SIMULATIONS OF ORGANIC SOLAR CELLS WITH AN EVENT-DRIVEN MONTE CARLO ALGORITHM

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SIMULATIONS OF ORGANIC SOLAR CELLS WITH AN EVENT-DRIVEN MONTE CARLO ALGORITHM

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Thesis

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ABSTRACT

The generation of photocurrent in organic solar cells starts with a photon being absorbed in the active layer and creating an excited electron/hole pair (exciton). The exciton is mobile and dissociates into electron and hole at an interface between donor and acceptor material, unless it decays before it reaches the interface. If they do not recombine, the charge carriers migrate toward the appropriate electrode and contribute to the photocurrent. Thus, the efficiency of organic solar cells depends strongly on the geometry and electronic properties of the donor/acceptor materials. Simulating in detail the processes described above is of interest since it enables the modeling of devices with different architectures and materials properties. Since processes such as exciton absorption, electron hopping, and recombination take place on vastly different time scales, we employ an event-driven Monte Carlo algorithm to simulate a coarse grained lattice model of the active layer of organic solar cells. We investigate devices of two geometries, one planar and one V-shaped, that differ significantly in the size of the donor/acceptor interface. The trends observed in our results agree with literature findings that show that, as the interface area increases, the current density, charge carrier density and internal quantum efficiency of the device also increase.
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CHAPTER I

INTRODUCTION

1.1 Motivation

Despite much effort, inorganic semiconductor photovoltaic devices such as crystalline silicon solar cells have remained expensive enough to prohibit their wide spread adoption [2]. Organic solar cells give the opportunity of lower production costs compared to their inorganic counterparts, in large part due to their materials and the processing techniques associated with their construction. The highest power conversion efficiencies of organic solar cells however, are on the order of eight percent [4]; far too low to warrant their large-scale production. A key challenge is to develop a predictive understanding of the relationship between the molecular structure of the polymer blends, the device geometry and the overall device performance [5]. This work investigates with computer simulations how device performance is affected by the geometry of the device.
1.2 Organic Solar Cell Principles

The modeled device consists of four parts, a transparent electrode at the top, a layer of donor material, a layer of acceptor material and finally an electrode at the bottom. Light passes through the transparent electrode, enters the donor material, interacts with the donor material and generates excitons. The excitons diffuse through the donor material and, upon reaching the donor acceptor interface, separate into hole-electron pairs. A built in electric field due to the difference in the work functions of the electrodes causes the holes to diffuse through the donor material and the electrons to diffuse through the acceptor material until being collected by the top and bottom electrodes respectively. After charge separation, it is possible for charges to recombine, additionally excitons have the ability to decay either radiatively (e.g. the generation of a photon) or non-radiatively if they do not reach a donor/acceptor interface within 100 ps to 1 ns [5].

In this work we model the following device: an organic solar cell with MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene) for donor material, PCBM (1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61} ) for acceptor material, Indium Tin Oxide (ITO) as a transparent top electrode and an aluminum electrode at the bottom, as depicted in Figure 1.1; Table 1.1 contains the X,Y, and Z dimensions of each material.
Figure 1.1: Illustration of the modeled device, at the top is the ITO electrode, in the $Z_1$ region is the donor material, in the $Z_2$ region is the acceptor material and at the bottom the aluminum electrode.

Table 1.1: $X$, $Y$, and $Z$ dimensions for each material in the modeled device.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>$X$ [nm]</th>
<th>$Y$ [nm]</th>
<th>$Z$ [nm]</th>
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<tbody>
<tr>
<td>ITO</td>
<td>20</td>
<td>20</td>
<td>$\infty$</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>20</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>PCBM</td>
<td>20</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Aluminum</td>
<td>20</td>
<td>20</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

The electronic properties of semiconducting organic materials come from the overlap of $p_z$ orbitals which create delocalized electron states [6, 7]. The overlapping of the $p_z$ orbitals on two adjacent $sp^2$-hybridized carbon atoms causes their degeneracy to split and form $\pi$-bonds [2, 6]. The interaction between $\pi$ bonds results in
delocalized $\pi$ electron states. In semiconducting organic materials, the delocalized $\pi$ electron states become continuous energy bands similar to the conduction and valence bands in inorganic semiconductors [2, 6], with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) separated by a band gap. Figure 1.2 illustrates the formation of the band structure.

Figure 1.2: Schematic energy diagram of electron energy levels, (a) $p_z$ electrons overlap causing degenerate orbitals, (b) the degeneracy splits creating $\pi$ and $\pi^*$ orbitals (c) when a number of these are brought together (such as in a polymer) a delocalized $\pi$-system is formed creating energy bands analogous to the conduction and valence bands of inorganic semiconductors. Modified from Ref [2].

Photoabsorption bands represent the lowest possible one-electron excitation processes. An electron at the HOMO level is excited to the next higher level; with the HOMO level empty, the monomer becomes positively charged and exerts an attractive Coulomb force on the excited electron [7]. The Coulomb force reduces the excitation energy below the gap energy, forming a coupled electron hole pair known as an exciton [7]. The coupling of electronic and mechanical excitations (vibrations)
of the molecular structure produces a broad photoabsorption band so that light over a range of frequencies can be absorbed [7].

