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Separation of geminate electron-hole pairs at donor-acceptor interfaces in the approximation of prescribed diffusion

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ABSTRACT

It is generally believed that electrons and holes in organic solar cells are generated by dissociation of excitons at the interface between donor and acceptor materials in the form of geminate, coulombically bound electron-hole pairs. The further motions of electrons and holes are restricted to the acceptor material and donor material, respectively. Using the method of prescribed diffusion, we solve the Smoluchowski equation describing evolution of the spatial distribution of electrons and holes. The separation probability of electron-hole pairs is found as a function of an initial intrapair separation and external electric field.

1. Introduction

Organic photovoltaic cells are usually constructed using blends or bilayers of the electron donor and electron acceptor dielectric materials. It has been established [1–3] that the conversion of photons into charge carriers in organic photovoltaic cells occurs in several sequential steps. (1) At first, photon absorption leads to the generation of an exciton (an electronically excited state) in a donor or acceptor material. (2) The exciton diffuses towards the interface between donor and acceptor (D-A) materials. (3) In the vicinity of the D-A interface, the exciton can dissociate into a geminate pair of oppositely charged particles bound by the Coulomb attraction. A positive charge of the geminate pair, below called a hole, is formed in the electron donor material, and a negative charge, below called an electron, is formed in the electron acceptor material. (4) The electron-hole pair initially produced at the D-A interface can either recombine or escape from the Coulomb potential well and separate into free charge carriers, which are not bound by the Coulomb attraction.

Improvement of the performance of organic photovoltaic cells requires an understanding of all optical and electronic processes that determine the conversion efficiency. However, the key process, that is, how the electron-hole pair created at the D-A interface dissociates into free charge carriers, is still obscured. One of the challenges is the development of methods to find the separation probability of geminate charges, *i.e.* the probability for a geminate electron-hole pair to escape geminate recombination and become free charge carriers. The separation probability and dynamics of geminate charge separation have been studied in a number of theoretical papers including the renowned work of Onsager [4] and a series of works of Hong and Noolandi [5–8], Tachiya with co-workers [9–11], and Berlin et al. [12]. In the papers, the motion of a geminate pair of charged particles produced by ionization in the bulk of dielectric media was approximated by the Smoluchowski equation describing evolution of the distribution function $w(\vec{r},t)$ for geminate charged particles, so that wd^3r is the probability to find a negatively charged particle (electron) in the volume element d^3r at a position $\vec{r}$ relative to a positively charged particle (hole) at time t. Onsager [4] has assumed that recombination of geminate charged particles occurs at an infinitely short distance between charges at which they can approach each other, *i.e.* at zero recombination radius. More realistic model of geminate recombination takes into account that recombination of the charges occurs when they encounter at the encounter separation R_0 (also called the recombination radius, or the distance of the closest approach). Assuming the spherical symmetry in the absence of an external electric field, the boundary condition at the encounter separation is written as follows [5,9]

$$D\left[\frac{\partial w(r,t)}{\partial r}+\frac{r_c}{r^2}w(r,t)\right]_{r=R_0}=\kappa w(R_0,t) \tag{1}$$

where D is the sum of the diffusion coefficients of the two charged particles, r is the distance between them, $r_c=e^2/(4\pi\varepsilon_0\varepsilon k_BT)$ is the Onsager length, k_B is the Boltzmann constant, T is temperature, ε is dielectric constant, ε_0 is permittivity of free space, e is the elementary charge, and κ is the intrinsic recombination velocity on a sphere of radius R_0. Eq. (1) states that the flux density through the reaction surface of radius R_0 is proportional to the probability

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density at the reaction surface [5,9]. It is assumed that in the final stage of recombination the charged particles may react with the intrinsic rate determined by the reactivity velocity κ when the distance between them reaches the reaction radius R_0. The separation probability of a pair of geminate charged particles in the absence of an external electric field is given by [5,9]

$$q = \frac{\exp(-r_c/a) + (\xi - 1)\exp(-r_c/R_0)}{1 + (\xi - 1)\exp(-r_c/R_0)} \tag{2}$$

where $\xi = Dr_c(R_0^2\kappa)^{-1}$, and a is the initial distance between geminate charges. A large body of theoretical and experimental data on diffusion-limited reactions stimulated by light or high-energy radiation in solutions was summarized in reviews [13,14].

