Stochastic models of charge transport in disordered media

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***Abstract*—Charge transport in disordered materials, such as organic and amorphous inorganic semiconductors, is often modeled in a stochastic framework. The microstructure of the disordered material is interpreted as a realization of a stochastic model and, given a realization of this model, the charge transport process itself is treated as a random process. In this paper, we give an introduction to this combined stochastic modeling approach. We first describe the basic physics underlying charge transport in disordered materials. Then, we discuss stochastic models of the material and the charge transport process. In organic semiconductors, charge transport is modeled either by a continuous-time random walk in a random environment or an interacting particle system in a random environment. In amorphous inorganic semiconductors, charge transport is modeled by a continuous-time random walk in a deterministic environment. In the organic semiconductor case, the resulting stochastic models need to be solved using numerical methods. As such, we discuss Monte Carlo methods for estimating charge transport properties. In particular, we discuss a recently developed method, Aggregate Monte Carlo, which can be used to significantly speed up Monte Carlo simulations. Finally, we discuss the problem of modeling recombination in organic semiconductors.**

I. INTRODUCTION

The charge transport properties of organic semiconductors (and, to a lesser extent, amorphous inorganic semiconductors) are a major focus of research in condensed matter physics and materials science. These materials offer many advantages over conventional semiconductors. In particular, they are often cheap to produce, light-weight and can have attractive mechanical properties (for example, they may be very flexible). Applications of organic semiconductors include organic light-emitting diodes (OLEDs) and organic solar cells. A general introduction to the field is given in [1].

Stochastic modeling plays a key role in studying charge transport in these semiconductor materials. There are two reasons for this. Firstly, organic and amorphous inorganic semiconductors are disordered materials. Such materials can be interpreted as realizations of stochastic models. For example, a given spatial configuration of molecules could be thought of as a realization of a spatial point process and the corresponding molecular energies could be regarded as a realization of a Markov random field (whose neighborhood structure is induced by the spatial locations of the molecules). The second reason is that the modeling of the charge transport process is usually at a molecular level, where the motion of single and interacting charge carriers is best described by random processes.

This paper aims to give a brief introduction to the physics of charge transport in disordered semiconductors, to explain the links between the physics and various stochastic models, and to describe some recent achievements in stochastic modeling of charge transport. A particular focus is placed on efficient Monte Carlo methods for estimating charge transport properties.

II. CHARGE TRANSPORT IN DISORDERED SEMICONDUCTORS

A. *Types of Semiconductors*

Conventional inorganic semiconductors are made from crystalline solids such as silicon. These materials have highly ordered structures, with the molecules arranged into lattices. However, there are some defects in the structure caused, for example, by the vibration of the constituent molecules; see [2] for more details. Amorphous inorganic semiconductors do not have the crystalline structure of conventional inorganic semiconductors and are, thus, disordered materials.

Organic semiconductors are made from materials that primarily consist of hydrogen and carbon atoms. In contrast to conventional semiconductors, these materials can have highly disordered structures. This is often due to the way in which the materials are fabricated; see [3]. The disorder manifests itself in two different forms: *energetic disorder* and *spatial disorder* (often called *diagonal disorder* and *off-diagonal disorder* in the physics literature). Energetic disorder refers to the disorder in the energies of the molecules (or polymer segments) which form the material. Spatial disorder refers to the disorder in the locations of these molecules (or polymer segments).

B. *Charge Transport Basics*

In solids, electrons are confined to certain bands of energy. Electrons in the *conduction band* are able to move through the material. Electrons in the *valence band* are not. The *band gap* describes the difference in energy between the lowest unoccupied energy state in the conduction band and the highest occupied energy state in the valence band. In semiconductors, this band gap is quite small. When an electron has sufficient energy (which could be obtained, for example, from a photon), it is able to jump from the valence band to the conduction band and begin moving through the material. When an electron jumps into the conduction band, it leaves behind a free space in the highest occupied energy state of the conductance band. This free space, called a *hole*, also moves through the material. Both holes and electrons carry charges (they are different *species* of charge carriers). When holes and electrons moving through the material come into contact, they can *recombine*. That is, the electron can reoccupy its place in the conduction band, releasing energy. Recombination is an important process in semiconductors.

In conventional semiconductors, charge carriers are delocalized. This means they can be treated as if they are moving through a continuous state space. When an electric field is applied, this movement is well described using a modified version of the classical Drude model. In this model, the charge carrier (more precisely, a quasi-particle) moves according to Newton's laws of motion until it hits a defect. At this point it scatters, changing direction according to some probability distribution and changing speed according to the local temperature. For more details, see [2] and [4].