The binding energy of an exciton is on the order of 0.5 eV [2]. At room temperature \((kT = 25 \text{ meV})\) there is an almost zero probability of electron-hole separation [2]. However if an acceptor molecule is in proximity to the exciton, the electron in the bound pair can be transferred to the LUMO level of the acceptor while the hole is transferred to the HOMO level of the donor thus separating the exciton. The separation takes place because the energy difference between the LUMO levels of the donor and acceptor materials is greater than the binding energy of the electron/hole pair (e.g. \(\Delta E = 0.9 \text{ eV} > 0.5 \text{ eV} \)). The charge separation process is illustrated in Figure 1.3.
Figure 1.3: An illustration depicting the HOMO/LUMO levels of the device, exciton generation and separation and charge carrier collection. (A) an exciton (g) is generated in the donor material, (B) the exciton then diffuses to the the donor acceptor interface, (C) at the interface the energy difference between the LUMO levels of the donor and acceptor materials is greater than the binding energy of the exciton separating it into charge carriers, (D) both charge carriers diffuse (←,→) towards their respective electrodes and are subsequently collected. Modified from Ref. [3]

1.3 Monte Carlo Simulation

The goal of classical Monte Carlo simulations is to model a system in thermal equilibrium. To do this, a sequence of microstates is generated. First we define \( p_i \) as the probability to find the system in state \( i \) with energy \( E_i \) and \( p_j \) as the probability to find the system in state \( j \) with energy \( E_j \). Then if we let \( P(i \rightarrow j) \) be the probability to transition from state \( i \) to state \( j \) and \( P(j \rightarrow i) \) be the probability for the reverse
transition; we must demand the following in order for the simulation to approach equilibrium as time goes to infinity.

1. The transition probabilities do not vary with time.

2. The transition probabilities $P(i \to j)$ and $P(j \to i)$ only depend on states $i$ and $j$ and not the history of the system.

3. $\sum_j P(i \to j) = 1$; some state must be generated in each transition.

4. The Ergodic hypothesis (all microstates are accessible) must be satisfied.

5. The detailed balance condition must be satisfied:

$$p_i P(i \to j) = p_j P(j \to i) \Rightarrow \frac{P(i \to j)}{P(j \to i)} = \frac{p_j}{p_i} \quad (1.1)$$

An algorithm that satisfies demands one through three generates a sequence of states known as a Markov chain, which is used to describe a memoryless stochastic process. For a transition from state $i$ to $j$ the Metropolis algorithm for Monte Carlo simulations is implemented in the following manner:

1. $\alpha$ is drawn uniformly from the interval $[0,1]$.

2. $a = \frac{p_j}{p_i}$.

3. The transition is accepted if $a > \alpha$.

This algorithm presents a problem with respect to the computational time required to accept the transition from state $i$ to $j$ for systems with rare events. If one considers a system with only one transition available from $i$ to $j$ with the probability
10^{-15}$, then the likelihood the acceptance criterion ($10^{-15} > \alpha$) is satisfied would be on the same order as the transition probability. This situation leads to a condition where many $\alpha$ values must be generated for one transition to take place, meaning several runs through the acceptance criterion would not yield a transition.

To overcome this problem event-driven Monte Carlo algorithms have been developed, where every time the acceptance criterion is evaluated a transition occurs. This type of rejection free Monte Carlo simulation is referred to as the BKL algorithm, after Bortz, Kalos and Lebowitz [8]. Every possible event is associated with a probability, expressed as a rate $\omega_i$ [units s$^{-1}$]. In each step of the algorithm, the rates for all events for the current system configuration are determined and normalized according to Equations (1.2) and (1.3). Then a random number in the interval (0,1) is selected and the event corresponding to the number is executed. This process is illustrated in Figure 1.4.

$$\omega_{\text{Total}} = \sum_i \omega_i \quad (1.2)$$

$$\omega_{\text{normal}}^i = \frac{\omega_i}{\omega_{\text{Total}}} \quad (1.3)$$
Figure 1.4: Schematic showing the time line, constructed from normalized rates, and the selection of the next event based on the time line and a random number. In this example the random number $R$ is 0.375 which corresponds to event 2 indicating that this event will be executed next.

The output of our device simulations allows for the calculation of the charge carrier density, the current density and the internal quantum efficiency. Spatially resolved charge carrier densities are of interest because they give insight into the location of the charge carriers and space charge build up. The carrier density is given by:

$$\rho_{e/h} = \frac{1}{V} \langle n_{e/h} \rangle \quad (1.4)$$

where the $\rho_{e/h}$ is the carrier density, $V$ is the volume of the layer and $n_{e/h}$ is the average number of electrons/holes for a given layer [1].
The current density \( (J) \) is the electric current per unit area, and is the average number of holes and electrons collected at the electrodes over time \( \tau \),

\[
J = -\frac{K_j}{A} \langle (n^c_e + n^c_h) / \tau \rangle
\]  

(1.5)

where the prefactor \( K_j \) has the value \( 1.602 \times 10^{10} \) [mA ps nm\(^2\)/cm\(^2\)] [1], \( A \) is the electrode surface area in nm\(^2\), and \( n^c_e, n^c_h \) are the number of collected electrons and holes respectively [1]. The internal quantum efficiency \( (IQE) \) is defined as the ratio of the number of collected charge carriers to the number of generated excitons and is given by:

\[
IQE = \frac{n^c_e + n^c_h}{2n^g_{exc}}
\]  

(1.6)

where \( n^g_{exc} \) is the number of generated excitons with the factor of 2 accounting for the fact that one exciton generates two charge carriers [1].

Monte Carlo simulations have been applied to investigate different aspects of organic photovoltaics. For example, Ries and Bässler [9] investigated the charge transport properties of spatially random systems while varying the carrier concentration. Scheidler et al. [10] studied the dissociation dynamics of excitons in PPV and proposed a hopping scheme for exciton transport through PPV. Using an event-driven Monte Carlo simulation, Watkins et al. [11] studied the effects of morphology on the internal quantum efficiency of organic solar cells. They compared bulk heterojunctions with ordered chessboard morphologies of PFB/F8BT devices and concluded that the chessboard configuration had a higher internal quantum efficiency. Marsh et
al. [12] studied the process of charge carrier separation and recombination for various morphologies. They demonstrated that the device performance is strongly influenced by the competition between initial carrier separation and recombination. Yang and Forrest [13] compared planar and bulk heterojunction systems for a CuPc/C$_{60}$ solar cell with an ITO anode and Ag cathode. The conclusion was a confirmation of Watkin’s previous work that a chessboard morphology provided the overall best device performance. Casalegno et al. [1] focused on the modeling. They devised a more efficient way of implementing the Ewald summation method and compared simulations with a cutoff Coulomb potential to simulations with Ewald summation.