Braun [15] worked out an empirical approach for the field-assisted dissociation of the tightly bound charge-transfer (CT) states having a finite lifetime, which can either dissociate into separated charges or recombine radiatively or non-radiatively. He has assumed that the separation probability of a CT state initially separated by R_0 is given by the ratio $k_d/(k_d + k_f)$ where k_f and k_d are the first-order rate constants of recombination and separation, respectively. Braun [15] assumed that both the separation and recombination processes follow the first-order kinetics, and for the electric field dependence of k_d he used the field dependent rate constant found by Onsager [16] for ion pair dissociation in weak electrolytes. As noted [11], Braun's approach is based on the wrong assumption that the separation process of a pair of geminate charges follows exponential kinetics. Using the exact solution [8] of the separation probability in the presence of external electric field for a pair of geminate charges that can be partly absorbed by a recombination sphere, Wojcik and Tachiya [11] extended the Onsager theory to the case of a finite intrinsic recombination rate at a recombination sphere of finite radius R_0 and calculated the field dependent separation probability of CT states having the initial separation $a = R_0$.

It should be emphasized that the theoretical approaches [4–12] are applicable only to the case of ionization in the bulk of a homogeneous medium. As to organic photovoltaic cells, the electron acceptor and electron donor regions form a bulk heterojunction in an active layer of the cells. The motions of electrons and holes generated at a D-A interface are restricted to the acceptor region and donor region, respectively. As noted [17], this makes the available analytical theories [4–12] inapplicable to organic solar cells.

In this paper, we find the separation probability of electron-hole pairs in the framework of the diffusion model similar to that of Wojcik and Tachiya [17]. In the model, the D–A interface is assumed to be a plane with the coordinate $x = 0$. The donor and acceptor materials fill the semispace $x > 0$ and the semispace $x < 0$, respectively. An electron can move only in the acceptor region ($x < 0$) with a diffusion coefficient D_1 while a hole can move only in the donor region ($x > 0$) with a diffusion coefficient D_2. We consider an electron and a hole as classical thermalized particles executing a diffusion-drift motion in their regions. In addition, in the present paper it is assumed that an external electric field is applied across the D–A interface so that the vector of the external field strength coincides with a positive direction of the x-axis. The electric field applied along the x-axis assists the geminate charges to overcome the Coulomb potential barrier. Such a planar heterojunction with the external field applied normally to the D–A surface is particularly suitable for modeling the charge separation in bilayer photovoltaic cells for which important data on the initial electron–hole separations have been reported [18–21].

To obtain the separation probability, we solve below the Smoluchowski equation in the approximation of prescribed diffusion. This approximation has been widely used in the past in the diffusion kinetics of geminate ion pairs and radicals produced in a condensed medium by the passage of a high energy charged particle [22]. The charge separation probability is found below as a function of an external electric field and initial distance between an electron and its sibling hole. It is shown that the separation probability of geminate charges generated at a D–A interface is greater than that in the case of ionization in the bulk of a homogeneous medium.

2. Smoluchowski equation for electron-hole pairs produced at a D –A interface

Let $w(x_1,y_1,z_1,x_2,y_2,z_2,t)$ denote the probability density that an electron will be at (x_1,y_1,z_1) and its sibling hole will be at (x_2,y_2,z_2) at time t. The distribution function w satisfies the Smoluchowski equation given by [17]

