Charge separation in organic photovoltaic cells

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ARTICLE INFO

ABSTRACT

We consider a simple model for the geminate electron–hole separation process in organic photovoltaic cells, in order to illustrate the influence of dimensionality of conducting channels on the efficiency of the process. The Miller–Abrahams expression for the transition rates between nearest neighbor sites was used for simulating random walks of the electron in the Coulomb field of the hole. The non-equilibrium kinetic Monte Carlo simulation results qualitatively confirm the equilibrium estimations, although quantitatively the efficiency of the higher dimensional systems is less pronounced. The lifetime of the electron prior to recombination is approximately equal to the lifetime prior to dissociation. Their values indicate that electrons perform long stochastic walks before they are captured by the collector or recombined. The non-equilibrium free energy considerably differs from the equilibrium one. The efficiency of the separation process decreases with increasing the distance to the collector, and this decrease is considerably less pronounced for the three dimensional system. The simulation results are in good agreement with the extension of the continuum Onsager theory that accounts for the finite recombination rate at nonzero reaction radius and non-exponential kinetics of the charge separation process.

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1. Introduction

Photovoltaic cells utilizing organic semiconductors have attracted much attention due to their promising electronic properties, low cost, thin film flexibility, and high functionality. Although their present efficiency is not high enough, widespread interest in both the academic and, increasingly, the commercial communities promises fast progress in this direction [1,2]. Many attempts have been undertaken to understand the dissociation and recombination processes starting with the theoretical works of Onsager [3,4], Frenkel [5] and Eigen [6], where models of these processes were suggested and investigated. Later, these models were refined with using proper boundary conditions for more adequate description of different stages of recombination/dissociation [7–10]. In these models it is assumed that continuum phenomenological diffusion equations are applicable on molecular space and time scales. On the other hand, discrete models were developed and their computer simulations were performed [11–15].

The models of charge separation were widely used to find routes for increasing the efficiency of the organic solar cells whose internal structure is characterized by a variety of characteristics, e.g. the charge transfer routs can be of different space dimensionality. For example, discotic liquid–crystal porphyrins conduct almost exclusively along one-dimensional backbones, most π-conjugated polymers have quasi-two-dimensional character, while C_{60} and their derivatives are truly three-dimensional organic semiconductors [16].

The effect of space dimensionality on recombination/dissociation was discussed earlier [17]. It was shown that in the absence of interaction potential between two

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dissociating particles the escape probability (the probability that the particles can go away to infinity) is zero if the space dimension is smaller than or equal to two and increases with increasing space dimensionality.

Recently the entropy contribution with respect to the dimensionality of the organic semiconductor into charge separation after sunlight exciton production has been extensively discussed [1,16]. The equilibrium free energy of the electron–hole pair was used for estimating the charge separation efficiency in systems of different dimensionality. It was shown that the efficiency of three dimensional (3D) systems can be up to four orders of magnitude higher, as compared to a one dimensional (1D) system.

However, the equilibrium consideration does not take into account important features of the charge separation process as it was mentioned in Ref. [16] and is in more detail discussed below. Thus, we suggest a simple non-equilibrium model of geminate recombination/dissociation of electron–hole pairs and quantitatively investigate the electron yield on the collector depending on the system dimensionality with accounting of interparticle Coulomb interaction. The main focus of our work is the influence of the space dimensionality on the electron yield in zero electric field. The simulation results are compared with the extension of the Onsager continuum model [9,10]. Characteristic times of the processes are considered as well.

