MONTE CARLO SIMULATION OF DIFFUSION COEFFICIENT AND AVERAGE ENERGY OF CHARGE CARRIERS IN A DISORDERED ORGANIC SEMICONDUCTORS

By

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The undersigned hereby certify that they have read and recommend to the college of Natural and computational scienceGraduate Programs for the acceptance of a project entitled “ **MONTE CARLO SIMULATION OF DIFFUSION COEFFICIENT AND AVERAGE ENERGY OF CHARGE CARRIERS IN A DISORDERED ORGANIC SEMICONDUCTORS** ” by **FEKADU LEGESSE** in partial fulfillment of the requirements for the degree of Master of science in physics **Master of Science**.

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Table of Contents

List of Tables

List of Figures

Abstract

One of the most remarkable results known for energy relaxation of charge carriers in a Gaussian DOS is the existence of the so called equilibration energy. With the help of computer simulations, we study the relaxation of charge carriers and their corresponding diffusive character in a zero electric field region. The relaxation time is of key importance for the analysis of analytical and numerical results in this study because it determines the transition from dispersive to non dispersive (Gaussian) transport behavior. So this project reviews the strong dependence of relaxation time on temperature.

We propose also a Gaussian disordered model (GDM) based on the hopping transport theory of charge carriers (non-interacting particles) to study the relaxation phenomena, the equilibration energy $\langle \varepsilon_\infty \rangle$ and the effect of diffusion in thermal equilibrium in the absence of electric field.In addition we reproduced numerical results of the mean energy and dispersion of charged carriers using the model we have designed and compared our results with those in the literature, found using kinetic Monte-carlo simulation techniques for different values of temperature. Through our simulation, we observed that the mean energy of the particles and the carrier diffusion are both depend on temperature and our analytical discussion also approves the same phenomena.

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Chapter 1

Introduction

Organic semiconductors are a new technology for large area and flexible thin film electronics. Manufacturability and low production costs of these materials along with their specific charge transport properties make such systems extremely favorable. They have attracted much attention over the past fifty years for their potential applications in optoelectronic devices like large area flat displays, organic light emitting diodes (OLED), organic solar cells and organic photovoltaic(OPV). As a result, the research behind this area has risen sharply. In all these intended applications the active layer in the devices involves organic semiconductors whose transport properties of charge carriers in disordered thin films of typically 100 nm or less is very important. Their strong chemical bonding is confined to a molecular level only while intermolecular coupling is controlled by weak vander walls forces. Charge carrier mobility of this material is very less compared to hydrogenated amorphous silicon which is in the order of $1cm^2$v/s and their mean free paths are comparable to intermolecular spacing's. Hence over the last three decades, there has been considerable focus on understanding the physics of transport parameters of which charge-carrier mobility

(μ) has been the most studied. One of the transport models in these classes of materials is the Gaussian disordered model (GDM)[1].

In this model the energy of charge carriers at different sites are uncorrelated, and their distribution is assumed to be Gaussian. Organic disordered semi-conductors (ODSs) are a broad class of materials, which can essentially differ from each other in morphology and chemical composition. Most prominent representatives of the ODSs are conjugated polymers [2, 3], Molecularly doped polymers [4, 1], and low-molecular-weight organic glasses [5, 6].

The theory of how charge carriers perform charge transport in solid materials has been for many years mostly confined to crystalline systems with the constituent atoms arranged in regular ways. However these well-known concepts developed so far for crystalline solids essentially based on the assumption of long-range atomic order are not applicable to disordered materials. So it has been and still is a challenge task to develop a consistent theory for charge transport in disordered systems without translation symmetry in the atomic structure. The main problem to the researchers is the lack of reliable and precise information on the energy spectrum and on the structure of the wave function for most disordered systems. So the theory of charge transport in disordered systems should still be considered as a phenomenological one. To improve the properties of molecularly doped polymers requires knowledge concerning the mechanism by which carriers are generated and transported. So there have been many attempts to deduce the shape of the DOS and to develop a theoretical framework to understand their properties by fitting various experimental data using some particular assumptions on the energy spectrum.

Organic semiconductors are inherently insulators but they can be converted into a semiconductor if free charge carriers are introduced to them, which is possible by either injecting from metal contacts or by chemical doping or by optical excitation. They are carbon based materials that consists of large molecules with conjugated carbon chains as a key feature. Before the discovery of conductive polymers in 1977 by Alan.J,Heeger,Alan G. MacDiarmid and Hideki shirakawa [7, 8], conjugated polymers were considered as insulators. They found that the conductivity in polyacetylene films could be increased by doping with the halogens. The valence π electrons of the atoms in a conjugated polymer are united (delocalized) over the polymer. In practice the polymers in the thin films used in electronic devices form more of a spaghetti-like mass where kinks and twists are common. So the charge carriers are localized to this small segments of the polymer known as chromphores that make up the transport sites. The chromphores consists of small number monomer units that determine both the energy and the localization length of each site. The energy of a charge carrier in a site is related to the length of the segment. Since the lengths of chromophores are not uniform, the energies are also not uniform. For disordered organic semiconducters the distribution of these energies are considered to be Gaussian[1]. The consideration is based on the spectrum width of its light absorption [1].

One of the easiest ways to study charge transport in a random distribution of localized states is via Monte Carlo simulation [9, 10].The essential input parameter is the width σ of the distribution of the density of states (DOS). The Monte Carlo simulation reveals that charge carriers tend to relax to an equilibrium level located at σ^2/kT, where T is temperature in Kelvin and k is Boltzmann constant.

