Simulation of charge transport in organic semiconductors

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Summary

Solar energy is good candidate for large scale energy harvesting. The radiative power of all sunlight that is incident on the earth surface is more than enough to fulfil our ever increasing need for energy. The fraction of solar power that can be converted into electrical power depends on radiative limits, and on the type of solar cell under consideration. There is a growing need for cheap, efficient and durable solar cells that can convert sunlight into electrical power. Organic solar cells provide a low-weight solution that features good mechanical properties, and promising power conversion efficiencies. However, the efficiency of organic solar cells needs to be further improved to make the technology economically viable.

The performance of organic solar cells depends on the efficiency of the individual subprocesses that range from phonon absorption to charge carrier extraction at the electrodes. These processes include absorption of photons and the formation of excitons; separation of excitons into free electrons and holes; transport of the free electrons to the cathode, and free holes to the anode; and finally charge extraction at the electrodes. In order to improve the performance, a proper understanding of all individual processes is required. Although many work has already been done in this field, some details are still missing. This thesis focuses on some of these details that are related to charge transport and charge carrier recombination.

Unlike inorganic semiconductors, charge carrier transport in organic semiconductors occurs by phonon activated hopping through a disordered density of states. Therefore, there is no closed set of equations that describes the charge transport

dynamics in these materials. Instead, kinetic Monte Carlo methods model a large number of charge carriers that are allowed to move through a disordered density of states, by means of phonon activated hopping. Typically, the rate equations of this hopping mechanism are given by Miller-Abrahams or Marcus theory. Although these equations reproduce the experimental results at low electric field, they fail at high bias. Moreover, both theories predict that conductivity disappears at temperatures close to 0 K, whereas experiments show that conductivity becomes finite in this range.

Alternatively, nuclear tunneling hopping can be used to model charge transport in organic semiconductors. This model assumes that charge transport is driven by ground-state oscillations, and previous work on field effect transistors has shown that this results in finite conductivities at low temperatures. **Chapter 2** of this thesis extends the discussion of nuclear tunneling hopping to orthogonal thin film diodes. In this chapter, current-voltage measurements of hole-only MEH-PPV diodes are reproduced using a numerical drift-diffusion simulation that includes charge carrier mobilities based on nuclear tunneling hopping. Even though the active layer thickness and the experimental bias are varied over a wide range, the charge transport parameters that are required to fit the data are found to be equal is all cases. This proves that nuclear tunneling hopping is able to explain the charge transport in MEH-PPV hole-only diodes.

Kinetic Monte Carlo methods are computationally expensive due to the large number of iterations that are required before a physically relevant result is obtained. Moreover, including detailed mechanisms such as particle-particle interactions reduces the performance of these methods even further. **Chapter 3** of this thesis discusses a massively parallel approach to increase the performance of the kinetic Monte Carlo algorithm. The method is implemented on a computer graphics board, which features several thousand parallel threads. This approach allows larger systems to be simulated in the same amount of time, reducing the impact of disorder. Furthermore, the simulation includes a rapid algorithm for calculating the Coulomb interactions between individual charges, and features a method that prevents rounding errors.

In **chapter 4**, the massively parallel kinetic Monte Carlo simulation from chapter 3 is used to investigate charge carrier thermalization in organic solar cells. Photo generated and injected charge carriers are likely to be introduced in highly energetic sites of the density of states. These charges are more mobile than charges in the bottom of the density of states, since they are surrounded by free sites with comparable energy levels. Because these charges are more mobile than thermally relaxed carriers, they

may govern the charge carrier transport characteristics of organic solar cells and diodes. Since this would render space charge limited current analysis invalid, it is important to understand the implications of hot carrier thermalization. The chapter investigates the thermalization effect of both injected and photo generated carriers. For injected hot carriers, it is found that carriers reach their energetic equilibrium position within 12 nm from the injecting electrode. The effect of thermalization on the operation of organic diodes is therefore negligible. For photo generated hot carriers, the impact of thermalization depends on the generation rate of charge carriers. Only when this rate exceeds the values that are accounted in state-of-the-art solar cells, is a small deviation from space charge limited transport observed. The chapter concludes that the impact of charge carrier thermalization is negligible for steady-state operation of organic devices.

Chapter 5 treats the charge carrier recombination of holes at the cathode and electrons at the anode. Since this recombination pathway counteracts the beneficial current flow in the a cell, the process is regarded as a loss mechanism. This type of recombination is hard to investigate experimentally, because it cannot be distinguished from bimolecular recombination. However, numerical drift-diffusion simulations allow surface recombination to be investigated theoretically. The governing parameter for this recombination rate is the surface recombination velocity. The chapter first discusses the lower and upper limits of parameter. Next, the relation between surface recombination and bimolecular recombination is investigated. It is found that surface recombination will only become important once the amount of bimolecular recombination is highly reduced. Furthermore, the drift-diffusion simulations of a large number of organic solar cells are studied. This analysis shows that once surface recombination becomes the dominant loss mechanism, reducing the surface recombination velocity leads to an an increase in bimolecular recombination again. Finally, performance enhancements in organic solar cells that include charge blocking layers are attributed to a reduction of bimolecular recombination, rather than a reduction of surface recombination.