Inhomogeneous charge transport in organic photovoltaic devices

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Abstract

The current of charge carriers in organic photovoltaic devices were investigated using 1D and 2D computational models. It is shown here that analytic treatments of the current in photovoltaic devices based in electrostatics and the drift-diffusion equation make a faulty assumption that is not always valid. The charge density, potential, and current were simulated in 2D across two materials in contact: one n-type and one p-type. The results agree with the theoretical expectations.

I. Introduction

Photovoltaics devices (PVD) or in particular solar cells represent a clean-alternative to coal-produced electricity should they ever become cost effective. To become cost effective, photovoltaic devices must be able to produce electricity at a price comparable to that of coal-produced electricity. Presently, two avenues for improvement exist: make PVD's cheaper and easier to produce or make them more efficient. One of or a combination of these two efforts may allow PVDs to become a better source of electricity than coal and nuclear power. One promising device is the organic photovoltaic device (OPV).[1] An OPV differs from traditional PVDs in that it is made out of polymers rather than traditional semiconductors like silicon.[2] Although the polymers in OPVs produce electricity less efficiently, they reduce manufacturing cost to a

fraction of that of traditional PVDs.[3] Despite their cheap manufacturing cost, the efficiency of OPVs must be increased before they can compete with coal-produced electricity.

I investigated the physics behind an organic photovoltaic device and constructed a computer model to examine the physical properties of the device. By varying the structure of the device within my model, I hoped to possibly improve the efficiency of the device. The project did not reach this final stage in the ten week program; however, my computational models produced several interesting results and intriguing questions.

Physical properties of an OPV cell

The physics underlying polymer solar cells differs from traditional semiconductor solar cells in several ways. In traditional PVDs, absorbed light excites an electron from its atomic bound state, allowing it to move about the array. Since the array has two materials, one which accepts holes (p-type) and one which accepts electrons (n-type), an electric field between the two semiconductors forces the conduction electrons in one direction, creating a net current. The net current across the junction establishes a potential difference across the PVD and therefore makes the solar cell a generator of electricity.

OPVs do not function in the same way. According to Pichler, Friend, and Holmes[4], the photoconductivity of OPVs results from photogenerated excitons (electron-hole pairs), not from excited electrons. The electron and hole of the exciton can recombine at any time due to their mutual coulombic interaction. Traditional PVDs also produce excitons; however, the binding energy of the exciton is very small in semiconductors, so they ionize. Once the exciton has been generated by incoming light, it will diffuse throughout the material. Should the exciton reach the junction (the boundary between the two polymers) before recombination, the exciton will dissociate, allowing the hole to enter the p-type polymer and flow towards one electrode and

allowing the electron to enter the n-type polymer and flow towards the opposite electrode (See Fig. 1). The currents due to these two charged particles will provide a net current across the OPV and allow the OPV to generate electricity.

FIG. 1 Schematic depicting the resulting charge current after dissociation.

The goal of my computational modeling was to replicate as much of the experimental results as possible while incorporating as few physical principles as necessary. In the process of creating my model, I decided on five primary physical interactions. First, the conservation of charge must be upheld by using the continuity equation:

$$\nabla \cdot J = -\frac{d\rho}{dt}. \tag{1}$$

Secondly, the potential must satisfy Gauss's law:

$$\nabla^2 V = -\frac{\rho}{\epsilon}. \tag{2}$$

The current, j, must be calculated from the drift and from the diffusion of charge carriers. However, in my two dimensional simulations, I neglect the diffusion term due to empirical evidence and traditional analytical treatments (see next section for justification):

$$J \propto \rho E. \tag{3}$$

(Note ρ can be positive or negative for charge density). The resistance between the two materials must be accounted for in order to properly explain the current across the junction. Finally, the dissociation of excitons near the boundary creates a net current across the junction. To good approximation, the dissociation will occur continuously and be evenly dispersed along the junction due to the random nature of exciton generation and diffusion. Therefore, I can account for this behavior by adding a constant to the current across the junction.
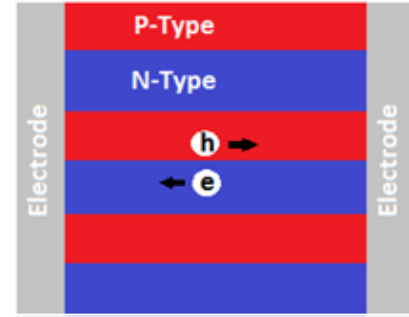
Computational model for a 1-D p-type material

Several 1D models were made to explore the role of diffusion in polymers, to ensure that my model follows Mott-Gurney's Law and to decide what boundary conditions were necessary to provide a complete and consistent solution. In particular, I will describe a 1D model which substantiates my claim that diffusion can not easily be neglected, and then I will describe a 1D model that served as the genesis for my 2D model.