In the presence of sufficient disorder in the material, however, the charge carriers become localized. In other words, they do not move freely through the material but rather hop from molecule to molecule (or polymer segment to polymer segment). The phenomenon of localization in the presence of disorder was first identified by Anderson in the seminal paper [5]. This localization can be explained by the presence of energy states within the band gap from which a charge carrier must escape; see [4]. As a result of the localization, the nature of charge transport in disordered semiconductors is very different to that in conventional semiconductors.

C. Charge Mobility

In the absence of an external electric field, charge carriers move about randomly within a material with no drift in any direction. When an external uniform electric field, F, is applied, the charge carriers begin to move in the direction of F. The *drift velocity*, v, of the transport process is the average speed of a charge carrier as it moves through the material in this direction. The *charge mobility*, μ, is the drift velocity normalized by the magnitude of the force. That is,

$$\mu = \frac{v}{|F|}.$$

Charge mobility is one of the most important quantities describing charge transport in semiconductors. It is closely related to the current and the conductivity of the material; see [1]. Charge mobility behaves very differently in organic semiconductors than it does in conventional semiconductors. In organic semiconductors, the behavior of the charge mobility is closely related to the nature and degree of disorder in the material being considered.

A number of techniques exist that are able to measure the charge mobility of a material experimentally. The most widely used of these techniques is *time of flight measurement* (ToF). In this approach, a slice of material of width L is sandwiched between two electrodes. Electron-hole pairs are generated at one of the electrodes using photoexcitation. One species of charge carrier is immediately absorbed at this electrode. The carriers from the other species travel through the material to the opposite electrode. The current at this electrode is measured as a function of time and the drift velocity, v, is estimated by

$$v = \frac{L}{\bar{t}},$$

where $\bar{t}$ is the average time taken for a charge carrier to reach the electrode. See [1], [6], [7] and references therein for more details on ToF.

D. Dependence on Temperature, Force and Carrier Density

Charge mobility depends on a number of macroscopic variables, in particular, temperature, T, the strength of the field F and the concentration of charge carriers, ρ. In conventional semiconductors the drift velocity is usually proportional to the field strength. As a result mobility is constant as a function of $|F|$. This changes, however, at high field strengths, where the drift velocity begins to increase only sub-linearly towards a limiting velocity, known as the *saturation velocity*, and the mobility begins to decline; see [2] for more discussion. Because temperature increases scattering, it decreases mobility. This dependence is usually of the form $\mu(T) \propto T^{-\alpha}$ for some $0.5 \leq \alpha \leq 3$; see [6].

ToF experiments have shown that charge mobility in highly disordered materials behaves very differently from charge mobility in conventional semiconductors. In particular, the mobility of disordered semiconductors exhibits a strong dependence on the strength of the external force. For a large range of field strengths, the mobility follows a Poole-Frenkel type-law of the form $\log \mu(F) \propto \sqrt{|F|}$. Much of the work on modeling charge transport in disordered media has focused on capturing this Poole-Frenkel behavior; see the discussion in [7]. The temperature dependence is also different for organic semiconductors, with the mobility following either an Arrhenius-like law of the form $\log \mu(T) \propto T^{-1}$ or a law of the form $\log \mu(T) \propto T^{-2}$; see [6]. Recently, the focus of much research has been on correctly describing the dependence of mobility on the density of charge carriers; see, e.g., [8], [9], [10], [11] and [12]. In experiments, it appears that mobility is more or less constant for very low charge carrier densities but begins to increase according to a power law beyond a given threshold.

The main reason for the markedly different behavior of mobility in highly disordered semiconductors is the presence of trap regions in the material. These are groups of molecules or polymer segments whose energies are markedly lower than the energies of surrounding molecules/segments. Charge carriers, which prefer lower energies, become trapped in these regions for long period of time (and, thus, do not move quickly through the material). Increasing the strength of the electric field, helps the charge carriers to escape these low energy regions. Likewise, when the density is increased, some of the charge carriers fill the low energy regions, allowing the other charge carriers to move easily through the material.

III. HOPPING MODELS FOR ORGANIC SEMICONDUCTORS

The motion of a single charge carrier through a highly disordered material is naturally modeled as a continuous time random walk in a random environment. The random environment represents the possible locations of the hopping sites and their associated energies and the random walk describes the location of the charge carrier. In practice, realizations of the random environment are simulated and mobilities are calculated for each realization. Conditioned on a realization of the random environment, the motion of a single charge carrier is described by a *continuous-time Markov chain* (CTMC). The mobility of the material is estimated by averaging over the mobilities of each realization of the random environment.

When multiple charge carriers are considered, their motion is again modeled by a stochastic process in a random environment. Given a realization of the random environment, each charge carrier attempts to move as it would if its dynamics were determined by a CTMC. In the simplest model of interactions, the transition rates of this CTMC are the same as in the single carrier case except that the charge carrier is not allowed to jump to a site if it is occupied by another charge carrier. Thus, given the environment, this process is an *exclusion process*. In more sophisticated models of the interaction between charge carriers, repulsive *Coulomb interactions* are included by changing the transition rates of the single carriers depending on the locations of nearby charge carriers.

