Computing Modeling of Organic Solar Cells - A Mesoscopic Scale Approach

Hélder M C Barbosa, Marta M D Ramos
Department of Physics, University of Minho, Campus de Gualtar, 4710 – 057 Braga,
Portugal
helder@fisica.uminho.ptl

In the last few years, great attention has been done to clean energy sources due to the greenhouse effect, which is responsible for the development of new energy converter systems. Until very recently, the development of energy photovoltaic systems, that convert solar energy into electric energy, have been related to inorganic semiconductors, in particular polycrystalline silicon which allows a maximum yield that approach 25%. Nevertheless, the high cost of fabrication of raw materials associated with their degree of pollution limit the commercial development against other energy sources. In this context, the use of organic semiconductors has been seen as a truly alternative to raw inorganic materials, due to their many advantages, such as easy fabrication and manipulation, flexibility, low weight and cost [1,2].

One of the most used organic solar cells consist of a blend of a low weight molecule with a polymer, that form what is known as bulk heterojunction [3]. When a photon is absorbed by the organic material it will generate a quasi-particle known as exciton that will diffuse through the material. During this process, and as long as the radiative decay of the exciton does not take place, the exciton can meet an internal electric field sufficient strong that allows electron-hole separation, which in turn will be collected at their respective electrodes. The use of a blend of two materials with different molecular properties (different ionization potentials and electron affinities) will allow efficient exciton dissociation at polymer/molecule interface [4], so the challenge is to efficiently diffuse an exciton until it finds one of those interfaces. Although the mechanisms associated with charge generation seems to be simple enough, the efficiency of organic solar cells depends on the balance of the competitions between exciton diffusion, decay and dissociation processes and between charge transport and recombination processes, and that can easily be altered depending of the nanostructure of the materials used [5-7]. Despite the fact the yield of organic solar cells is far from the values achieved with the inorganic counterparts, perspectives for the increase of their efficiency is foreseeable if a better understanding of the relationships between the different processes involving excitons and separated charges is achieved.

Here we present our mesoscopic model for organic photovoltaic cells that is distinguished from other models [8, 9] for taking into account: intra-molecular mobility along polymer chains and the zero-field energy barrier heights for charge and exciton inter-molecular mobility, both obtained with atomistic simulations [10-14]. Like other models, we use a dynamical Monte Carlo method that includes exciton diffusion and dissociation, and charge transport, recombination and collection by the electrodes, where the algorithm is based on the first reaction method (FRM) [15]. In our model we consider two processes for charge transport: intra-molecular charge transport along a polymer chain, where we assume that the coupling between the electronic and atomic motion in the polymer chain creates a quasi-particle known as polaron, that can move along the strand due the local electric field; inter-molecular charge transport between polymer chains and molecules, where charge transport occurs by a process thermally activated, known as hopping. Due to the nature of the materials simulated, we consider that only Frenkel-type excitons are created, and the diffusion of those excitons through the organic material involves a coulombic interaction of dipoles between two polymer chains/molecules (Forster energy transfer). In our simulations, the organic material is viewed as a mixture of cylinders that represent conjugated segments of polymer chains and dots that represent molecules. Although at this moment we do not use any molecular dynamic process to generating morphologies of polymer/molecule blends, the way

that the cylinders and dots distribute in the bulk are representative of the known morphology for the organic material used in solar cells.

When an exciton is created in the polymeric material, it will diffuse following a trajectory until eventually either recombine or dissociate into an electron-hole pair. The exciton hopping rate between two sites is given by:

$$w_{ij} = w_{0,dip-dip} \, g(r_{ij}) \, j(E_{ij}) f(\theta)$$

Where $g(r_{ij})$ is the distance dependence factor for the dipole-dipole interaction in Forster transfer mechanism between sites i and j, $j(E_{ij})$ is the energy dependence factor that considers the difference in exciton occupation energy between the two sites and presents Arrhenius type temperature dependence, $f(\theta)$ is a factor that depends on the angle between dipole orientation on both polymer chains. $w_{0,dip-dip}$ is the maximum hopping frequency for an exciton. After exciton dissociation, the hopping rate for an electron or hole is given by:

$$w_{ij} = w_{0,hop} \, f(\vec{E}) g(r_{ij}) \, j(E_{ij})$$

$j(E_{ij})$ is the energy barrier height dependence factor for charge hopping, $g(r_{ij})$ is the distance dependence factor for charge tunneling between two sites and $f(\vec{E})$ is a factor that depends on the angle between the local electric field direction and the jump direction. $w_{0,hop}$ is the maximum hopping frequency for a charge, and it depends on its sign.

Since in our model we use the molecular properties, obtained by atomistic simulations, of the materials used in organic solar cells and our results are strongly affected by the nanostructure of the organic bulk (e.g. polymer chain orientation that creates crystalline and amorphous regions, dimension of the aggregation zones for one kind of material, the presence of defects and impurities), we hope this new model can give some guidelines for improving organic solar cells efficiency.

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