One method examined the 1D case using a combination of the shooter method and the Runge-Kutta method in order to calculate the electric field and charge density across a p-type sample. The initial values of the model consisted of the electric field at both electrodes. By specifying the electric field and guessing its derivative at the left electrode (See Fig. 1), the shooter method uses the Runge-Kutta method to simultaneously solve the continuity equation and Eq. (7) to find the density of holes and the electric field throughout the material. The first attempt usually does not hit the correct electric field on the right, and therefore several guesses are necessary (See Fig. 2). By making wild guesses and then interpolating to find a best guess, the shooter method arrives at a quite accurate result.

A second method examined the 1D case using the finite element method (FEM) to determine the potential and the integrate-forward method to approximate the charge density. First I use a grid of points to represent the p-type sample (see Fig.3). The FEM relates the first and second derivates of a function at a single point to the functions neighboring values. A discrete version of Poisson's equation gives the finite element method as many equations as
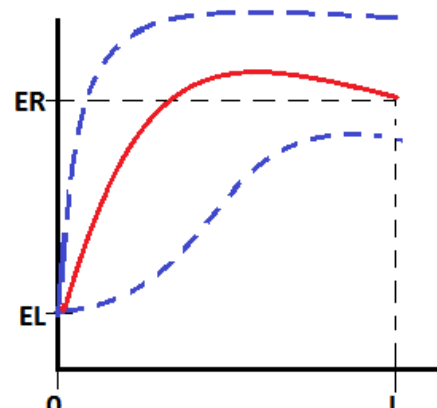

Fig. 2 Sketch showing the basics of the shooter method. The blue trajectories are guesses and the red trajectory is the best guess.

there are points. However, since the endpoints are the only points specified, the first iteration of the FEM returns a best guess. If I continually use these best guesses as the initial conditions of a next guess, the FEM returns more accurate results until eventually the correct solution will be known within some uncertainty (This process is known as the method of relaxation and works for equations such as Poisson's Equation). Meanwhile, between iterations of the FEM, the charge density is updated across the sample by manipulating a discretized version of the continuity equation. I used this discrete function to find the derivative of charge density with respect to x and then "integrated-forward" from the known density on the left. By alternating between these two methods, the steady state solution will be found as long as the initial values allow the method to converge.
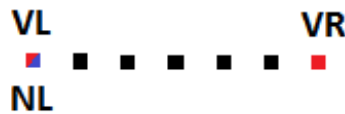
VL   **VR**
■ ■ ■ ■ ■ ■
NL

Fig. 3 A schematic showing the grid structure and the three initial values. The voltage is specified on the left and right as VL and VR respectively. The charge density is set as NL on the left.

Mott-Gurney law and the diffusion of charges

My 1D results challenge an approximation within the Mott-Gurney Law.[5] The Mott-Gurney Law states that the current across a slightly doped semiconductor with a potential difference, V, established across it by an ohmic contact will exhibit the following relations:

$$j \propto V^2 \ for \ small \ V \quad\quad\quad (4)$$

$$j \propto V \ for \ large \ V.$$

PVDs and OPVs exhibit this behavior experimentally and have been explained analytically by Mott and Gurney.

To understand why my model did not observe the Mott-Gurney law, the underlying approximations of the Mott and Gurney derivation must be examined. Free charges within a material will diffuse; however, following the derivation of the Mott-Gurney Law explicitly requires that the diffusion term be neglected due to its small size when compared to the drift term. Mott and Gurney's derivation is as follows:

The drift-diffusion equation in one dimension is:

$$j = \rho e \upsilon E - De\frac{\partial \rho}{\partial x}. \tag{5}$$

This is the standard equation for the current where ρ is the charge density, e is the charge of an electron or hole, υ is the mobility constant of the material, E is the electric field, and D is the diffusion coefficient. Using Gauss's Law, Eq. (6), to eliminate ρ from Eq. (5) and then integrating with respect to x, one arrives at Eq. (7):

$$\frac{\partial E}{\partial x} = 4\pi\rho e \tag{6}$$

$$4\pi j x + C = \frac{1}{2}\upsilon E^2 - D\frac{\partial E}{\partial x}. \tag{7}$$

By noting that D=kTυ/e and assuming dE/dx~E/L,

$$D\frac{\partial E}{\partial x} \ll \frac{1}{2}\upsilon E^2 \quad if \quad kT \ll eEL. \tag{8}$$

Since Eq. 8 holds for most cases, Mott and Gurney neglect diffusion term. The assumption that V~E/L, however, seems to be problematic.