A. Hopping Transport

Usually, the random environment considered is not infinite. Instead, for computational reasons, it is restricted to a bounded window, $W \subset \mathbb{R}^3$, with periodic boundary conditions (thus, approximating an infinite environment). A realization of the random environment typically consists of a geometric graph, $G = (V, E)$, and the generator, $Q = \{q_{i,j}\}$, of a V-valued CTMC describing the dynamics of a single charge carrier. The set of vertices of the graph, $V \subset \mathbb{R}^3$, records the locations of the hopping sites. These sites are labeled $1, \ldots, M = |V|$. The set of edges, E, describes possible transitions that a charge carrier can make. There is an edge between two sites, i and j, if and only if $q_{i,j} \neq 0$. The calculation of the rate matrix depends on a number of factors, foremost amongst them the locations and energies, $\{\mathcal{E}_i\}_{i=1}^M \subset \mathbb{R}^M$, of the hopping sites. In addition, the transition rates may depend on additional information about the hopping sites (for example, when the hopping sites are molecules, their orientations may effect the transition rates).

The choice of transition rates depends on the nature of the material, the values of macroscopic parameters and how detailed the model of the random environment is. The simplest, and most widely used, rates are the *Miller-Abrahams rates*; see, e.g., [1], [3]. In this framework, the transition (or 'hopping') rate between sites i and j is given by

$$q_{i,j} = \begin{cases} v_0 \exp\{-2\,\gamma\, R_{i,j}\} & \text{if } \mathcal{E}_j \leq \mathcal{E}_i \\ v_0 \exp\{-2\,\gamma\, R_{i,j}\} \exp\left\{-\frac{\Delta_{i,j}}{k_B T}\right\} & \text{if } \mathcal{E}_j > \mathcal{E}_i \end{cases},$$

where $\Delta_{i,j} = \mathcal{E}_j - \mathcal{E}_i - q(\mathbf{v}_j - \mathbf{v}_i) \cdot \mathbf{F}$ and q is the charge of the charge carrier. Here, $R_{i,j} = \|\mathbf{v}_i - \mathbf{v}_j\|$ is the distance between the locations, $\mathbf{v}_i$ and $\mathbf{v}_j$, of sites i and j, k_B is the Boltzmann constant, v_0 is a constant determining the hopping frequency and γ is a constant that gives the inverse localization radius of the electron wave function.

Another popular choice of rates is the Marcus transfer rates; see [6] and [13]. Here, the hopping rate between site i and site j is given by

$$q_{i,j} = \frac{2\pi}{\hbar} \frac{J_{i,j}^2}{\sqrt{4\pi\lambda_{i,j} k_B T}} \exp\left\{-\frac{(\Delta_{i_j} - \lambda_{i,j})^2}{4\lambda_{i,j} k_B T}\right\},$$

where $\hbar$ is the reduced Planck's constant, $\lambda_{i,j}$ is the reorganization energy between sites i and j and $J_{i,j}$ is the transfer integral between sites i and j. Note that, in order to obtain realistic values of $\lambda_{i,j}$ and $J_{i,j}$, much more detailed information about the microstructure of the material is required than in the Miller-Abrahams case; see [14] and [13].

Usually, transitions rates below a certain threshold are set to zero (this minimizes the number of edges in G). Alternatively, only transitions to nearby sites may be considered. When this thinning of E is performed, care should be taken to ensure that the resulting Markov chain is still irreducible.

Regardless of the choice of transitions rates, the resulting Markov chain has the following important qualitative features:

1) Charge carriers prefer to jump to sites with lower energies.
2) The transition rates from low energy to high energy sites can be several orders of magnitude smaller than other transition rates.

It is these features that cause charge carriers to become trapped in low energies regions of the state space for long periods of time.

If Coulomb interactions are not modeled in the multiple charge carrier setting, then the transition rates derived in the single carrier setting are used to describe the rates at which hopping attempts are made by the carriers. If a carrier attempts to jump to an unoccupied site, it does so successfully. If it attempts to jump to an occupied site, it remains where it is. Note that the rates of the exclusion process describing the configuration of charge carriers can be written out explicitly. However, this does not make sense in practice, due to the size of the state space. Coulomb interactions can be incorporated into the rate models by adding an additional term into the energy difference, $\Delta_{i,j}$. This term depends on the locations of nearby charge carriers. See [8] for more details.