The remainder of this thesis is organized as follows: the second chapter details the events and interactions modeled as well as their implementation in the simulation. Chapter three discusses the implementation of the BKL algorithm, chapter four presents results from the simulations and a discussion of the results, and chapter five contains a summary and conclusions.
CHAPTER II

EVENTS AND INTERACTIONS

2.1 Introduction

This chapter describes the events and interactions used to simulate light conversion into electricity in an organic photovoltaic cell. The interactions described comprise Coulombic interactions, hard core repulsion and the interaction with the external potential. Seven types of events are simulated; the first five are necessary to generate a current the remaining two result in the loss of charge carriers internal to the device. The events are illustrated in Figure 2.1.

For this work a three dimensional lattice model was used, the distance between lattice sites in all three dimensions is 1 nm [1]. A lattice site is considered “occupied” when a particle is present at that lattice site, and is “unoccupied” when a particle is not present. The lattice consists of a donor and an acceptor material, two different donor/acceptor geometries were used, one planar bilayer and one V-shaped. Cross sections of the geometries are shown in Figure 4.1, in both cases the active layers were between single layers representing electrodes. Excitons and holes are only allowed on donor material sites, and electrons are only allowed on acceptor material sites. The diffusion of charge carries and excitons occurs through the use of discrete
Figure 2.1: Illustrations of events in the simulated solar cell; the circles labeled ‘p’, ‘g’, ‘e’ and ‘h’ represent the photons, excitons, electrons and holes respectively. The top electrode is assumed to be ITO the bottom aluminum, between these is the hole conducting donor material and the electron conducting acceptor material. The diffusion of particles through a material is denoted by arrows (↗↘).
hopping between one lattice site and the next. Single occupancy has been taken into consideration; only one particle can occupy a given lattice site at a time. Cross hopping (electrons hopping from acceptor to donor sites or holes/excitons hopping from donor to acceptor) is not allowed, although it does rarely happen in real materials. This approximation is acceptable since the differences in the HOMO/LUMO levels between acceptor and donor sites are on the order of 1 eV which equates to a hopping rate of about $1 \times 10^{-17}$ ps$^{-1}$ at room temperature see equation (2.3) [1].

2.2 Exciton Generation

Figure 2.1(a) depicts the photoexcitation of a conducting polymer generating an exciton. We assume unoccupied sites of the donor material act as exciton creation sources each with the same probability to generate an exciton, $\omega_{exg} = 4.0 \times 10^{-12}$ ps$^{-1}$ nm$^{-3}$ [1]. The total exciton generation rate is given by

$$\omega_{Total}^{exg} = \omega_{exg} n,$$  \hspace{1cm} (2.1)

where $n$ is the difference between the total number of donor material sites and occupied donor sites:

$$n = n_{sites} - n_{occupied}.$$  \hspace{1cm} (2.2)
2.3 Exciton Diffusion

Excitons diffuse by hopping to nearest neighbor sites \([10]\) as illustrated in Figure 2.1(b). If an exciton attempts to hop to a site already occupied or to an acceptor site the move is rejected. The exciton hop rate is set to \(\omega_{\text{exh}} = 0.2 \text{ ps}^{-1} [1]\).

2.4 Exciton Dissociation

If an exciton meets a donor/acceptor interface it may dissociate into an electron/hole pair with a rate of \(\omega_{\text{exs}}\), as illustrated in Figure 2.1(c). This is simulated by placing an electron and hole at neighboring acceptor and donor sites, respectively. The estimated time for exciton dissociation is 45 fs \([1]\) which leads to an exciton dissociation rate of

\[
\frac{1}{45 \text{ fs}} = 20 \text{ ps}^{-1}.
\]

2.5 Charge Carrier Diffusion

After exciton dissociation, charge carriers diffuse through their respective materials, via nearest neighbor hopping. \(\Delta E_{ij}\) is the sum of the energies associated with Coulombic interactions, hard core repulsion and potential interactions. The hopping rate for charge carriers is given by:

\[
\omega_{\text{hop}} = \omega_{\text{elh/hoh}} \exp\left(-\frac{2\gamma r_{ij}}{\Delta E_{ij}}\right)
\]

\[
\times \begin{cases} 
1 & \text{for } \Delta E_{ij} \leq 0, \\
\exp\left(-\frac{\Delta E_{ij}}{k_B T}\right) & \text{for } \Delta E_{ij} > 0,
\end{cases}
\]

where \(\Delta E_{ij} = \Delta E_{\text{Potential}} + \Delta E_{\text{HardCore}} + \Delta E_{\text{Coulomb}}\). Further discussions of contributions to \(\Delta E_{ij}\) can be found in sections 2.9 - 2.11. The exponential term depends on
a localization constant \( \gamma = 2.0 \, \text{nm}^{-1} \) [1]. The electron hopping rate is \( \omega_{elh} = 1.683 \, \text{ps}^{-1} \), the hole hopping rate is \( \omega_{ho} = 2.523 \times 10^{-1} \, \text{ps}^{-1} \) [1, 11].

Due to the potential gradient caused by the difference in the work functions of the electrodes the charge carriers diffuse towards their respective electrode as seen in Figure 2.1(d).

2.6 Charge Carrier Collection

Charges are collected by their respective electrodes as illustrated in Figure 2.1(e). The charge collection rate for both holes and electrons was taken to be \( \omega_{elc(hoc)} = 0.01 \, \text{ps}^{-1} \). This value is an estimate by Casalegno et al. [1] who reported that no adequate experimental data were found in the literature and chose a value that yields reasonable estimates for device performance.