A simplified model of transport is assumed and relation between observable quantities such as (mobility, electric field, temperature and charge carrier density) is derived analytically or from numerical simulations.

The Gaussian Disorder Model (GDM) and recent improvements are prototypes of this modeling paradigm. When this model is applied to a set of experimental data it provides a structure-property relation and suggest a means for improving the charge-property of a material rather than using other models for the study of highly disordered solids.

So in this work, using the model described above, we discuss the temperature dependence of the mean energy of the charge carriers in disordered organic semiconductors and diffusivity property at thermal equilibrium both analytically and numerically using computer simulation.

The rest of this work is organized in four chapters. In Chapter two we present a general overview of the hopping transport which is the main building block of our work. We will briefly discuss the concept of variable range hopping, transport energy, charge carrier relaxation and analytical derivation of the equilibration energy. Our methodology will be presented in Chapter 3, we present a simple device model (lattice Monte Carlo method is introduced) and the simulation employed in this work. In Chapter four, we will present the results of our MC simulations. We analyze and discuss in detail what we get from the simulation and to validate the algorithms. Finally we will present summary and conclusions.

Chapter 2

Theory of charge transport in organic disordered semi-conductors

In contrast to ordered crystalline semiconductors with well -defined electronic energy structure consisting of energy bands and energy gaps, disordered materials are distinguished as extended and localized states. In the former states, the charge carrier wave function is spread over the whole volume of a sample, while in the latter states the wave function of a charge carrier is localized in a spatially restricted region which usually fill the energy spectrum continuously.

In amorphous organic systems there exist some energy level called the mobility edge that separates the extended states from the localized ones. The energy region between the mobility edges for holes and electrons is called the mobility gaps where the spatially localized states are found. Each of the sites, that can accept a charge carrier, has some binding energy. The energies of these localized sites are different from site to site due to the disorder of the material and the energetic correlations between neighboring states. The energy regions of localized states in the vicinity of the mobility edge are called band tails. The charge transport properties depend essentially on the energy spectrum in the vicinity and below this area. But precise structure of this energy spectrum in the band tails for all disordered materials is in its early stage.

2.1 Hopping Transport

Hopping transport for disordered organic semi-conductors where the Fermi energy is located with in the mobility gap, the charge transport is taking place in the localized state. This type of charge transport is called hopping charge transport and the states are usually called transport sites. The motion of charge carriers in this picture happens when they tunnel from one localized state to another. This tunneling events are the 'hops' in hopping transport. So a hope refers to a transition of a charge carrier between two different localized states. One is mostly interested in the transition rate of the hops for the purpose of finding transport properties like the mobility and diffusivity of the charge carriers. Numerous models were developed to describe these rates, the most successful one was suggested by Millers and Abrahams [11] that gives the hopping rate as

$$\nu_{ij} = \nu_0 \exp\left[\frac{-2r_{ij}}{\alpha}\right] \begin{cases} \exp\left[\frac{\varepsilon_j-\varepsilon_i}{k_BT}\right] & \texttt{if} \quad \varepsilon_i < \varepsilon_j \\ 1 & \texttt{if} \quad \varepsilon_i > \varepsilon_j \end{cases} \tag{2.1}$$

Eq(2.1), which describes the tunneling transition rate between two sites i and j that are separated from each other by the distance r_{ij} with the energies ε_i and ε_j. When the charge carrier relaxes downwards in energy, a phonon is emitted and in the case of an activated transition, the required energy is taken up by the absorption of a phonon. ν_0 is the attempt to escape frequency and is typically of the order of $10^{12}s^{-1}$

[7], k_B is the Boltzmann constant,T is temperature in K and α is the localization length which describes the decay strength of the localized wave functions. Eq.(2.1) consists of two exponentially decaying factors. The first one, the tunneling part of the rates account for the distance between the sites that take part in the transition and the second exponential function accounts for the energy difference between the sites. The higher the value of the binding energy of the state $'\varepsilon'$, the deeper in the spectrum the state lies.

In general a tunneling transition probability of charged carrier from a localized state i to a lower in energy localized state j depends on the spatial separation r_{ij} between sites i and j as

$$\nu_{ij} = \nu_0 exp(\frac{-2r_{ij}}{\alpha}) \tag{2.2}$$

2.2 Density of states

The density of states (DOS) refers to the distribution of the sites in space and energy and their concentration usually decreases when the energy moves away from the mobility edge towards the center of the mobility gap. The energy difference between two localized states plays a crucial role for the probability of a charge carrier to hop between them. When studying the charge transport in the system as a whole these energy differences are conveniently described by using the energies of each site which is found based on the density of states. For the energy distribution of the sites, the two most popular assumptions are the exponential and the Gaussian distribution. In inorganic materials, an exponential density of states is assumed [10].

$$g(\varepsilon) = \frac{N}{\varepsilon_0} exp\left(\frac{\varepsilon}{\varepsilon_0}\right) \tag{2.3}$$

Here N is the spatial density of sites (the number of sites per cm^3),ε is the energy of each site while ε_o gives the energy scale of the distribution. For organic disordered materials, the density of states is described by the Gaussian distribution. Bassler(1981)[7].

$$g(\varepsilon) = \frac{N}{\sqrt{2\pi\sigma^2}} exp\left(\frac{-\varepsilon^2}{2\sigma^2}\right) \tag{2.4}$$

where σ, indicates the width of the density of states (DOS), whose value for disordered organic semiconducter is, in the range between 0.05 eV up to 0.15 eV depending on the material. In this work, a Gaussian energy distribution has been used, assuming that the energies ε_i of different sites are independent of each other i.e, not correlated.