Using the Runge-Kutta method and the shooter method in 1D, Fig. 4 and Fig. 5 resulted from solving Eq. (5) with the drift coefficient set to .01 and to 1.0 respectively. Both cases use a small voltage and thus in both cases, Mott and Gurney predict that the entire diffusion term should be negligible in comparison to the entire drift term. Fig. 4 and Fig. 5 do not show this

behavior. Instead, reducing the diffusion coefficient to almost zero does approximately give the results Mott and Gurney predict; however when the diffusion coefficient was set to 1.0, a linear electric field is produced and the drift term and diffusion term are of the same order. In fact, only in regions where the change in charge density is small does the diffusion term become negligible. Therefore I found that one can not easily account for the small nature of the diffusion term using electrostatics and the drift-diffusion equation alone. Knowing that the Mott-Gurney law can be derived by other methods besides the drift-diffusion equation, I decided to drop the diffusion term from my model for physically accurate results. Without the diffusion term, the current does vary as the Mott-Gurney law suggests as shown in Fig. 6.
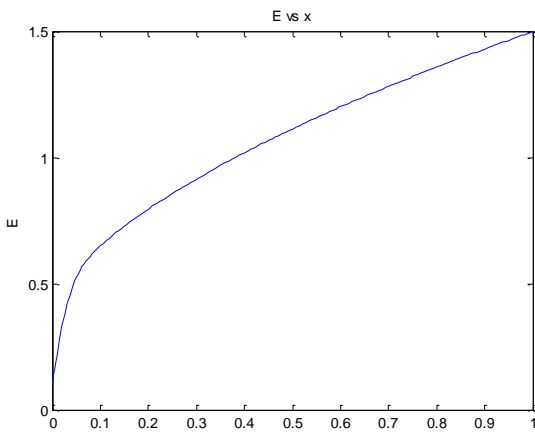

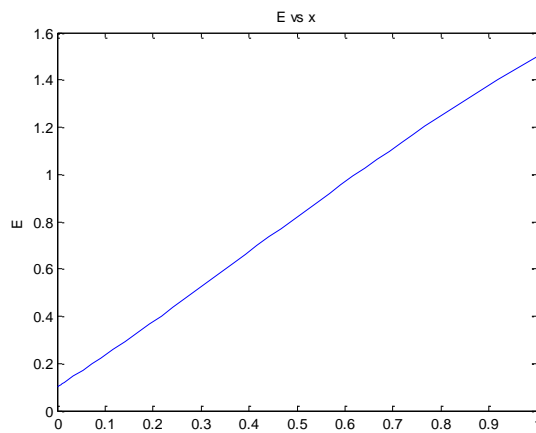**Fig. 4** Solving for the electric field using low drift coefficient.

Fig. 5 Solving for the electric field using high drift coefficient.
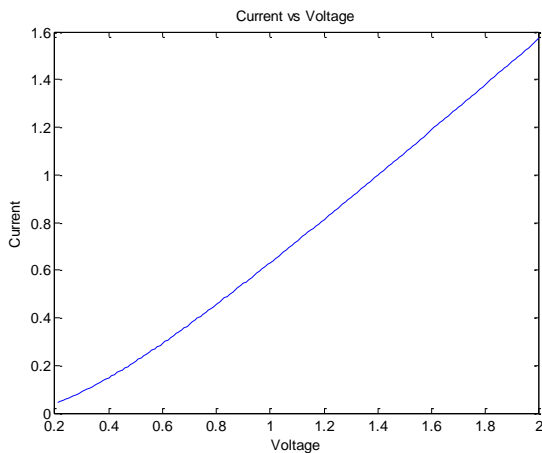

Fig. 6 IV curve created using 1D code. Due to instability, the solution from higher voltages was fed as an initial guess to the next lowest voltage.

