DENSITY AND TEMPERATURE DEPENDENT OF CHARGE CARRIERS MOBILITY IN DISORDERED ORGANIC SEMICONDUCTORS : MONTE CARLO SIMULATION METHOD

BY

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Abstract

We begin the analysis of transport of charge carriers in organic semiconductors, focusing on the dependence of charge carriers mobility on density, external electric field and temperature. We start with the formulation of the main relationships that provides the current density as a function of conductivity and electrical field. Conjugated polymer films are composed of carbon-based molecular chains, which are held together by weak van der Waals interactions. Such type of weak intermolecular interaction gives rise to a soft and flexible molecular system. This flexibility character and its other properties, which include electronic properties, have made the material attractive for scientific investigations since it has shown possible applications in electronic devices such as light emitting diodes, field-effect transistors (FETs), and solar cells.

The electronic states in disordered semiconductors are localized and the transport of charge carriers occurs by hopping between the localized states. The hopping transitions between localized states and the exchange of electrons between localized and extended states form a variety of complex phenomena that determine the charge carrier transport. we discuss a variety of transport phenomena known as hopping transport mechanisms. The description of the relationship between current density and charge carrier density in disordered organic-semiconductors is complicated by the effects of diffusion and a charge-carrier mobility that depends on the disorder nature of the material, charge concentration, electric field and temperature. With the help of computer simulations, we study the mobility of charge carriers and their corresponding diffusive character at different temperatures. The ratio between mobility and diffusion parameters is derived for a Gaussian like density of states. This steady-state analysis is expected to be applicable to a wide range of organic materials (polymers or small molecules) as it relies on the existence of quasi-equilibrium only. Our analysis shows that there is an inherent dependence of the transport in disordered organic-materials on the charge carrier density.

We investigate the effects of disorder on the external electric field and charge carrier density dependence of the mobility in disordered organic semiconductor with a Gaussian shape of the density of states. The results we found are compared with recently published numerically exact expressions for the dependence of the charge-carrier mobility on the carrier density, temperature and the electric field in such organic semiconductor materials.

We consider the MillerAbrahams expression to describe the hopping rate of charge carriers and employ kinetic Monte Carlo simulation methods to generate data from which we can analyze a charge carrier mobility as a function of applied electric field, temperature, localization length, and energetic

disorder parameters. Based on our results, we discuss the effects of these parameters on charge carrier mobility. Our results show the importance of the energetic disorder parameter and localization length on the effects of temperature dependence on charge carrier mobility, and we also evaluate the value of localization length that has been mostly considered as 0.1a, where a is the lattice parameter. Finally, the temperature dependence is markedly different in single crystals and in disordered materials. In single crystals, the hole and electron mobilities generally decrease with temperature.

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GENERAL LIST OF ACRONYMS

DOS	density of states
FET	field-effect transistor
HOMO	highest occupied molecular orbital
kMC	kinetic Monte Carlo
LED	light-emitting diode
LUMO	lowest unoccupied molecular orbital
OFET	organic field-effect transistor
OLED	organic light-emitting diode
VRH	variable-range hopping
MA	Millar-Abrahams hopping rate
TE	Transport energ

Chapter 1

Introduction

The daily reality, based on consumption life-style, let us easily forget about the concepts of the semi-conductor materials surrounding us. They are a new technology for large area and flexible thin film electronics devices. Low production costs of these materials along with their specific charge transport properties make Such systems extremely favorable [1]. Due to their role in the fabrication of electronic devices, semiconductors are an important part of our lives. Imagine life without electronic devices. There would be no radios, no TV's, no computers, no video games, and poor medical diagnostic equipment. Although many electronic devices could be made using vacuum tube technology, the developments in semiconductor technology during the past 50 years have made electronic devices smaller, faster, and more reliable. Think for a minute of all the encounters you have with electronic devices. How many of the following have you seen or used in the last twenty-four hours? Each has important components that have been manufactured with electronic materials. We just use what someone has produced for us. Nevertheless, it is always good to know what is the crystal structure of the matter like, how the objects of daily used may be produced, and how they may be improved and protected in order to be useful for a long time. Semiconductors materials such as silicon (Si), germanium (Ge) and gallium arsenide(GaAs) have electrical properties some where in the middle between those of a conductor and an insulator. They are not good conductors nor good insulators (hence their name semiconductors). They have very few free electrons because their atoms are closely grouped together in a crystalline pattern called a crystal lattice but electrons are still able to flow, but only under special conditions [2, 3].