B. Modeling the Material

As mentioned above, a realization of the random environment typically consists of a geometric graph $G = (V, E)$

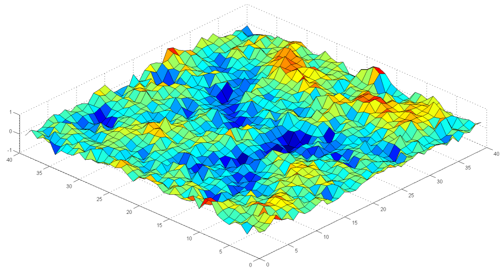

Fig. 1. A correlated energy surface for a 2D lattice model of hopping sites

and a matrix, Q, of transition rates. Many models have been developed for these environments, ranging from simple lattice models to sophisticated models that use computationally-intensive molecular dynamics simulations.

The most well-established model, described in [15], is the *Gaussian disorder model* (GDM). In this model, the set of locations, V, of the hopping sites is given by the vertices of a cubic lattice. Thus, there is no spatial disorder whatsoever. The energies of the hopping sites, $\{\mathcal{E}\}_{i=1}^{M}$, are independent normal random variables with mean 0 and some variance, σ^2. The transition rates are then given by the Miller-Abrahams rates.

Although the GDM model is able to capture a number of qualitative features of charge transport in organic semiconductors, it is not able to describe the field dependence of mobility outside a narrow range of field strengths; see [3] and [7]. A modification of the GDM that has proven successful at capturing the field dependence is the correlated disorder model (CDM). As in the GDM case, the model is lattice-based and has normally distributed site energies. However, these site energies are now positively spatially correlated. Such correlated site energies can be modeled, for example, using a Markov random field. Figure 1 shows a realization of a Markov random field describing the energies of hopping sites on a 2D lattice. Note, in particular, that the correlation encourages the formation of low energy regions. Although the CDM appears to be an improvement on the GDM, [11] argues that field dependence can be properly modeled using the GDM (without the need for correlated energies) so long as the mobility is calculated for interacting charge carriers, rather than a single charge carrier.

In the last few years, increases in computational power have made much more sophisticated models of the random environment possible. In [14], the structure of Alq3, a material commonly used in OLEDs, is simulated at a molecular level using Monte Carlo methods to simulate the deposition process that is used to produce the material. In [16], the microstructure of Alq3 is simulated using molecular dynamics. This approach is further described in [17]. These approaches are able to simulate highly realistic configurations of molecules, which contain the additional information needed in order to use the Marcus transfer rates. However, they are also computationally intensive. As a result, the systems sizes that are considered cannot be too large.

Recently, realistic models of material microstructures based on stochastic geometry have been developed. Alq3 is modeled in [18]. DCV4T, which is used as an electron donor in organic solar cells, is modeled in [19]. These approaches treat the hopping site locations as a realization of a spatial point processes. The energies of the hopping sites are then described by a Markov random field. Additional information, which is needed in order to use the Marcus transfer rates, is produced using stochastic models fitted to data from molecular dynamics simulations. The advantage of the stochastic geometry approach is that it is much less computationally intensive than molecular dynamics simulations. As a result, much larger system sizes can be simulated, avoiding finite size effects.

C. Calculating Mobility

In the single carrier case, the mobility of a given realization of the random environment is calculated as follows. The position of the charge carrier is given by a CTMC, $\{X_t\}_{t\geq 0}$, taking values in V and starting at i_0. Because the random environment is typically restricted to a bounded window $W \subset \mathbb{R}^3$ with periodic boundary conditions, $\{X_t\}_{t\geq 0}$ has a finite state space and is irreducible. Thus, $\{X_t\}$ has a stationary distribution, π. The drift velocity can then be written in terms of the stationary distribution as

$$v = \sum_i \sum_{j\neq i} -\frac{q_{i,j}}{q_{i,i}} \pi_i \, \mathsf{d}(\mathbf{v}_i, \mathbf{v}_j),$$

where $\mathsf{d} : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}$ is the projection onto F of the signed component-wise distance (taking into account periodic boundary conditions) between $\mathbf{v}_i$ and $\mathbf{v}_j$. For example, if $W = [0, \mathsf{b}_\mathsf{x}] \times [0, \mathsf{b}_\mathsf{y}] \times [0, \mathsf{b}_\mathsf{z}]$, then the signed x-component of the distance is given by

$$\mathsf{d}_x(\mathbf{v}, \mathbf{v}') = \begin{cases} v_x' - v_x & \text{if } |v_x' - v_x| \leq \mathsf{b}_\mathsf{x}/2, \\ \mathsf{b}_\mathsf{x} + v_x' - v_x & \text{if } |v_x' - v_x| > \mathsf{b}_\mathsf{x}/2, v_x > v_x', \\ -\mathsf{b}_\mathsf{x} + v_x' - v_x & \text{if } |v_x' - v_x| > \mathsf{b}_\mathsf{x}/2, v_x < v_x', \end{cases}$$

where $\mathbf{v} = (v_x, v_y, v_z)$ and $\mathbf{v}' = (v_x', v_y', v_z')$. The other components, $\mathsf{d}_y(\mathbf{v}, \mathbf{v}')$ and $\mathsf{d}_z(\mathbf{v}, \mathbf{v}')$, are calculated in a similar fashion. The function $\mathsf{d}(\mathbf{v}, \mathbf{v}')$ is then given by

$$\mathsf{d}(\mathbf{v}, \mathbf{v}') = (\mathsf{d}_x(\mathbf{v}, \mathbf{v}'), \mathsf{d}_y(\mathbf{v}, \mathbf{v}'), \mathsf{d}_z(\mathbf{v}, \mathbf{v}')) \cdot F$$