Computational model for a 2-D array with two materials

By using the finite element and integrate-forward methods, I found the approximate potential and density throughout two materials in two dimensions. Similar to the 1D case, I established a grid of points to replicate the material in two dimensions (See Fig. 7). I then repeatedly used the finite element method in two dimensions to update the potential and used the "integrate-forward" method to calculate the density. Because of the second material, the initial values are slightly different: the charge density is specified on the left for the p-type material and on the right for the n-type material. The change in the initial value points does not stop the method from finding the steady state solution. By alternating between updating the two different materials, my method found a steady state solution, again provided that the initial values allowed the method to converge. To probe smaller potential differences across the device, ones that typically cause the code to diverge, I used the solution from a higher voltage as an initial guess.
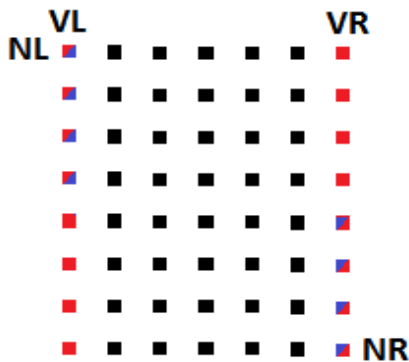

Fig.7 A sketch of the grid of points in 2D with the three types of initial value points. The P-type material is on top and the n-type material is on bottom in this diagram. The voltage is specified on the left as VL and on the right as VR. The charge density in the p-type material is specified on the left as NL. The charge density in the n-type material is specified on the right as NR.

Steady state solution for an OPV without light

The initial conditions for the three figures are summarized in Fig. 8. My two dimensional, two material results are shown in Figs. 9-11. From observing the three figures, I

saw several parallels between my computational result and accepted theory. The charge density has a build up of charge at the interface, and the charge densities for the p-type and n-type materials are symmetric, exactly as expected from accepted theory. In a 1D p-type material, the charge density progressed as $x^{-1/2}$ as Mott and Gurney suggest; in the 2D case, near the center of the p-type material it follows the same relation as it should. The potential has a negative curvature in the p-type region and a positive curvature in the n-type region as expected by Poisson's equation and the generated density map. Finally, there exists a small current flowing from n-type to p-type as I had expected. One can see that this should be the case by looking at the slope of the potential near the interface. The negative of the slope gives the direction of the electric field. By using Eq. (3), one can easily see that there should be current flowing over the junction.

Voltage Left	1.00
Voltage Right	0.00
Density p-type	1.00
Density n-type	-1.00

Fig.8 A Table that gives the initial values used in my computational model to find Fig. 8-10
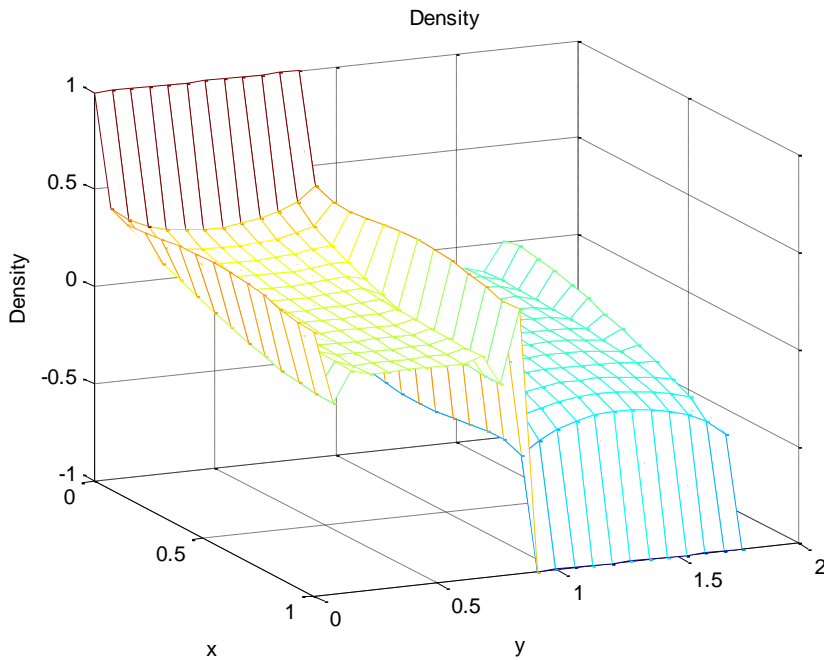