The ability of semiconductors to conduct electricity can be greatly improved by replacing or adding certain donor or acceptor atoms to this crystalline structure there by, producing more free electrons than holes or vice versa. That is, by adding a small percentage of another element to the base material, either silicon or germanium. On their own Silicon and Germanium are classed as intrinsic semiconductors, that is they are chemically pure, containing nothing but semi-conductive material. But by controlling the amount of impurities added to this intrinsic semiconductor material it is possible to control its conductivity. Various impurities called donors or acceptors can be added to this intrinsic material to produce free electrons or holes respectively. This process of adding donor or acceptor atoms to semiconductor atoms (the order of 1 impurity atom per 10 million or more atoms of the semiconductor) is called Doping. As the doped silicon is no longer pure, these donor and acceptor atoms are collectively referred to as impurities, and by doping these silicon material with a sufficient number of impurities, we can turn it into an N-type or P-type semi-conductor material [4].

The most commonly used semiconductor basics material by far is silicon. Silicon has four valence electrons in its outermost shell which it shares with its neighboring silicon atoms to form full orbitals of eight electrons. The structure of the bond between the two silicon atoms is such that each atom shares one electron with its neighbor making the bond very stable. As there are very few free electrons available to move around the silicon crystal, crystals of pure silicon (or germanium) are therefore good insulators, or at the very least very high value resistors. Silicon atoms are arranged in a definite symmetrical pattern making them a crystalline solid structure. A crystal of pure silica (silicon dioxide or glass) is generally said to be an intrinsic crystal (it has no impurities) and therefore has no free electrons. But simply connecting a silicon crystal to a battery supply is not enough to extract an electric current from it [5, 6]. To do that we need to create a positive and a negative pole within the silicon allowing electrons and therefore electric current to flow out of the silicon. These poles are created by doping the silicon with certain impurities. Although the valence band of these substances is almost filled and the conduction band is almost empty as in the case of insulators. But the forbidden energy gap between the valence band and the conduction band is very small. Therefore, an electric field, smaller than insulators and greater than conductors is required to push the valence electrons to the conduction

band [6]. Few of the electrons cross the conduction band even at room temperature as some of the heat energy are imparted to the valence electrons. As the temperature increases, more and more number of valence electrons cross over to the conduction band and the conductivity of the material increases. Thus, these materials have negative temperature co-efficient of resistance. In terms of energy bands, semiconductors can be defined as those materials which have almost an empty conduction band and almost filled valence band with a very narrow energy gap (of the order of 1 eV) separating the two [7]. The ratio between mobility and diffusion parameters is derived for a Gaussian like density of states in a disordered organic materials. The electronic carrier mobility in semiconductors is strongly dependent on scattering processes. Mobility is almost constant for low doping concentrations and is basically affected by phonon scattering. At higher doping concentrations, mobility decreases due to scattering by ionized impurities. Values of electron mobility in crystalline semiconductors can be as large as $10^4 cm^2 V^{-1} s^{-1}$ [2, 8, 9].