Using the above formulation, the calculation of the mobility reduces to solving for the stationary distribution, π. In the physics literature, π is usually obtained by solving the steady state form of the *master equation* (Kolmogorov's forward equation), which is given by the system of equations

$$\sum_{j\neq i} q_{i,j}\, \pi_j - \sum_{j\neq i} q_{j,i}\, \pi_i = 0$$

for all $i \in \{1, \dots, M\}$; see, e.g., [13].

In the multiple carrier case, the configuration of k charge carriers is given by a CTMC, $\{C\}_{t\geq 0} = \{(X_t^{(1)}, \dots, X_t^{(k)})\}_{t\geq 0}$, taking values in a subset of V^k and starting at $C_0 = (i_0^{(1)}, \dots, i_0^{(k)})$. Given the stationary distribution of this chain, the velocity can be calculated in a similar manner to the single carrier case (however, to avoid excessive notation, we do not give the explicit formula). In contrast to the single carrier case, it is not practical to calculate the velocity in terms of the stationary distribution. This is because the size of the state space is $\binom{M}{k}$, which becomes prohibitively large very quickly.

An often used approximation in the physics literature is the so-called mean field approximation; see, e.g., [13], [20], [21]. Here, the location of each charge carrier at stationarity is assumed to be independently and identically distributed according to the vector $\widetilde{\pi}$, where $\widetilde{\pi}$ is the solution to the system of equations

$$\sum_{j \neq i} q_{i,j}\, \widetilde{\pi}_j (1 - \widetilde{\pi}_i) - \sum_{j \neq i} q_{j,i}\, \widetilde{\pi}_i (1 - \widetilde{\pi}_j) = 0$$

for all $i \in \{1, \dots, M\}$. This approximation clearly allows multiple charge carriers to occupy the same state. However, a repulsive term is included in the master equation. Note that, unlike in the single carrier case, the latter equation is non-linear and is usually solved using an iterative solution technique as in [22].

IV. MONTE CARLO METHODS FOR ESTIMATING MOBILITY

Monte Carlo methods are often used to estimate the mobility of a given realization of the random environment. Such methods are clearly necessary in the multiple carrier case (except when using the mean-field approximation). In the single carrier case, the main motivation for using Monte Carlo methods is that that they can be easily extended to more complicated settings. For example, it is straightforward to add additional charge carriers or another species of charge carriers; see [13].

A. Kinetic Monte Carlo

The standard approach to estimating mobility using Monte Carlo methods is called *kinetic Monte Carlo* (KMC) in the physics community (as it simulates the actual dynamics of the charge carriers). In the single carrier case, a sample path of $\{X_t\}_{t \geq 0}$ is simulated. Then, a point estimate of the mobility, μ, is obtained by normalizing the velocity, v, which is obtained by dividing the distance the charge carrier has traveled by the time taken to travel it. More formally, $\{X_t\}_{t \geq 0}$ is simulated for N steps of the embedded jump chain, $\{Y_n\}_{n \in \mathbb{N}_0}$, where $\mathbb{N}_0$ denotes the non-negative integers.. The velocity is then estimated by

$$\widehat{v} = \frac{1}{T_N} \sum_{n=1}^{N} \mathsf{d}\left(\mathbf{v}_{Y_{n-1}}, \mathbf{v}_{Y_n}\right),$$

where T_N is the time of the Nth jump of $\{X_t\}_{t \geq 0}$. By the ergodic theorem, this estimator converges to the correct value almost surely. The complete procedure is described in Algorithm 4.1.