Fig.9 A charge density map. Note that positive values represent holes and negatives values represent electrons.
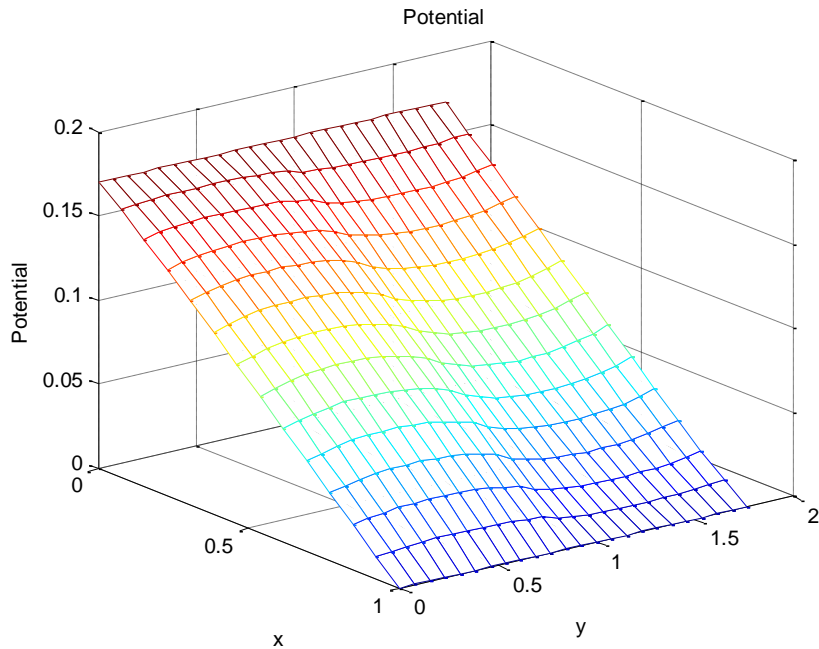
Fig.10 A Potential landscape. Both Fig. 8,9 are oriented with the p-type material on the left and the n-type material on the right.
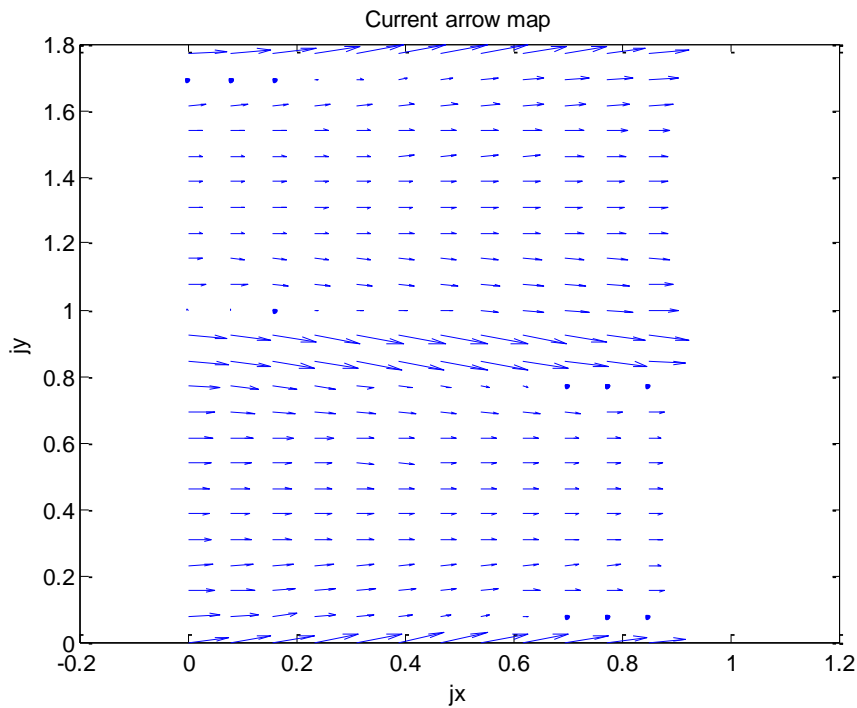

Fig.11 Current arrow map, oriented left to right with the n-type material on top and the p-type material on bottom.

Conclusion

My 1D and 2D models of an OPV device confirmed my theoretical expectations and provided insight into the physics behind OPV. From my 1D modeling, I learned that the Mott-

Gurney Law can not be accounted for using electrostatics and the drift-diffusion equation, and that more complicated phenomena, such as trapped states, must be used to adequately correlate the experimental findings to Mott-Gurney's result. Due to several experimental findings that PVDs follow the Mott-Gurney law to good approximation, I neglected the diffusion term to allow my simple model to achieve more accurate results. My 2D results corroborate my expectations as to how the potential, density, and current relate in 2D across two differing materials. The stability of my 2D method leads us to believe that more physical interactions could be accounted for within this model without causing the method to diverge away from a steady state solution.

Several questions remain to be answered. A follow up simulation might attempt to answer the following questions: When resistance is added to the junction, how will the potential, density, and currents maps be displaced? When the dissociation of excitons is accounted for, by how much will the current increase across the device? What geometry will offer the highest efficiency? Can my 2D model evolve directly into a 3D model?

Acknowledgments

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