2.3 Variable range hopping model

It is widely accepted that charge carrier transport in disordered semiconductors is governed by variable range hopping (VRH) among the system of localized states. As it was put forward by Mott [12], VRH is the more general regime of hopping transport which is valid also at low temperature . In this case, all transport happens with in the energy ($\Delta\varepsilon$) around the Fermi energy(ε_f). Variable range hopping is closely connected with the millers and abrahams(MA) hopping rates. As long as a carrier can find shallow and unoccupied sites with energies below its current state, it will perform a nearest neighbor hopping (NNH), where the rates are only limited by the spatial tunneling distances. This type of hopping is similar to the conduction through impurity levels in heavily doped crystalline semi-conductors. Whereas at low temperature, the probability of NNH decreases . In this situation between two sites whose transfer integral smaller leads the activation energy to be small and hopping is most probable over a long distance known as variable range hopping. This model (VRH) suggests that charge carriers may either hop over a small distance with high activation energy or hop over a long distance with low activation energy.

If the thermal energy kT is smaller than the energy scale of disorder σ, which is the case for ODS_s where at room temperature $kT \approx 0.3\sigma$ [13], charge transport occurs in the VRH regime, i.e. the interplay between the spatial and energy factors determines the transport path.

2.4 Transport energy

The concept of the transport energy (TE) has proven to be one of the most powerful theoretical approaches to describe charge transport in organic semi-conductors.

Grunewald and Thomas [14] first recognized the crucial role of the transport energy level in the hopping transport of electrons via localized band-tail states with purely exponential DOS. This particular energy level dominates the hopping transport of electrons in the band tails. They have also achieved an analytical formula for this level and showed its position does not depend on the Fermi-energy.

Along with many analytical approaches the position of the transport energy was also studied using computer simulation techniques[1]. As Oelerich *et al.*[15] recently suggested a computer algorithm that allows one to determine the energy range that dominates the charge transport. By most definitions, it is the energy path of conducting charge carriers that replace the mobility edge within the framework of the multi-trapping model [16].

It has been shown in the derivations for transport energy at low temperature, $(kT < \varepsilon_0, \sigma)$ and as it was later discussed by Arkhipov *et al.*[17] the concept of transport energy is applicable practically for all realistic DOS distributions.

2.5 Charge carrier relaxation

If some small electrons are inserted into a DOS (disordered organic semiconducter film) with a Gaussian DOS at temperatures such that $kT < \varepsilon_0$, charge carriers would continuously relax in energy diving energetically deeper and deeper thereby lower their energy in the course of time. More over, during the relaxation the charge carriers will be trapped on sites with increasingly from lower energy site to high energy site one by one until they fill all the available empty sites on the vicinity of the equilibration energy level. The diving of these energy carriers in energy stops when they arrive in the vicinity of some limiting energy called the equilibration energy $< \varepsilon_\infty >$. This energy, $< \varepsilon_\infty >$, lies above the Fermi-level is a well-defined quantity even in the empty system without any interactions between the relaxing carriers [13]. The time required to reach this equilibrium distribution (called the relaxation time) τ_{rel} is of key importance for the analysis of experimental results[18]. Indeed, at time scales shorter than τ_{rel}, charge carriers initially randomly distributed over localized states perform a downward energy relaxation during which transport coefficients depend on time and charge transport is dispersive.

At time scales longer than τ_{rel}, the energy distribution of charge carriers stabilizes around the equilibrium energy $< \varepsilon_\infty >$, even in a very dilute system with non-interacting carriers. In such a regime, transport coefficients are time independent.in otherwards, at $(t = \tau_{rel})$ dispersive transport is succeeded by the non-dispersive (Gaussian) transport behavior. This is one of the most important results for charge carrier transport in disordered organic media.

2.6 Analytic solution of the Equilibration energy

As we mentioned in the introduction, even-though the study of charge transport in the field of organic materials are based on computer simulations, researchers develop some analytical theories that are consistent with a special efficient numerical methods putting a restrictive conditions, and one of them is the analytical solution for the equilibration energy.

In section (2.5) above, we noted that, most charge carriers in a Gaussian DOS of low density charge carriers (n) are distributed not around the Fermi level but are instead situated around the so-called equilibrium energy level. It is a specific feature of a Gaussian DOS that the mean energy $\langle \varepsilon_\infty \rangle$ of the whole ensemble of charge carriers stop to go down from transport energy level and saturates at long times indicating attainment of dynamic equilibrium. This energy is usually identified as the average carrier energy equals to $\frac{-\sigma^2}{k_b T}$. In such a case, transport in the Gaussian DOS is due to a carrier transitions via energy levels in the range between $\langle \varepsilon_\infty \rangle$ and (ε_t). Neither of these energies depends on the charge carrier density (n). Furthermore, the occupation number of state in the range between $\langle \varepsilon_\infty \rangle$ and (ε_t) is very low. Therefore the carrier mobility in the Gaussian DOS at low 'n' does not depend on 'n', which is totally opposite to the situation in the exponential DOS, where the mobility depends on all n values. The equilibration energy $\langle \varepsilon_\infty \rangle$ of the charged carriers at zero electric field can be calculated as follows.