2.7 Exciton Decay

An exciton lifetime of 500 ps is assumed yielding an exciton decay rate of \( \omega_{exd} = 2.0 \times 10^{-3} \, \text{ps}^{-1} \) [1]. Since all excitons have the same average decay rate the total exciton decay rate can be calculated as:

\[
\omega_{exd}^{Total} = n_{excitons} \omega_{exd}
\] (2.4)

In the simulation, the total decay rate is calculated using equation (2.4), and the decaying exciton is chosen from all currently in the device. The event, see Figure 2.1(f), is executed by deleting the particle and clearing its position on the lattice.
2.8 Charge Carrier Recombination

When charge carriers occupy adjacent sites they have the ability to recombine into a non-particle state with a rate of $\omega_{ehr} = 5 \times 10^{-7} \text{ ps}^{-1}$ [1, 12], illustrated in Figure 2.1(g). This value of $\omega_{ehr}$ has been used in simulations of bilayer devices in Refs [12] and [1]. Table 2.1 contains all event rates used in our simulations.

Table 2.1: Modeled events and associated rates

<table>
<thead>
<tr>
<th>Event</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exciton Generation ($\omega_{exg}$)</td>
<td>$4.0 \times 10^{-12}$</td>
<td>ps$^{-1}$nm$^{-3}$</td>
</tr>
<tr>
<td>Exciton Diffusion ($\omega_{exh}$)</td>
<td>$2.0 \times 10^{-1}$</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Exciton Dissociation ($\omega_{exs}$)</td>
<td>20.0</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Electron Diffusion ($\omega_{eth}$)</td>
<td>1.682</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Hole Diffusion ($\omega_{hoh}$)</td>
<td>$2.523 \times 10^{-1}$</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Electron Collection ($\omega_{elc}$)</td>
<td>$1.0 \times 10^{-1}$</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Hole Collection ($\omega_{hoc}$)</td>
<td>$1.0 \times 10^{-1}$</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Exciton Decay ($\omega_{exd}$)</td>
<td>$2.0 \times 10^{-3}$</td>
<td>ps$^{-1}$</td>
</tr>
<tr>
<td>Recombination ($\omega_{ehr}$)</td>
<td>$5.0 \times 10^{-1}$</td>
<td>ps$^{-1}$</td>
</tr>
</tbody>
</table>
2.9 Potential Interactions

The difference of the electrode work functions (\(\phi_{ITO} = 4.3 \text{ eV}\) and \(\phi_{Al} = 4.3 \text{ eV}\)) produces a potential that is assumed to be a linear function of \(Z\). If an external field \((V_{ext})\) is applied then the energy difference of hopping from site \(i\) to site \(j\) is given by [1]:

\[
\Delta E_{ij}^{\text{Potential}} = \pm \frac{m_j^z - m_i^z}{M_z + 1} (eV_{ext} - \Delta \phi),
\]

where \(m_j^z\) and \(m_i^z\) are the \(Z\) positions of sites \(j\) and \(i\) respectively, \(M_z\) is the maximum \(Z\) value, and \(e\) is the elementary charge.

The positive and negative sign denote the contributions for holes and electrons, respectively. Under short circuit conditions \((V_{ext} = 0)\) the difference in the electrode work function produces a field driving the electrons downward and the holes upward. To determine device performance absent of the field \(eV_{ext}\) is set to \(\Delta \phi\) [1].

2.10 Hard Core Repulsion

Single occupancy is imposed for all particle types by setting \(\Delta E_{ij}^{\text{HardCore}}\) to infinity for the cases where one particle tries to occupy the space of another. This energy contribution is not taken into account for the case of charge carrier recombination. Figure 2.2 illustrates an example of hard core repulsion:
2.11 Coulomb Interaction

The final contribution ($\Delta E_{\text{Coulomb}}^{ij}$) is from the electrostatic interactions of the particles. We will model the device as a system of point charges in a dielectric layer sandwiched between two infinitely conducting electrodes. The point charges lead to an induced charge density on the electrodes. To calculate the electrostatic potential of the system, a charge image system is employed, where the real charges have image charges of opposite sign symmetrically arranged about the electrode [14]. The image charges then create secondary image charges and so forth, as illustrated in Figure 2.3.
Figure 2.3: An illustration of a charge image system, a charge is placed between two conductors which then creates image charges setting up a system of one physical cell and image cells at periodic intervals, modified from Ref. [1].

The interaction energy contribution for charge $q$ to hop from site $i$ to site $j$ can be calculated according to Coulomb’s law as:

$$\Delta E_{ij}^C = \frac{1}{2} q (V_j - V_i),$$

where the potential $V_i$ for a periodic system with $N$ real and $N$ image charges is given by:

$$V_i \equiv V(\vec{r}_i) = \frac{1}{4\pi\epsilon_r\epsilon_0} \left[ \sum_{\vec{n}} \sum_{j=1}^{2N} \frac{q_j}{|\vec{r}_{ij} + \vec{n}|} \right],$$

where $\vec{r}_i = (x_i, y_i, z_i)$, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ and $\vec{n} = (n_x X, n_y Y, n_z Z)$ with $n_{x,y,z} = 0, \pm 1, \pm 2, \cdots$, $X, Y,$ and $Z$ the dimensions of the physical cell, and $\epsilon_r$ is the permittivity of the dielectric material.
Equation (2.7) is computationally intensive with the processing time scaling as $4N^2$ [1]. There are two different approaches to make the implementation more efficient. The first is an approximation that involves setting a cutoff distance that limits the interactions of charge $i$ with the rest of the charges in the system to a subset of those charges within a sphere of radius $r_{\text{cutoff}}$. This distance is generally defined as twice the Debye length [1], or equal to the thermal capture radius which is on the order of 10-16 nm [1, 11, 13]. The second approach uses Ewald summation and provides in principle an exact treatment of the electrostatic interactions. The general idea behind this method is to apply a Fourier transform to equation (2.7), thereby converting the slowly converging summation into two fast converging sums and a constant term given by:

$$V_{\text{Total}} = V_{\text{direct}} + V_{\text{reciprocal}} + V_{\text{self}}$$

$$V_i = \frac{1}{4\pi \varepsilon_r \varepsilon_0} \left( \sum_n \sum_{j=1}^{2N} q_j \frac{\text{erfc}(\alpha |\vec{r}_{ij} + \vec{n}|)}{|\vec{r}_{ij} + \vec{n}|} \right) + \frac{4\pi}{V} \sum_{k \neq 0} \sum_{j=1}^{2N} q_j \frac{|\vec{k}|^2}{2\alpha^2} \exp\left(\frac{|\vec{k}|^2}{4\alpha^2}\right) \cos(\vec{k}\vec{r}_{ij}) - q_i \frac{2\alpha}{\sqrt{\pi}}$$