$$\begin{aligned}\frac{\partial w}{\partial t} &= D_2\left[\frac{\partial^2 w}{\partial x_2^2} + \frac{\partial^2 w}{\partial y_2^2} + \frac{\partial^2 w}{\partial z_2^2}\right] \\ &+ D_2\left[\frac{\partial}{\partial x_2}\left(w\frac{\partial u}{\partial x_2}\right) + \frac{\partial}{\partial y_2}\left(w\frac{\partial u}{\partial y_2}\right) + \frac{\partial}{\partial z_2}\left(w\frac{\partial u}{\partial z_2}\right)\right] \\ &+ D_1\left[\frac{\partial^2 w}{\partial x_1^2} + \frac{\partial^2 w}{\partial y_1^2} + \frac{\partial^2 w}{\partial z_1^2}\right] \\ &+ D_1\left[\frac{\partial}{\partial x_1}\left(w\frac{\partial u}{\partial x_1}\right) + \frac{\partial}{\partial y_1}\left(w\frac{\partial u}{\partial y_1}\right) + \frac{\partial}{\partial z_1}\left(w\frac{\partial u}{\partial z_1}\right)\right]\end{aligned} \tag{3}$$

Here, $u = V/k_BT$, and $V(x_1,y_1,z_1,x_2,y_2,z_2)$ is the potential energy of an electron-hole pair determined by

$$V = -\frac{e^2}{4\pi\varepsilon_0\varepsilon\left[(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2\right]^{1/2}} - e(x_2 - x_1)F \tag{4}$$

where F is the strength of an external electric field, and the elementary charge $e > 0$. The initial condition describing coordinates of a geminate electron-hole pair at $t = 0$ can be written as follows: $x_1 = -a/2$, $x_2 = a/2$, $y_1 = y_2$, and $z_1 = z_2$ where a is the initial distance between geminate charges.

To describe the relative motion of an electron and hole in the yz-plane, Wojcik and Tachiya [17] have used only four independent variables: x_1, x_2, $y = y_2 - y_1$, and $z = z_2 - z_1$. In these variables, Eq. (3) takes a form [17]

$$\begin{aligned}\frac{\partial w}{\partial t} &= D_1\frac{\partial^2 w}{\partial x_1^2} + D_2\frac{\partial^2 w}{\partial x_2^2} + (D_1 + D_2)\times\left[\frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2}\right] \\ &+ D_1\frac{\partial}{\partial x_1}\left(w\frac{\partial u}{\partial x_1}\right) + D_2\frac{\partial}{\partial x_2}\left(w\frac{\partial u}{\partial x_2}\right) \\ &+ (D_1 + D_2)\times\left[\frac{\partial}{\partial y}\left(w\frac{\partial u}{\partial y}\right) + \frac{\partial}{\partial z}\left(w\frac{\partial u}{\partial z}\right)\right]\end{aligned} \tag{5}$$

where $w = w(x_1,x_2,y,z,t)$, and the reduced potential energy $u = V/k_BT$ can be written as follows

$$u = u_c - e(x_2 - x_1)F/k_BT \tag{6}$$

$$u_c = -\frac{r_c}{\sqrt{(x_2 - x_1)^2 + y^2 + z^2}} \tag{7}$$

Here, u_c is the energy of a Coulomb attraction divided by k_BT. Using the relationship $\partial^2 u/\partial x_j^2 + \partial^2 u/\partial y^2 + \partial^2 u/\partial z^2 = 0$ (where $j = 1, 2$), we can rearrange Eq. (5) as follows

$$\begin{aligned}\frac{\partial w}{\partial t} &= D_1\frac{\partial^2 w}{\partial x_1^2} + D_2\frac{\partial^2 w}{\partial x_2^2} + (D_1 + D_2)\times\left[\frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2}\right] \\ &+ D_1\left(\frac{\partial u}{\partial x_1}\cdot\frac{\partial w}{\partial x_1}\right) + D_2\left(\frac{\partial u}{\partial x_2}\cdot\frac{\partial w}{\partial x_2}\right) \\ &+ (D_1 + D_2)\times\left[\frac{\partial u}{\partial y}\cdot\frac{\partial w}{\partial y} + \frac{\partial u}{\partial z}\cdot\frac{\partial w}{\partial z}\right]\end{aligned} \tag{8}$$