The energy distribution of most carriers occupying thermal equilibrium energy level corresponds to the maximum of the product of the density of states $g(\varepsilon)$ and the Fermi distribution function $f(\varepsilon, \varepsilon_f)$.

Let us assume a system with a small amount of charge carriers ($\frac{n}{N} \ll 1$)[15]. Where N is the number of sites per cm^3, n is the number of charge carriers per cm^3. In this case the Fermi distribution function can be approximated by the Boltzmann distribution function. Which means

$$f(\varepsilon,\varepsilon_f) = [exp(\frac{\varepsilon-\varepsilon_f}{k_bT})+1]^{-1} \approx exp-(\frac{\varepsilon-\varepsilon_f}{k_bT}) \tag{2.5}$$

So the product $g(\varepsilon)f(\varepsilon,\varepsilon_f)$ becomes,

$$g(\varepsilon)f(\varepsilon,\varepsilon_f) \approx g(\varepsilon)exp(\frac{-\varepsilon}{k_bT})exp(\frac{\varepsilon_f}{k_bT}) \tag{2.6}$$

but (ε_f) is just a scaling factor and can be dropped out. Our interest here is to find the average of the energy of the carrier distribution (ε). Note that $'\varepsilon'_\infty$ is defined as the average energy of the charged carriers in the distribution. $g(\varepsilon)exp(\frac{-\varepsilon}{k_bT})$. It is therefore calculated as

$$\langle\varepsilon_\infty\rangle = \frac{\int_{-\infty}^{\infty}\varepsilon g(\varepsilon)f(\varepsilon)d(\varepsilon)}{\int_{-\infty}^{\infty}g(\varepsilon)f(\varepsilon)d(\varepsilon)} \tag{2.7}$$

The reason for using $'\infty'$ at the subscript is to show that the average energy is attained after a long time close to infinity.

Substituting the values of of $g(\varepsilon)$ and $f(\varepsilon)$ in Eq.(2.7), by their values from Eq.(2.4) and Eq.(2.5) an expression for $\langle\varepsilon_\infty\rangle$ becomes

$$\langle\varepsilon_\infty\rangle = \frac{\int_{\infty}^{\infty}\varepsilon\, exp(\frac{-\varepsilon^2}{2\sigma^2})exp(\frac{-\varepsilon}{k_bT})d(\varepsilon)}{\int_{-\infty}^{\infty}exp(\frac{-\varepsilon^2}{2\sigma^2})exp(\frac{-\varepsilon}{k_bT})d(\varepsilon)} \tag{2.8}$$

The constant term of Eq.(2.4), $\frac{N}{\sqrt{2\pi\sigma^2}}$,in the above equation is already taken out from both the integrals and canceled each other. So now Eq.(2.8) can be evaluated by using the integration by parts method.

Consider the terms in the denominator. Let

$u = exp(\frac{-\varepsilon^2}{2\sigma^2})$, $du = \frac{-2\varepsilon}{2\sigma^2}\left[exp(\frac{-\varepsilon^2}{2\sigma^2})\right]$,

$dv = \int_{-\infty}^{\infty} exp(\frac{-\varepsilon}{K_bT})d(\varepsilon)$,and $v = -k_bT\,exp\frac{-\varepsilon}{k_bT}$, So applying the formula of integration by parts, the equation becomes

$$\underbrace{-k_bT\,exp(\frac{-\varepsilon}{k_bT})\,exp(\frac{-\varepsilon^2}{2\sigma^2})}_{1}\,|_{-\infty}^{\infty} - \underbrace{\frac{k_bT}{\sigma^2}\int_{-\infty}^{\infty}\varepsilon\,exp(\frac{-\varepsilon^2}{2\sigma^2})\,exp(\frac{-\varepsilon}{k_bT})}_{2} \tag{2.9}$$

The first term of the equation vanishes when it is evaluated from $(-\infty)$ to (∞) , and the remaining term (second term) of Eq.(2.9) is replaced for the denominator of Eq.(2.8) and the final equation can now be written as

$$\langle\varepsilon_\infty\rangle = \frac{-\sigma^2}{k_bT}\left[\frac{\int_{\infty}^{\infty}\varepsilon\,exp(\frac{-\varepsilon^2}{2\sigma^2})\,exp(\frac{-\varepsilon}{k_bT})d(\varepsilon)}{\int_{\infty}^{\infty}\varepsilon\,exp(\frac{-\varepsilon^2}{2\sigma^2})\,exp(\frac{-\varepsilon}{k_bT})d(\varepsilon)}\right] \tag{2.10}$$

Similar terms canceled each other and the equation is finally reduced to

$$\langle\varepsilon_\infty\rangle = \frac{-\sigma^2}{k_bT} \tag{2.11}$$

and this equals to $\langle\varepsilon_\infty\rangle = -\hat{\sigma}\sigma$, where$\hat{\sigma} = \frac{\sigma}{k_bT}$.

Using the formula we got in Eq.(2.11), the equilibration energy can be calculated for different values of $(\frac{\sigma}{k_bT})$ as shown below. We keep the same parameter of $(\frac{\sigma}{k_bT})$ and calculate $\langle\varepsilon_\infty\rangle$ using MC simulation method. The disorder parameter in our case is taken 0.15eV, since the energy disorder of most organic amorphous semi-conductors ranges from 0.05eV to 0.15eV.