(2.9)

where $\alpha$ is the so-called Ewald parameter, $\vec{k}$ is the reciprocal-space vector given by $\vec{k} = (2k_x\pi/X, 2k_y\pi/Y, 2k_z\pi/Z)$, where $k_{x,y,z} = 0, \pm 1, \pm 2, \cdots$, $V$ is the volume of the charge/image cell in this case $V = XY2Z$ and $\text{erfc}$ is the complementary error function. Although the Ewald summation is computationally more efficient than a direct summation it is still very demanding since equation (2.9) must be evaluated for sites $i$ and $j$ for each attempted hop, the total evaluation time of this sum will be on
the order of $N(N_{\text{hop}} + 1)$ \cite{1}. To achieve greater computational efficiency Casalegno et al. \cite{1} noted that the sum given in equation (2.7) may be rearranged into a sum of pairwise terms:

$$V(\vec{r}_i) = \sum_{j=1}^{2N} q_j \left[ \frac{1}{4\pi \epsilon_r \epsilon_0} \sum'_{\vec{n}} \frac{1}{|\vec{r}_{ij} + \vec{n}|} \right].$$  \hspace{1cm} (2.10)

Since the inner sum’s numerical value depends on the difference between particle positions, we introduce the pairwise function

$$V^{\text{pair}}(\vec{r}_i) = \left[ \frac{1}{4\pi \epsilon_r \epsilon_0} \sum'_{\vec{n}} \frac{1}{|\vec{r}_{ij} + \vec{n}|} \right].$$  \hspace{1cm} (2.11)

With the aid of Equation (2.11), Equation (2.10) takes the form:

$$V(\vec{r}_i) = \sum_{j=1}^{2N} q_j V^{\text{pair}}(\vec{r}_i),$$  \hspace{1cm} (2.12)

As the numerical value of equation (2.11) depends only on the lattice and not its occupation and it may be computed once prior to initializing the simulation. A Fourier transform is applied to equation (2.11) for a computationally more efficient summation yielding:

$$V^{\text{pair}}(\vec{r}_i) = \frac{1}{4\pi \epsilon_r \epsilon_0} \left[ \sum_{\vec{n}} \text{erfc}(\alpha |\vec{r}_{ij} + \vec{n}|) \right] + \frac{4\pi}{V} \sum_{k \neq 0} \frac{1}{|k|^2} \exp\left(\frac{|k|^2}{4\alpha^2}\right) \cos(k \cdot \vec{r}_{ij}).$$  \hspace{1cm} (2.13)

$V^{\text{pair}}(\vec{r}_i)$ given by equation (2.13) is substituted into equation (2.12). Table 2.2, on the next page, contains the values associated with calculating the electrostatic interactions.
Table 2.2: Electrostatic and material parameters from Ref.[1]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_r$</td>
<td>3.5</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.03</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>2.0nm$^{-1}$</td>
</tr>
<tr>
<td>Real cells</td>
<td>2</td>
</tr>
<tr>
<td>Periodic cells</td>
<td>5</td>
</tr>
</tbody>
</table>
3.1 Software and hardware

To perform simulations with the BKL algorithm we wrote C programs for the simulations and Matlab (7.7.0 R2008B) scripts for system setup and some of the evaluations. The C-code was developed with the gnu C-compiler under the Cygwin bash shell. Production simulations were performed on a cluster of Intel Pentium (3.0 GHz) processors and typically took between fourteen and 28 days to complete. The C-code for the simulation consists of five header files, Material_Lattice.h, Ewald_Lattice.h, Rnox.h, Start_Data.h and Event_header.h, and eight program files Event_Driven.c (main program), Config_Lattice.c, Coulomb_Energy.c, Material_Energy.c, Move.c, Potential_Energy.c, Record.c and Total_Energy.c. A “make” file, Event_Driven.make contains the compilation and link instructions. Figure 3.1 illustrates the initialization, simulation loop and recording.
Figure 3.1: Schematic drawing of the simulation and the step wise process that makes up the initialization, event execution, determination, and recording loop.
3.2 Initialization

The first step in initializing a simulation involves two separate scripts in MatLab. The first “Material.m” generates the material lattice (Material_Lattice.h) file containing the numerical values corresponding to the acceptor and donor material for a lattice of size $X \times Y \times Z$. In this file the boundaries of the donor and acceptor materials are set determining the geometry of the solar cell. This script also plots the material lattice in three dimensions and provides lattice statistics such as the number of donor/acceptor sites for a given configuration. The second script is called “Ewald.m” which calculates the values for a lattice of size $X \times Y \times 2Z$ corresponding to the real- and reciprocal-space contributions of $V_{\text{pair}}(m^{x}_{ij}, m^{y}_{i}, m^{z}_{ij})$ defined in equation (2.13). The script generates the file Ewald_Lattice.h.

