further investigations.

5. Conclusions

In this paper we performed the Monte-Carlo simulations of geminate-carrier recombination in systems with exponential energetic disorder. The main conclusions are as follows.

1. For the systems in approximate thermal equilibrium, at $T > T_e$, the yield of free carriers is almost independent of disorder degree and its temperature dependence at zero field has an Arrhenius form. The simulation results are in reasonable agreement with predictions of the classical Onsager theory.
2. For the non-equilibrium systems, at $T < T_e$, the free-carrier yield at low field significantly increases with growing disorder degree and its temperature dependence is a sub-Arrhenius one. At sufficiently low temperatures the zero-field carrier yield approaches constant value. The simulation results are well described by modified Onsager theory, with T replaced by T_e.
3. In general, the deviations of carrier yields in disordered systems from the Onsager theory are mainly due to violation of the classical Einstein relationship in non-equilibrium conditions. For this reason, the experimental investigations of geminate-carrier dissociation yield in disordered materials may be valuable tool for verifying the applicability of Einstein relation and determining the energy distribution of localized states.

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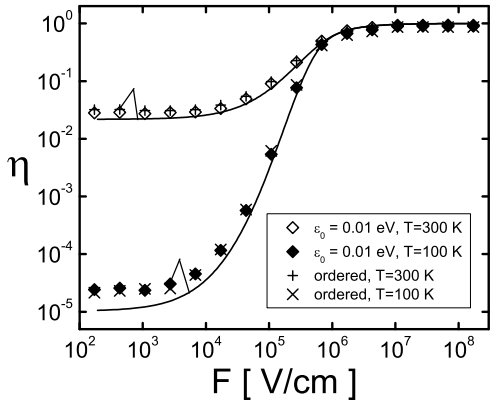

Figure 1: Field dependencies of geminate-pair dissociation probability at two temperatures, simulated for system with exponential disorder, characterized by parameter $\varepsilon_0 = 0.01$ eV (points) and for ordered system (crosses), as well as calculated from Onsager theory (full lines)

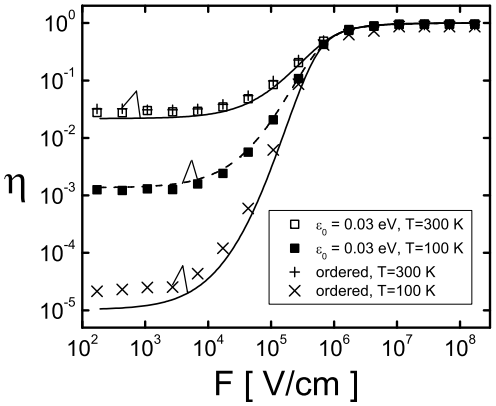

Figure 2: Field dependencies of geminate-pair dissociation probability at two temperatures, computed for system with exponential disorder, characterized by parameter $\varepsilon_0 = 0.03$ eV (points) and for ordered system (crosses), as well as calculated from Onsager theory (full lines) and its low-temperature version (dashed line)

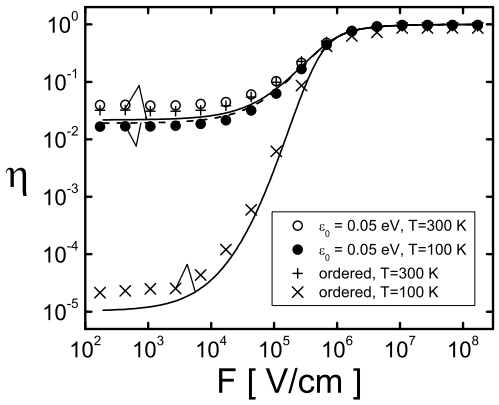

Figure 3: Field dependencies of geminate-pair dissociation probability at two temperatures, simulated for system with exponential disorder, characterized by parameter $\varepsilon_0 = 0.05$ eV (points) and for ordered system (crosses), as well as calculated from Onsager theory (full lines) and its low-temperature version (dashed line)

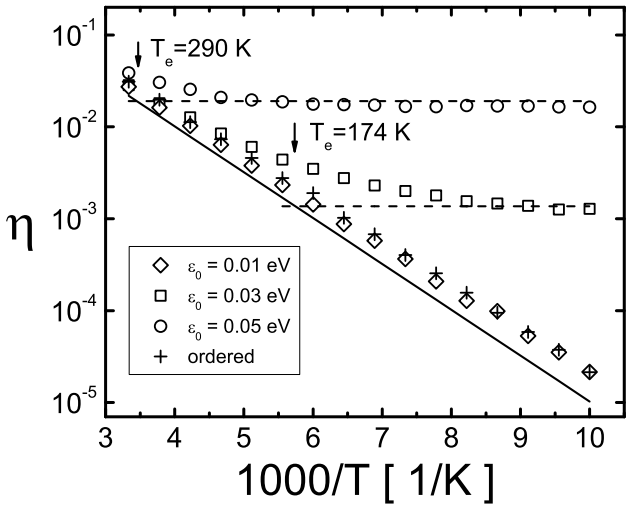

Figure 4: Temperature dependencies of zero-field dissociation probability of geminate-pair, computed for system with exponential disorder at several disorder parameters ε_0 (points) and for ordered system (crosses), as well as calculated from Onsager theory (full line) and its low-temperature version (dashed lines)