Table 2.1: the corresponding value of the equilibration energy in eV for different values of temperature

$\frac{\sigma}{k_bT}$	1	1.5	2	2.5	3	3.5	4
$\langle\varepsilon_\infty\rangle$	-0.5	-0.225	-0.3	-0.375	-0.45	-0.525	-0.6

The equilibration energy of the charge carriers for different values of $(\frac{\sigma}{k_bT})$ is calculated and the numbers in the table indicates, a decrease in temperature is accompanied by the decrease in the mean energy of the charged carriers. Looking at the values, for $\frac{\sigma}{k_bT} < 2$, the higher the temperature, the faster the charge carriers to go down and attain an equilibrium state, and for the lower the temperature $\frac{\sigma}{k_bT} > 2$, the longer it takes for the charge carriers to relax to the steady state mobility. This can be explained by the fact that the waiting time is on average smaller, when $(\frac{\sigma}{k_bT})$ is smaller, and higher when $(\frac{\sigma}{k_bT})$ is relatively larger. We found similar results using MC simulation technique. Comparative analysis is given on chapter(4)

2.7 Diffusion of charge carriers in a Gaussian DOS

Diffusion of charged carriers is another phenomenon that are observed at finite temperature in zero field region. During the process of charge carrier relaxation at low density from the center of the DOS towards quasi-equilibrium energy level, charge carriers motion show also diffusion. This gives the spreading of the carrier packet when they move around randomly at the equilibration level. The dense carrier packet diffuses and therefore broadens. So diffusion should be seen as a local displacement of charge carriers around an average position. In the absence of any external potential transport, the motion of charge carriers is purely diffusive and the diffusion coefficient is defined for a packet of charge carriers by the equation.

$$D = \frac{\langle X^2 \rangle - \langle X \rangle^2}{2t_{ave}}, \tag{2.12}$$

where the equation is for one dimensional case.

So, $\langle X^2 \rangle - \langle X \rangle^2$ is the dispersion of position distribution of charge carriers at equilibrium. If we consider the mean position is zero, it means that, the charge carriers on either side of the mean in equilibrium are equal. The diffusivity is simply defined as the mean square free path of a transition divided by its average time.

$$D = \frac{\langle X^2 \rangle}{2t_{ave}} \tag{2.13}$$

Then, the variance which is the measure of dispersion can be calculated by

$$X_{var} = \frac{1}{N_p} \left(\sum_{i=1}^{N_p} X^2 \right) \tag{2.14}$$

The standard deviation is another measurement for the average deviation of this distribution from the mean and is given by-

$$X_{std} = \sqrt{X_{var}} \tag{2.15}$$

In the limit of small electric field the diffusion coefficient D and the mobility μ are related by the Einstein relation [19]

$$De = \mu k_b T \tag{2.16}$$

where 'e'is the electric charge on electron and the equation is best suit for the steady state condition because the relation is derived for a finite, closed system where there is no net current flows.

Chapter 3

Methodology

3.1 Monte Carlo simulation technique

Monte Carlo methods are a broad class of computational algorithms that relay on repeated random sampling to obtain numerical results. Their essential idea is using random numbers to solve problems that might be deterministic in principle. The Monte Carlo (MC) simulation was the numerical approach to find charge transport properties in disordered semiconductors. It is the most popular and widely used tool in this field of research.

In this work, we study the influence of temperature on mobility and diffusivity of charged carriers using Monte Carlo simulation method. We consider holes or electrons as charge carriers and limit the study to the low charge carrier density in a zero field regime, so that the interaction between charge carriers in the simulations is neglected.

As soon as a charge carrier performs a hop in the simulation, the destination position is chosen randomly on the basis of the probabilities of hopping to each possible destination site. The probability of hopping from one position to another is found based on the hopping rate which is given by Eq.(2.1). The total rate of hopping of all charge carriers is used to randomly choose the carrier dwell time on each site. During the actual simulation, the distance that the carriers travel in each direction and the simulation time is stored. So transport coefficients like the mobility and diffusivity can hence be evaluated after the simulation.

3.2 Model of the simulation

The sample material is modeled as a simple cubic lattice of L_x, L_y,L_z sites, whereL_x, L_y,L_z denote the size of the lattice in the x, y and z directions respectively. Periodic boundary conditions are considered in all the three dimensions, with no applied electric field applied to the system. Simulation is performed on a regularly arranged three dimensional lattice sites, with the assumption that the hopping among the lattice site is governed by Miller-Abrahams rate equation in which the jump rate ν_{ij} of the charge carrier from the site i to site j is given by Eq.(2.1). We only consider the situation of uncorrelated Gaussian disorder model. The energies ε_i and ε_j are then randomly drawn from a Gaussian density of states given by Eq.(2.4).These disordered energies are uncorrelated.

Each simulation step starts with a random distribution of charge carriers (Np), provided that Np divided by the number of sites (charge carrier density) is low, with the constraint that, one site must not be occupied by more than one charge carrier at a time or avoid double occupancy. Since we are mainly interested in charge transport at a very low carrier density, we neglect the effect of electrostatic interactions. Then number of charge carriers is 100, or $\frac{N_p}{N} = \frac{100}{50\times50\times50a^3} = \frac{8\times10^{-4}}{a^3}$, where a is a lattice parameter which is about 1 nm for disordered organic semiconducter.