The file “Event_Header.h” defines variables for the lattice size (SIZEX, SIZEY, SIZEZ) and number of simulation steps (TST). The file also contains the system dependent parameters given in Table 2.1. Note that the exciton generation rate is calculated from $\omega_{\text{exg}} = 4.0 \times 10^{-12} \text{[ps}^{-1} \text{nm}^{-3}] \times N_{\text{Donor Sites}}$. The number of times the output files are written during the course of the simulation is set by the variable “EVAL”, and the external potential is set by the “Vext” variable. To start a simulation from a previous set of conditions the variable “START” must be set to one, the variable “LINES” must equal the number of lines in the input file Start_Data.h, which is generated by copying and pasting the starting conditions from the file Configuration_Data.txt to a file saved as Start_Data.h.
3.3 Simulation Loop

The simulation loop in Figure 3.1 is composed of four primary parts, choosing an event, executing the event, recording the configuration and determining the new set of events.

3.3.1 Choose an Event

To choose an event the function “Move” in the file Move.c is called. This function depends on the current occupation of the charge/image lattice, the fixed Ewald lattice, and the fixed event rates. Within the Move function, a data structure is built containing the initial and final positions for all possible events of all particles along with the associated rates. These rates are then normalized, and an event time line (see Figure 1.4) is constructed. A random number $R \in (0, 1)$ is generated and compared to the event time line, this selects the next event to be executed on the lattice.

The update time is calculated according to,

$$T_{update} = -\frac{\ln R}{\omega_{Total}}$$

(3.1)

where $\omega_{Total}$ is the sum of all event rates as given by Equation (1.2). This value along with the event type represented by a unique integer and initial and final particle positions are the output of the Move function; they are passed in the one by eight variable “moveVector” to the main program.
3.3.2 Event Execution and Time Update

The output variable moveVector is evaluated in the main program (file Event_Driven.c) to identify the type of move (element 7 of the array) and the initial and final coordinates (elements 0 to 5) of the particle[s] involved in the event. For example, for the event electron/hole recombination, the elements 0 to 2 of moveVector correspond to the $X,Y$ and $Z$ positions of the electron, and the elements 3 - 5 represent the position of the hole. The event is then executed on the lattice. For instance, in the case of a particle move, the original lattice site is set to zero and the new lattice site is set to the unique integer of the particle (-1 for electrons, 1 for holes, and 2 for excitons). After the event is executed on the lattice the update time in the eighth element of moveVector is added to the current simulation time.

3.3.3 Record Configuration and Check Time

After the simulation time has been updated, it is compared with the target simulation time. If the simulation time is greater than or equal to the target time, the simulation is stopped and the final lattice configuration is recorded. If the simulation time is less than the target time, and if the current number of simulation steps is a multiple of the recording interval set by the variable EVAL, the function “Record” (file Record.c) is called. Record writes to file the current lattice configuration along with the update time and event type.
3.3.4 Determine New Events

To determine all possible events of the new configuration, the function Move sweeps through all lattice points, determines what (if any) particle exists on the lattice point and what events can be associated with that particle. The energy difference of the current configuration and a possible new configuration is calculated using the “Total_Energy” function in file Total_Energy.c. The Total_Energy function determines the energy contribution for each interaction, as described in Chapter 2, and then applies Equation (2.3) to the event rate for hopping events. The information regarding the event type, event rate, final and initial positions for all events is stored in a structure which is accessed by the function Move when an event is chosen, as described in 3.3.1.

3.4 Output Files

Each simulation generates three output files; the first, “seeds.txt”, contains the seed value for the random number generator so that a particular simulation can be executed again if needed. The second file “Current_Configuration.txt” is periodically updated, with the periodicity set by the variable EVAL, and contains the X, Y and Z coordinates of each particle, the particle type, the simulation step number, and the simulation time. The file “Configuration_Data.txt” is updated for every simulation step and contains the simulation step, simulation time, time interval between steps,
the number of each particle type, total number of particles and the last event that
took place. Tables 3.1 and 3.2 contain the output format of the variables in each file.

Table 3.1: Recorded quantities and their output formats for the Current_Configuration.txt file. Step is the step number, time is the simulation time in seconds, $\Delta T$ is the time interval between steps, $N_e$, $N_H$, $N_X$, $N_P$ are the number of electrons, holes, excitons and total particles respectively and $E_n$ is event number.

<table>
<thead>
<tr>
<th>Step</th>
<th>Time[s]</th>
<th>$\Delta T$</th>
<th>$N_e$</th>
<th>$N_H$</th>
<th>$N_X$</th>
<th>$N_P$</th>
<th>$E_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%12d</td>
<td>%12.10e</td>
<td>%12.10e</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
</tr>
</tbody>
</table>

Table 3.2: Recorded quantities and their output formats for the Configuration_Data.txt file. Step is the step number, time is the simulation time in seconds, $P_X$, $P_Y$, and $P_Z$ are the X, Y, and Z positions of the particle, $T_P$ and $T_M$ are the particle type and the material type.

<table>
<thead>
<tr>
<th>Step</th>
<th>Sim Time[s]</th>
<th>$P_X$</th>
<th>$P_Y$</th>
<th>$P_Z$</th>
<th>$T_P$</th>
<th>$T_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%12d</td>
<td>%12.10e</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
<td>%12d</td>
</tr>
</tbody>
</table>
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Simulated systems

Two different bilayer geometries with the same total size (20 × 20 × 10 lattice sites corresponding to 20 × 20 × 10 nm$^3$) were investigated by simulation. One configuration is a planar bilayer with donor and acceptor layer thicknesses of 5 nm. The second configuration is a modified bilayer that appears to be V-shaped. At the thickest point, the donor material is 9 nm thick and at the thinnest point only 1 nm thick. The simulated geometries are shown in Figure 4.1.

![Two-dimensional illustrations of the bilayer geometries used in this work. The shaded region represents the donor material while the white region represents the acceptor material.](image)

Figure 4.1: Two-dimensional illustrations of the bilayer geometries used in this work. The shaded region represents the donor material while the white region represents the acceptor material.
Reaching a steady state is important for an accurate evaluation of the performance of the device. In this work we determine if the system has reached steady state from a graph of the number of particles in the system as a function of time. As the system evolves from a completely unoccupied lattice to one where particles are entering and leaving the system at equal rates, it is expected that the number of each particle type will initially increase and later stabilize. When the particle numbers fluctuate about a constant mean value the system has reached a steady state. Figure 4.2 shows the evolution of an example system; notice that the number of holes increases until stabilizing about a mean; this is interpreted as steady state.