Algorithm 4.1: Single Carrier KMC

```
1) Set $Y_0 = x_0$. Set $t = 0$. Set $n = 0$.
2) Set $t = t + \tau$, where $\tau \sim \mathsf{Exp}(-q_{Y_n,Y_n})$.
3) Draw $Y_{n+1}$ from the distribution given by
       $\mathbb{P}(Y_{n+1} = j \,|\, Y_n) = -\frac{q_{Y_n,j}}{q_{Y_n,Y_n}}.$
4) If $n < N-1$ set $n = n+1$ and repeat from 2. Otherwise,
   return
       $\widehat{v} = \frac{1}{t} \sum_{n=1}^{N} \mathsf{d}\left(\mathbf{v}_{Y_{n-1}}, \mathbf{v}_{Y_n}\right)$
```

A major disadvantage of the KMC approach is that it often requires large amounts of computer time in order to return accurate estimates. The main reason for this is the presence of trap regions in the energy landscape. A trap region usually consist of a small number of hopping sites, whose energies are significantly lower than those of the surrounding sites. When a charge carrier enters a trap region, it makes an extremely large number of jumps between the constituent sites before it is able to escape and continue moving through the material. This means that most of the computational effort involved in simulating the Markov chain is spent on jumps between sites in trap regions (often an order of 10^6 or 10^7 jumps may occur before the carrier leaves the trap region). The end result is that the Markov chain does not mix quickly enough and requires a very large number of steps to converge to stationarity; see [23] for more detailed discussion. This limits both the size of the random environment and number of realizations that can be considered.

In the multiple carrier case, the process $\{C_t\}_{t \geq 0}$ is simulated for a given number of jumps and the average distance traveled by a charge carrier is returned. That is, the velocity is estimated by

$$\widehat{v} = \frac{1}{k} \frac{1}{T_N} \sum_{i=1}^{k} \sum_{n=1}^{N} \mathsf{d}\left(\mathbf{v}_{Y_{n-1}^{(i)}}, \mathbf{v}_{Y_n^{(i)}}\right),$$

where $Y_n^{(i)}$ is the position of the ith particle after the nth jump of $\{C_t\}_{t \geq 0}$ and T_N is the time of the Nth jump of $\{C_t\}_{t \geq 0}$. The procedure is described in Algorithm 4.2.