Our simulation procedures begin by the formation of the three dimensional lattice of 50 × 50 × 50 unoccupied sites. When placing charge carriers at randomly chosen sites their energy distribution will be that of the sites, with time, they move to sites with lower energies. Note that, a step in a random walk for a hopping charge carrier is based on the position and the energy of the site is the main cause for the transition rates between the sites. The sites to which a charge carrier can hop is limited to only 26. The number is restricted to 26 because it strongly reduces the amount of possible hops one must store and involving more number of possible destinations are computationally expensive. Two random variants are needed to complete a step in the random walk of the charged carrier. First, a dwell time τ must be drawn to determine the time the charge will spend on the current site before hopping to the next. The second random variant is the site to make the transition to. Then we solve for the normalized transition probability and make use of a stochastic approach to move the charge carriers around.

The probability that a charge carrier hops from an occupied site i to an unoccupied site j, is described as [16].

$$p_{ij} = \frac{\nu_{ij}}{\sum_{j\neq i} \nu_{ij}} \tag{3.1}$$

where i=1,2,3,...Np and j=1,2,3,...26

Here, the summation is done over all possible hops of all the particles and the total probabilities are normalized to 1. Once a dwell time and site index to transition has been drawn, the charge carrier can be moved to the new site and the process is repeated. This is counted as one Monte Carlo Time Step.

The mean dwelling time t_{ave} at site i is given by

$$t_{ave} = \frac{1}{\sum_{j\neq i}} \nu_{ij} \tag{3.2}$$

where the minimum and maximum limits approach zero and infinity, the exact dwelling time is approximated from the relation

$$t = t_{ave} \ln(1 - r) \tag{3.3}$$

where r is a random number taken from a uniform distribution between 0 and 1.

The steady state distribution is then obtained via the Monte Carlo steps. We let the system pass through (10^7) Monte Carlo time steps (MCTS), to ensure that the system has reached a steady state distribution. One MCTS is a step in which the hopping of one particle is performed after trial move of all the particles. Through the simulation, the average carrier energy of the charge carriers is calculated after each step and recorded in every 1000 MCTS. Therefore results are averaged on 10 different configurations of energy distribution. The same simulation procedure is repeated for different values of temperature by changing our parameter ($\frac{\sigma}{KT}$),from 1-4 in the step of 0.5.The distribution width (σ) in all cases is constant. So the computer keep track of all the time weighted mean energy(ε_∞) of the ensemble as a function of time for different values of temperature.

The dispersions of the particles are also numerically calculated using the same parameter following the same procedure. The simulations were carried out to obtain the temporal evolution of the dispersion of the charged particles relative to their mean position at the equilibrium energy level. The numerical data obtained by the simulation shows the spatial fluctuation of these carrier charge density measured relative to the average position ($\bar{X}$). The average position for every charged carrier (x_i) in every 1000 relaxing steps has been calculated and these results are then averaged 10 times so the spatial distribution of the carriers was determined. We did the same simulation repeatedly varying the value of ($\frac{\sigma}{K_b T}$).

Chapter 4

Results and Discussions

In our simulation, we considered a model of Gaussian DOS with a Gaussian width σ. To calculate the mean energy and diffusion of charged carriers (non-interacting) in disordered organic semi-conductor in three dimensional system, we used different values of $\frac{\sigma}{k_b T}$. The results of our MC calculations are shown by the plots in Figs.(1 and 2).

Figure (1) shows the mean energy per distribution width (σ) versus time (MCTS) for different temperature or ($\frac{\sigma}{k_b T}$).

Two clear features attract the attention in the first figure. Charge carriers that are introduced into a Gaussian DOS, under gone a relaxation from high energy states downward in energy until it arrives at the equilibration energy $\langle \varepsilon_\infty \rangle$. Initially the energy distribution of charge carriers concides with that of the DOS. In the course of time the charge carrier energy distribution moves downward until its maximum $\langle \varepsilon(t) \rangle$ arrives at the energy $\langle \varepsilon_\infty \rangle = \lim_{t\to\infty} \langle \varepsilon(t) \rangle = -\frac{\sigma^2}{k_B T}$. This result was shown analytically. The time required to reach this equilibrium distribution (known as relaxation time) demarcates dispersive transport from non dispersive one,and hence very important. In dispersive transport (or during the time before relaxation time) mobility is time dependent which is succeeded by non dispersive one at relaxation time. During relaxation, charges are always trapped on sites which increases with the decrease of energy. This leads to a longer waiting times for a charge carrier to leave the site which in fact depends on the temperature of the given system. It is clearly visible that, all the graphs in the figure behave the same way as the mean energy of the carrier packet saturates or occupy sites around the so-called equilibration energy $< \varepsilon_\infty >$. In all cases the mean energy of the charge carriers decrease with time until a certain threshold value is attained for each graph after which, their corresponding energy becames time independent.

At zero electric field region,the value of $'\varepsilon_{\infty'}$, depends on energetic disorder(σ) and temperature. But in this simulation, we observed the dependence of (ε_∞), at different temperature regions taking (σ) constant. The energy needed for a charge transport to occur is usually taken from phonon in the system, which is the reason why hopping charge transport is said to be phonon assisted. This makes the temperature dependence of hopping. For hopping transport, increasing the temperature of the system, increases the number of available phonons and charges becomes more energetic. In the contrary reducing the temperature reduces the number of available phonons and their respective mean energy. Hence their mobility decreases.