![Figure 4.2: The number of charged particles as a function of time for a 20 × 20 × 10 V-layer system with \( V_{\text{ext}} = 0 \) eV in a simulation of 704,000 steps. Each symbol represents an average over 10,000 simulation steps. The vertical dashed line indicates the time after which simulation data are evaluated.]
We performed eight simulations in total, one half of these were started from an empty lattice and executed for two weeks to ensure a steady state was achieved. The other half started from a steady state configuration (the final configuration of the previous set) and ran for a day. For each of the two geometries, planar bilayer and V-layer, we performed simulations under short circuit conditions \((V_{\text{ext}} = 0)\) and with an applied voltage equal to the work function difference \((V_{\text{ext}} = 0.4 \text{ eV})\). Tables 4.1 and 4.2 summarize the simulation parameters; steady state simulation results are presented in Tables 4.3 and 4.4.

Table 4.1: Simulation parameters for the planar bilayer and V-layer systems starting from an empty lattice. The simulation reference number (Sim No.), the lattice type (lattice), the applied external potential \((V_{\text{ext}})\), number of simulation steps (steps) and total simulation time (time) in milliseconds are given below.

<table>
<thead>
<tr>
<th>Sim No.</th>
<th>Lattice</th>
<th>(V_{\text{ext}}) [eV]</th>
<th>Steps</th>
<th>Time [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bilayer</td>
<td>0</td>
<td>(1 \times 10^6)</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>Biayer</td>
<td>0.4</td>
<td>(1 \times 10^6)</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>V-Layer</td>
<td>0</td>
<td>(7 \times 10^5)</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>V-Layer</td>
<td>0.4</td>
<td>(7 \times 10^5)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 4.2: Simulation parameters for the planar bilayer and V-layer systems starting from steady state conditions. The simulation reference number (Sim No.), the lattice type (lattice), the applied external potential ($V_{ext}$), number of simulation steps (steps) and total simulation time (time) in milliseconds are given below.

<table>
<thead>
<tr>
<th>Sim No.</th>
<th>Lattice</th>
<th>$V_{ext}$ [eV]</th>
<th>Steps</th>
<th>Time [ms]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bilayer</td>
<td>0</td>
<td>$1.2 \times 10^5$</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>Biayer</td>
<td>0.4</td>
<td>$1 \times 10^5$</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>V-Layer</td>
<td>0</td>
<td>$7 \times 10^4$</td>
<td>0.06</td>
</tr>
<tr>
<td>4</td>
<td>V-Layer</td>
<td>0.4</td>
<td>$6.6 \times 10^4$</td>
<td>0.04</td>
</tr>
</tbody>
</table>

4.2 Current Density and Internal Quantum Efficiency

Figure 4.2 shows the current density as a function of time calculated according to Equation (1.5) for the four simulations of Table 4.1. A comparison of the results for short circuit conditions, Figure 4.2 (a) and (b), with the results for an external potential that cancels the work function difference, Figure 4.2 (c) and (d), shows an increase in current fluctuations when the external potential is applied.
Figure 4.3: Current density as a function of time for: (a) planar bilayer system with $V_{\text{ext}} = 0$ eV, (b) V-layer with $V_{\text{ext}} = 0$ eV (c) planar bilayer system with $V_{\text{ext}} = 0.4$ eV, (d) V-layer with $V_{\text{ext}} = 0.4$ eV. Simulations were performed for $1 \times 10^6$ and $7 \times 10^5$ steps for the planar and V-layer systems, respectively. The system size was $20 \times 20 \times 10$ in each case.

Equation (2.5) for the energy due to the potential difference across the active layers shows that, as the external potential increases toward $\Delta \phi$, the energy from the interaction with the potential decreases to zero. In this case, only the interactions with the image charges across the electrodes bias the random walk of the charge carriers towards their respective electrodes. The reduction in driving force due to the absence of a potential difference is the probable reason for the observed increase in current fluctuations.
After the steady state has been reached the internal quantum efficiency and current density are calculated using Equations (1.6) and (1.5), respectively. Two simulations were evaluated for comparison, the first started from an empty lattice and evolved to a steady state the second system started from a steady state configuration, as described in section 4.1 and Tables 4.1 and 4.2.

Table 4.3: Current density (CD) and internal quantum efficiencies (IQE) for the planar bilayer and V-layer for systems starting from an empty lattice with two different external potentials $V_{ext}$, see Table 4.1 for parameters.

<table>
<thead>
<tr>
<th>$V_{ext}$ [eV]</th>
<th>Bilayer-IQE [%]</th>
<th>V-layer-IQE [%]</th>
<th>Bilayer-CD [mA/cm²]</th>
<th>V-layer-CD [mA/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35.1 ± 3.6</td>
<td>40.9 ± 3.2</td>
<td>0.45 ± 0.06</td>
<td>0.51 ± 0.06</td>
</tr>
<tr>
<td>0.40</td>
<td>36.2 ± 3.5</td>
<td>40.9 ± 2.7</td>
<td>0.46 ± 0.07</td>
<td>0.52 ± 0.08</td>
</tr>
</tbody>
</table>

Table 4.4: Current density (CD) and internal quantum efficiencies (IQE) for the planar bilayer and V-layer for systems starting from the steady state with two different external potentials $V_{ext}$, see Table 4.2 for parameters.