Algorithm 4.2: Multiple Carrier KMC

```
1) Set $Y_0^{(1)} = i_0^{(1)}, \dots, Y_0^{(k)} = i_0^{(k)}$. Set $t = 0$. Set $n = 0$.
2) Set $t = t + \tau$, where $\tau \sim \mathsf{Exp}\left(-\sum_{i=1}^{k} q_{Y_n^{(i)},Y_n^{(i)}}\right)$.
3) Draw $i^*$ according to the distribution given by
       $\mathbb{P}(i^* = i) = -\frac{q_{Y_n^{(i)},Y_n^{(i)}}}{\sum_{j=1}^{k} q_{Y_n^{(j)},Y_n^{(j)}}}.$
4) Draw $\check{Y}$ from the distribution given by
       $\mathbb{P}(\check{Y} = j \,|\, Y_n^{(i^*)}) = -\frac{q_{Y_n^{(i^*)},j}}{q_{Y_n^{(i^*)},Y_n^{(i^*)}}}.$
5) If $\check{Y} \neq Y_n^{(i)}$ for all $i \in \{1, \dots, k\}$, set $Y_{n+1}^{(i^*)} = \check{Y}$ and
   $Y_{n+1}^{(i)} = Y_n^{(i)}$ for all $i \neq i^*$. Otherwise, set $Y_{n+1}^{(i)} = Y_n^{(i)}$
   for all $i \in \{1, \dots, l\}$.
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6) If $n < N$ set $n = n + 1$ and repeat from 2. Otherwise, return

$$\widehat{v} = \frac{1}{k}\frac{1}{t}\sum_{i=1}^{k}\sum_{n=1}^{N} \mathsf{d}\left(\mathbf{v}_{Y^{(i)}_{n-1}}, \mathbf{v}_{Y^{(i)}_{n}}\right).$$

The multiple carrier KMC algorithm suffers from the same limitation as the single carrier algorithm. That is, it spends most of its computational time simulating charge carriers jumping back and forth in trap regions, although this can be somewhat mitigated by dynamically setting hopping rates to occupied sites to zero. Because multiple charge carrier KMC already requires far more simulation steps than single carrier KMC (the number of steps required is roughly proportional to k), this means that multiple KMC can only be effectively applied in settings where the system system size and number of carriers are quite small.

B. Aggregate Monte Carlo for Single Charge Carriers

The aggregate Monte Carlo method (AMC), described in [23] and [24], was developed to overcome the computational limitations of the KMC approach. The basic idea is to avoid simulating the full dynamics of the charge carrier within trap regions. This is done by coarsening the state space, essentially aggregating all states within a trap region into a single state. It is possible to do this in such a way that the resulting estimator of mobility is consistent; see [19].

The first step in the AMC method is to identify the trap regions. This is done by considering the jump chain $\{Y_n\}_{n\in\mathbb{N}_0}$. Although this chain is irreducible, the probability of leaving a trap region in any given step is very small. Thus, the chain has a nearly completely decomposable structure. This allows methods for partitioning the state space of nearly completely decomposable Markov chains to be used to identify the trap regions; see [23] and references within.

Given the trap regions, the state space is coarsened by removing transitions between states inside the traps and then removing states that become isolated as a result. Thus, when a charge carrier jumps into a trap region, the next jump will be to a state outside the trap region. Figure 2 illustrates this. The left-hand diagram shows the possible transitions the charge carrier can make in the KMC approach. These transitions can typically occur in either direction. The right-hand diagram shows the possible transitions the corresponding stochastic process, $\{\widetilde{Y}_n\}_{n\in\mathbb{N}_0}$, can make in the AMC approach. Note that some of these transitions are only in one direction. When a charge carrier enters a trap region, it can exit to any state neighboring the trap region, even if it is itself not a neighbor of that state. However, the state to which it exits must neighbor the trap region.

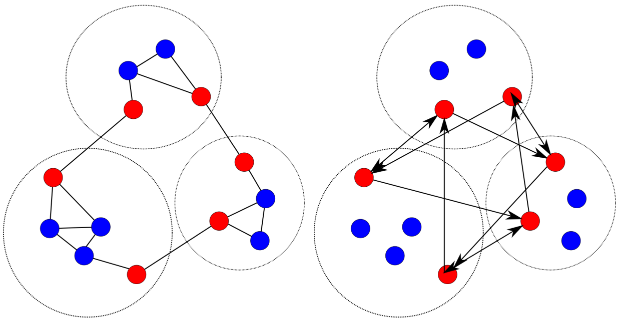

Fig. 2. Possible transitions for carriers in KMC (left) and AMC (right), with trap regions depicted by circles. In KMC all possible transitions are two way, but in AMC jumps may only be possible in one direction.

In order to ensure that the mobility estimator is consistent, the time spent in each trap region must be correctly measured and the distribution of states to which the charge carrier can jump on exit should be correct. This is achieved by treating each trap region as an absorbing CTMC (with the neighboring states acting as absorbing states). When the charge carrier jumps into a state in a trap region, the time it then spends in the trap is taken to be the expected time until absorption for the corresponding absorbing CTMC. Likewise, the distribution of exit states is calculated by determining the probabilities of the absorbing chain being absorbed in each of the neighboring states. The expected absorption times and absorption probabilities can be computed using standard numerical linear algebra packages and are, in practice, precomputed. The procedure is described in more detail in Algorithm 4.3.

Algorithm 4.3: Single Carrier AMC

1) Set $\widetilde{Y}_0 = i_0$. Set $t = 0$. Set $n = 0$.
2) If $\widetilde{Y}_n$ is in a trap region, set τ to be the expected time to absorption of the CTMC starting at $\widetilde{Y}_n$ (where the neighboring states of the trap region are the absorbing states). Otherwise, set $\tau \sim \mathsf{Exp}(-q_{\widetilde{Y}_n,\widetilde{Y}_n})$.
3) If $\widetilde{Y}_n$ is in a trap region, simulate $\widetilde{Y}_{n+1}$ according to the distribution given by the absorption probabilities of the jump chain starting at $\widetilde{Y}_n$ (where the neighboring states of the trap region are the absorbing states). Otherwise, draw $\widetilde{Y}_{n+1}$ from the distribution given by
$$\mathbb{P}(\widetilde{Y}_{n+1} = j \mid \widetilde{Y}_n) = -\frac{q_{\widetilde{Y}_n,j}}{q_{\widetilde{Y}_n,\widetilde{Y}_n}}.$$
4) If $n < N-1$ set $n = n+1$ and repeat from 2. Otherwise, return
$$\widehat{v} = \frac{1}{t}\sum_{n=1}^{N} \mathsf{d}\left(\mathbf{v}_{\widetilde{Y}_{n-1}}, \mathbf{v}_{\widetilde{Y}_{n}}\right)$$

The AMC method requires significantly less steps, N, of the simulation algorithm than KMC in order to obtain an accurate estimate of the mobility. In both [19] and [23], improvements of roughly two orders of magnitude are reported.

C. Aggregate Monte Carlo for Multiple Charge Carriers

It would clearly be very beneficial if the AMC algorithm could be extended to the multiple charge carrier setting, where Monte Carlo methods are necessary. However, the single carrier AMC algorithm described above is not easily adapted to the case of multiple charge carriers. This is because carriers outside trap regions can interact with carriers inside trap regions and, as a result, the dynamics of charge carriers within trap regions cannot be completely ignored. In particular, if a charge carrier attempts to jump into a trap region that is already occupied, it is necessary to know where the carriers are within the trap region.