As Fig.(1) shows, energetic charges at higher temperature such as $\frac{\sigma}{k_bT} = 1, 1.5, 2$ arrives at equilibrium earlier because their mobility is relatively fast. At lower temperature or as temperature decreases, in the case $\frac{\sigma}{k_bT} = 2.5, 3, 3.5, 4$ the mean energy of the charge carriers also decrease their mobility and this makes charges to take a long time to attain an equilibrate state. This condition is similar to the data shown on table [1]. But we see some numerical discrepancy between the analytical result and

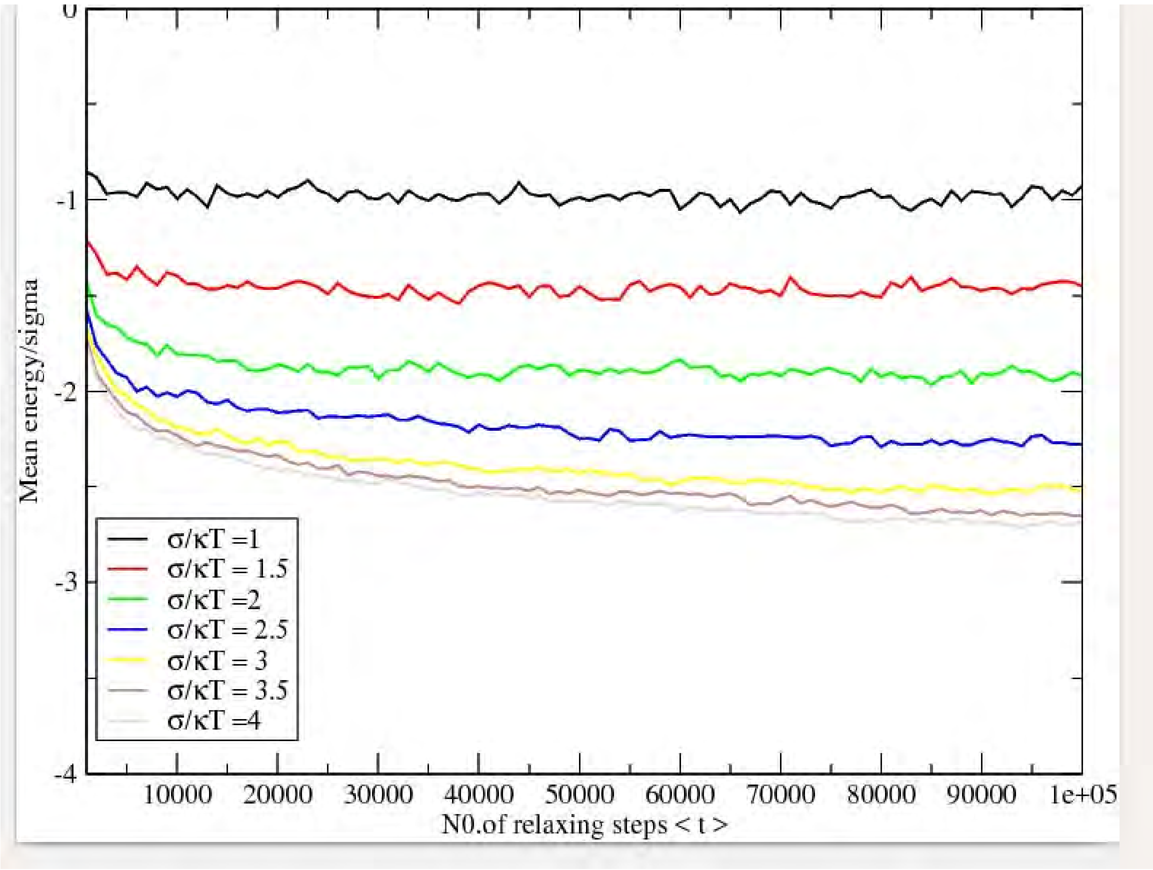

Figure 4.1: Temporal decay of the mean energy of an ensemble of carriers in a Gaussian DOS of variable normalized width $\frac{\sigma}{k_b T}$

the result we obtained using computer simulation method. This might be associated with the computational accuracy of the computer and the simulation may not be able to equilibrate the charges to the maximum desired value. However, even though the numbers show some little differences, the charge transport mechanism at thermal equilibrium in both cases (analytical or computer simulation) values show the above mentioned analysis were the same. Once a steady state is established, the transport is Gaussian and parameters such as mobility and diffusion constant are defined and calculated.

Figure(2) shows the dispersion of charge carriers as a function of time (MCTS) for different values of $\frac{\sigma}{k_b T}$ (or temperature).

In Fig.2. the results of our MC calculation show, the temperature dependence of the scattering or dispersion of the charged carriers for different values of $\frac{\sigma}{k_b T}$ is presented. As we can see from the figure, the plots have different slops indicating that, at higher temperature $\frac{\sigma}{k_b T} = 1$, the dispersion becomes large as compared to the low temperature $\frac{\sigma}{k_b T} = 4$. This means dispersion increases, at higher temperature and decreases at a lower temperature of the system. The diffusion coefficient in each case does not vary with time and it is the same for the same temperature when the charge carriers distribution is at equilibrium. This can be easily observed from the slope of each graph which is the same as the slope is constant. The slope in this figure representing the diffusion coefficient which decreases with the decrease of the temperature.