<table>
<thead>
<tr>
<th>$V_{ext}$ [eV]</th>
<th>Bilayer-IQE [%]</th>
<th>V-layer-IQE [%]</th>
<th>Bilayer-CD [mA/cm²]</th>
<th>V-layer-CD [mA/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38.2 ± 1.3</td>
<td>40.3 ± 2.6</td>
<td>0.47 ± 0.02</td>
<td>0.51 ± 0.05</td>
</tr>
<tr>
<td>0.40</td>
<td>36.2 ± 1.7</td>
<td>44.1 ± 6.6</td>
<td>0.48 ± 0.07</td>
<td>0.52 ± 0.08</td>
</tr>
</tbody>
</table>
The values presented in Table 4.3 represent averages over the last $10^5$ steps of the simulation. To estimate the uncertainties, the data are divided into ten blocks of $10^4$ steps each and the standard deviation of the block averages is calculated. The values presented in Table 4.4 represent block averages and standard deviations of all the data generated in the simulations from steady state configuration.

Casalegno et al. [1] simulated a planar bilayer device of the same material but of a larger size ($100 \times 100 \times 50 \text{ nm}^3$) and with longer simulation times (0.5 s). Their values for the internal quantum efficiency are $36.29 \pm 5 \times 10^{-2} \%$ for $V_{\text{ext}} = 0$ and $28.12 \pm 5 \times 10^{-2} \%$ for $V_{\text{ext}} = \Delta \phi$, while they find current densities of $-2.329 \pm 4 \times 10^{-3} \text{ mA/cm}^2$ for $V_{\text{ext}} = 0$ and $-1.802 \pm 3 \times 10^{-3} \text{ mA/cm}^2$ for $V_{\text{ext}} = \Delta \phi$.

For the planar bilayer our results for the internal quantum efficiency agree with Casalelegno et al. for short-circuit conditions ($V_{\text{ext}} = 0$) but not for $V_{\text{ext}} = \Delta \phi$. None of our calculated average values show any significant effect due to the applied external potential. This may be due to the small system size and the resulting small distance between the electrodes and any part of the active layers. Simulations of larger systems are in progress but will take several more weeks to complete.

Our results for the current density in the planar bilayer device is about a factor five smaller than that of Casalegno et al.. This is expected since the height of our device is also about a factor five smaller.

A comparison of the results for the planar bilayer and the V-layer device suggests a somewhat higher internal quantum efficiency and current density for the V-layer devices. While uncertainties are too large to draw firm conclusions, these
differences are not unexpected. The interface area is approximately 400 nm$^2$ for the bilayer and 720 nm$^2$ for the V-layer. Considering that charge carrier separation takes place only at the interface one might expect that the V-layer should have nearly twice the current density and internal quantum efficiency. However, the number of charge carrier recombination events is a function of the number of electrons and holes within nearest neighbor proximity to each other. As the interface area increases, the number of sites where electrons and holes are within nearest neighbor distance also increases. Furthermore, since the recombination rate is twice that of the hole diffusion rate the separation of charge carriers is in competition with the recombination of charge carriers immediately after the dissociation of an exciton. Thus the increase in interface area in the V-layer system does not lead to a marked increase in device performance.
4.3 Local Charge Carrier Density

Figures 4.4 and 4.5 show the average charge carrier density as a function of position $Z$ perpendicular to the electrodes for the planar bilayer system and V-layer system, respectively.

![Diagram showing charge carrier density](image)

Figure 4.4: Charge carrier density for a planar bilayer (a) when $V_{\text{ext}} = 0$ and (b) $V_{\text{ext}} = 0.40$ eV. ○ and • represent the average number of electrons and holes at position $Z$ perpendicular to the electrodes, respectively.
Figure 4.5: Charge carrier density for a V-layer (a) when $V_{ext} = 0$ and (b) $V_{ext} = 0.40$ eV, ○ and • represent the average number of electrons and holes at position $Z$ perpendicular to the electrodes, respectively.
In Figures 4.4 and 4.5 the electrodes are located at $Z = -1$ and $Z = 10$. Since the simulation only records the locations of charge carriers in the donor/acceptor material and not in the electrodes the density is zero at $Z = -1$ and $Z = 10$. For the planar bilayer in Figure 4.4 the donor/acceptor interface, located between $Z = 4$ and $Z = 5$ is a region of higher charge density. The donor material in the V-layer extends from $Z = 1$ to $Z = 9$ and the acceptor material extends from $Z = 0$ to $Z = 8$ (see Figure 4.1(b)). The carrier density in the V-layers is on average greater than the carrier density in the planar bilayer, which is due to the increased area of the donor/acceptor interface. The increase in carrier density with increased interface area is in agreement with the work of Casalegno et al. [1], who reported carrier densities of $0.24 \times 10^{21}$ for a planar bilayer versus $0.74 \times 10^{21}$ for a chessboard configuration. In the V-layer configuration, there are significantly more holes than electrons; this is caused primarily by the electrons’ diffusion coefficient being an order of magnitude greater than that of the holes.
CHAPTER V
SUMMARY AND CONCLUSION

In this work we performed Monte Carlo simulations for bilayer organic photovoltaic devices. Since processes within such devices take place on vastly different time scales, we used an event-driven Monte Carlo algorithm to simulate a coarse grained lattice model of the active layer of organic solar cells. We simulated the creation, diffusion, dissociation, and decay of excitons and the diffusion, recombination and transfer to the electrodes of the charge carriers. All particles were subject to excluded volume interactions; interactions between charged particles were evaluated with an Ewald summation technique. Simulations starting from an empty lattice allowed us to observe how the systems approach the steady state. Data for device performance calculations were taken only for the final part of these simulations and confirmed by simulations starting from steady state configurations. We investigated bilayers of two geometries, one with a planar and one with a V-shaped donor/acceptor interface. Our result for the internal quantum efficiency and the current density of planar device are consistent with results reported by Casalegno et al. [1] for a larger device of the same material and geometry.

Our results for the V-layer device suggest a better performance for this geometry. Since the donor/acceptor interface for the V-layer device is larger than for the
planar device, our observations agree with literature results that show that, as the interface area increases, current density, charge carrier density and internal quantum efficiency of a device also increase.