Recently, a breakthrough has been made in extending the AMC algorithm to the multiple carrier setting; see [25]. The basic idea is to consider the full exclusion process restricted to the trap region (with the neighboring states collapsed into a single absorbing state). In order for the AMC procedure to work, the following information needs to be obtained from this process:

- The random time at which a carrier first tries to exit the trap region.
- The state to which the carrier attempts to jump.
- If necessary, the distribution of charge carriers within the trap region at a time prior to the first attempted exit time.

As it transpires, these quantities can be obtained by simulating a simple birth-death type process (described in [26]), whose transitions are determined by the eigenvalues of the generator of the exclusion process restricted to the trap region. As a result, all the information needed to describe the dynamics inside the trap region can be obtained in a small number of simulation steps (say, 20 or 50) without the need to simulate the whole process, which could make in the order of 10^6 or 10^7 jumps within the trap region.

V. CONTINUOUS-TIME RANDOM WALK MODELS FOR AMORPHOUS INORGANIC SEMICONDUCTORS

Models of charge transport in amorphous inorganic semiconductors occupy something of a middle ground between models for conventional semiconductors and models for organic semiconductors. This is because charge transport in these materials can often be modeled as a mixture of a band transport process and a hopping transport process. In this setting, the charge carrier moves freely through the material until it comes into contact with a localized state (trap). It then spends a random amount of time in this state before escaping and continuing through the material.

A continuous-time random walk model of such a process was introduced by Scher and Montroll in [27]. In this model, the traps are taken to be spatially disordered and the charge carrier is thought of as hopping between these traps. The time the carrier spends in a trap is random and depends on the number and location of nearby traps. Scher and Montroll argued that this process could be modeled as a continuous-time random walk on a 3D lattice. The jumps of the random walk are modeled by a discrete time random walk biased in the direction of the applied field, F. The waiting times between jumps have a probability density function, $\psi(t)$, whose tails follow a power law. More precisely, for $t > t_{\mathsf{min}}$,

$$\psi(t) \propto t^{-(1+\alpha)},$$

where $\alpha > 0$. Each random waiting time is supposed to model both the time spent in the trap and the time taken to traverse the distance to the next trap. Thus, this model incorporates the randomness in the environment directly into the waiting time distribution. Using this approach, Scher and Montrol were able to explicitly solve for the mobility and other key quantities; see [27] and [28] for more detailed discussion. A related model, which was shown to exhibit similar behavior, is the multiple-trapping model; see [29] and [30]. In this continuum model, charge carriers diffuse through the material until they hit a trap state, at which point they wait for a random period of time before continuing on. Although these models successfully describe charge transport in amorphous inorganic semiconductors, they are not good models for organic semiconductors; see [1] and [31].

VI. RECOMBINATION

Recombination is an important process in many organic semiconductors. In OLEDs, recombination is a desirable process that produces light. In organic solar cells, recombination is an undesirable loss process that reduces the efficiency of the cells; see [32]. Recombination occurs when an electron and hole come close to one another and the electron reoccupies its place in the valence band, ceasing to move through the material. When deep trap regions are not present in the material, the recombination rate is determined by the mobilities of the holes and electrons; see [1]. However, when the hole and electron mobilities are highly asymmetric, the role of traps can dominate the recombination process. In this case, the carriers of the slower species become caught in traps and are stuck in them until they come into contact with the faster moving species.

Recombination can be modeled within the hopping transport framework described above. Generally, an attractive Coulomb force between the two species should be included in the transition rate model. The recombination rate can then be studied using Monte Carlo methods. When modeling OLEDs, the material is treated as finite (i.e. there are no periodic boundary conditions). One end of the material is specified as the anode and the other as the cathode. The two species are then injected at opposite ends of the material, and the number that successfully make their way across the material without recombining is recorded.

The simulation of such a complicated process as recombination is clearly computer intensive. It is possible to extend the multiple carrier AMC method to this setting. However, this does not completely alleviate the speed issues. One particular issue is that the event that an injected charge carrier successfully reaches the opposite end of the material may be a rare event. It is well established that standard Monte Carlo approaches to rare event simulation do not work well; see, e.g., [33] and [34]. Recently, [35] used importance sampling, a classical technique from rare event simulation, to develop a more efficient estimator for a toy model of recombination. The idea of importance sampling is to simulate a stochastic process under a different probability measure, under which the event of interest is more likely, and then to reweigh the resulting estimator so that it is unbiased. In [35], the change of measure was effected by reducing the rate of any transition of the particle system that could lead directly to recombination. This approach led to moderate speed-ups.

VII. OUTLOOK

With advances in computational power, it is now possible to use increasingly sophisticated and realistic models of charge transport within disordered semiconductors. However, these models are often very computationally intensive. For this reason, there is a clear need to develop more efficient numerical tools for studying charge transport. For example, improved Markov chain Monte Carlo methods for estimating mobility need to be developed, as do techniques for efficiently simulating interacting particle systems.

As it stands, little rigorous theoretical investigation of the stochastic models underpinning charge transport in disordered media has been undertaken. Rigorous analysis of simple but indicative models using techniques developed in the study of random motion in random media would represent a major development in the field.

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