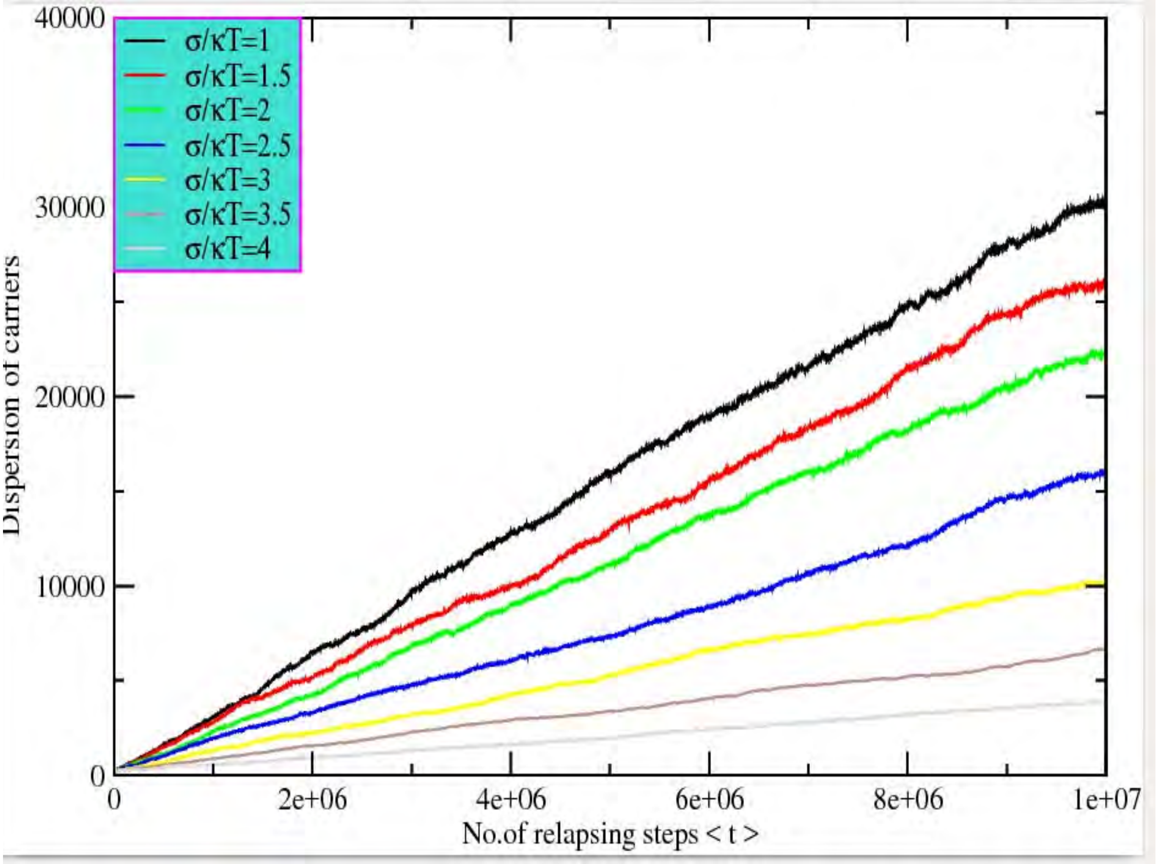

Figure 4.2: Temporal evolution of the dispersion of an ensemble of carriers in a Gaussian DOS of variable normalized width $\frac{\sigma}{K_b T}$

Chapter 5

summary and conclusions

Organic semiconductors which are nowadays used as an active media in optoelectronic devices. One of the main driving forces in research on amorphous semiconductors has been, and still is, the ability of these materials to be economically prepared for large areas of applications. These class of materials have a significant advantage over their crystalline counter parts. What makes them different is typically the charged carriers in organic semiconductors, are localized molecular entities and their movement is governed by incoherent hopping among adjacent sites with statistically variable energies. But the central problem is the understanding of the overall mechanisms related to charge transport. This is important because it is the charge transport which limits the performance and applicability of organic electronic devices.

Many modeling of the charge transport in ODS has been suggested but above all the Gaussian disordered model (GDM) with the miller Abraham transition rate is the best representing a disordered semi-conducting organic material, which is the basis of the theoretical as well as the numerical method approaches of our study in this project.

An analytical model describing the charge carrier relaxation is proposed based on the hopping transport theory.So many factors like the electric field, the material disorder, the charge carrier density etc...are affecting the transport coefficients mobility and diffusivity but, in particular we discuss in this study how this transport parameters are affected by temperature in the absence of electric field.

We used Monte Carlo simulation of hopping transport. We briefly explain the Monte-Carlo simulation technique, energy relaxation of charge carriers, and their mean energy at thermal equilibrium with the related variance. We analyzed and compared the result we got from the simulation with the analytic solution. Even though the analytical result is not fully consistent with the simulation finding, the characteristics we got turn out to be in a good agreement with the simulation findings.

We have shown how the steady state mobility and diffusion constant of a charge carrier are calculated. We investigated the charge transport property in a zero field Gaussian DOS regime. we showed that the normalized Gaussian width $\frac{\sigma}{k_bT}$ is an important factor and the Gaussian DOS is entirely reliable for a low carrier concentration regime.

Finally, we display the equilibration energy $\langle\varepsilon_\infty\rangle$ and diffusion as a function of the average time in a zero-field limit for various values of $\frac{\sigma}{k_bT}$.The graph demonstrates the validity of the analytical approach for revealing the position of the equilibration energy.

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