2. Model description

To make the model as simple as possible we consider an electron that moves in a regular lattice and in the Coulomb field of the immobile hole [1,16]. Then, the electron can be considered as moving in the external Coulomb field of the hole and in the approximation of uniformly distributed lattice sites, its equilibrium distribution function can be written as

$$f(r) = Q^{-1} n_r \exp[-\beta u(r)]$$
$$= Q^{-1} \exp[-\beta[u(r) - k_B TS(r)]], \qquad (1)$$

where Q is a normalization constant; $n_r = 1$, $2\pi r$, $4\pi r^2$ for one, two and three dimensional systems, respectively, and it determines the density of the number of lattice sites as a function of r that can be occupied by the electron with equal probability; r is the electron–hole distance; T is the absolute temperature; k_B Boltzmann constant; $\beta = 1/(k_B T)$ is the inverse temperature. The energy of Coulomb interaction for the electron on a cubic lattice with the lattice parameter a is inversely proportional to electron–hole distance

$$u(r) = \frac{-e_0}{\sqrt{i^2 + j^2 + k^2}}, \quad e_0 = \frac{e^2}{4\pi\varepsilon_0\varepsilon a}, \qquad (2)$$

where ε is the medium dielectric constant; e electron charge; ε_0 electric constant; i, j, k are integers that determine lattice sites positions. For 1D and 2D systems the expression for the interaction energy has to be modified correspondingly. The second part of Eq. (1) is rewritten in such a way that the configuration entropy $S(r) = \ln n_r$

appears in a natural way. The expression in the square brackets determines the Helmholtz free energy

$$\Delta G(r) = u(r) - k_B TS(r), \qquad (3)$$

that cumulatively takes into account the equal probability of occupying a number of equivalent lattice sites (with the same distance r) and the attractive electron–hole interaction that makes smaller r distances much more preferable. Of course, this expression for ΔG is the same as given in [1,16]. The distribution function is normalized to unity and the normalization constant

$$Q = \sum_{i,j,k} \exp(-u(i,j,k)/k_B T), \qquad (4)$$

where the sum runs over all sites between the source and the collector.

We used kinetic Monte Carlo method with the Metropolis algorithm [18] to perform simulations of the equilibrium distribution functions. The parameters were taken from paper [16]: $\varepsilon = 4$, $a = 1$ nm, $T = 300$ K. Then, the characteristic energy $e_0/k_B T \cong 13.9$ and the normalization constants are $Q \cong (1.0882; 4.4448; 6.8888) \times 10^6$ for 1D, 2D and 3D cases, respectively. In the equilibrium simulation the electron can jump from the initial site to any other site inside of the collector $(i^2 + j^2 + k^2 \leqslant N^2 + N)$ except zero site $(i^2 + j^2 + k^2 = 0$ where the hole is situated). The lattice sites are prescribed to the distance r if (in 3D case with the corresponding changes in 2D and 1D cases) $r^2 - r < i^2 + j^2 + k^2 \leqslant r^2 + r$, i, j, k, r and N are integers and the collector is on the distance $(N + 0.5)a$ from the hole. The configuration entropy in Monte Carlo simulation is taken into account indirectly through the interrogation of the lattice sites.

The electron energy difference Δu between the destination and the initial state was used for calculating the probability of the electron transition between these two sites. The transition probability was taken equal to $\exp(-\Delta u/k_B T)$ if $\Delta u > 0$ or 1 if $\Delta u \leq 0$. The free energy was calculated from the probabilities for the electron to occupy the lattice sites in accordance with Eq. (1)

$$\Delta G(r) = -k_B T[\ln f(r) + \ln Q - \ln n_r]. \qquad (5)$$

Definitely, in a true geminate recombination/dissociation process the electron cannot be in equilibrium with the hole. However, if the recombination rate is very small and can be neglected then the equilibrium model can be used for crude estimation of the electron spatial distribution around the hole.

3. Results and discussion

3.1. Equilibrium results

The results are shown in Fig. 1a for $N = 30$ (for the sake of uniformity in distribution of the lattice sites over distance r, the distance to the collector was taken equal to $30.5a$) and they confirm the equilibrium distribution function (1) and the conclusion of papers [1,16] about higher efficiency of 3D systems. Small fluctuations of the Monte Carlo simulation results around the analytical curves are