Drift is charged particle motion under an applied electric field. The hopping transport model describes charge transport in a semiconductor materials. It has been applied to semiconductors materials, such as silicon, and also to organic semiconductors such as Π-conjugated polymers. For a material to be conductive, it must contain some mobile charge carriers which are electrons or holes. We are interested in the movement of these charge carriers, typically in response to an electric field [10]. When transport of electrons or holes in an organic molecular solid is considered, one has to bear in mind that this involves ionic molecular states. In order to create a hole, e.g., an electron has to be removed to form a radical cation M+ out of a neutral molecule M. This defect electron can then move from one molecule to the next. One of the easiest ways to study charge transport in a random distribution of localized states is via Monte Carlo simulation [9, 11, 12, 13]. The essential input parameter is the width σ of the energy distribution or the density of states (DOS). The Monte Carlo simulation reveals that charge carriers tend to relax to an equilibrium level located at $\frac{\sigma}{kT}$ at T = 290K, where T is temperature in Kelvin and k is Boltzmann constant. A simplified model of transport is assumed and the relation between observable quantities such as mobility, diffusion coefficient, electric field, temperature and charge carrier density can be analyzed easily using numerical simulations.

So in this work, using the model described above, we discuss the mobility variation with

temperature for different charge carriers density in disordered organic semiconductors and diffusivity property at thermal equilibrium based computer simulation results. 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 the hopping transport model, effective temperature for hopping transport, hopping rate, charge carrier relaxation and analytical derivation of the equilibration energy [14, 13]. Our methodology will be presented in Chapter 3; which is a kinetic Monte Carlo (MC) method applied for lattice model. In Chapter four, we will present the results of our MC simulations results, and analyze and discuss in detail comparing with the previous related experimental and simulation results. Finally we will present summary and conclusions.

Chapter 2

Organic semiconductor materials

This chapter introduces the principles of the electronic properties of conjugated organic semiconductors and the basic concepts of charge carrier motion in these materials. Organic semiconductors usually have a molecular structure that features alternating single and multiple bonds, which gives rise to overlapping π-orbitals.

2.1 Basic properties of organic semiconductors

An organic semiconductor is the organic material that shows semi-conducting property. Organic small molecules and polymers are representative materials that consist of hydrogen and carbon. They can be crystalline or amorphous structure on thin films depending on the materials. Normally, they are insulators, but convert to semiconductors when charge carriers are introduced by charge injection from electrode, doping and photo-excitation. Semi-conducting properties originated from a conjugated system in carbon atoms. Carbon has four outermost electrons, i.e., a group four element in the periodic table. Each electron occupies separately in 2s, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals. They can be hybridized in various ways that lead to numerous bonding configurations, e.g., sp_1, sp_2 and sp_3 depending on the number of p atomic orbitals that participates in the hybridizations. When 3p atomic orbitals get involved with four neighboring atoms, four sp_3 hybrid orbitals with equal energy are composed. When 2p atomic orbitals get involved with three neighboring atoms, three sp_2 hybrid orbitals are created.

The nature of bonding in organic semiconductors is fundamentally different from their in-

organic counterparts. Organic molecular crystals are van-der-Waals-bonded solids implying a considerably weaker intermolecular bonding as compared to covalently bonded semiconductors like Si or GaAs. As a consequence, the width of the valence (HOMO) and conduction(LUMO) bands is two orders of magnitude lower in organic semiconductors. The energy range between HOMO and LUMO without states is referred to as the energy gap between HOMO and LUMO or sometimes said band gap like that in inorganic semiconductor. The overall splitting among the π orbitals is generally larger for a larger number of atoms and the energetic difference between HOMO and LUMO gets smaller. The situation in polymers is some what different since the morphology of polymer chains can lead to improved mechanical properties. Nevertheless, the electronic interaction between adjacent chains is usually also quite weak in this class of materials [15]. Both have in common a conjugated p-electron system formed by the p^z orbitals of sp^2-hybridized C atoms in the molecules.

In comparison to the σ bonds constituting the backbone of the molecules, π bondi is significantly weaker. Therefore, the lowest electronic excitations of conjugated molecules are the $\pi\pi^*$ transitions with an energy gap typically between 1.5 and 3 eV leading to light absorption or emission in the visible spectral range. In detail, the electronic properties of a molecule depend on factors like the conjugation length or the presence of electron donating or withdrawing groups. Thus organic chemistry offers a wide range of possibilities to tune the optoelectronic properties of organic semi-conducting materials. An important difference between the two classes of materials lies in the way how they are processed to form thin films. Whereas small molecules are usually deposited from the gas phase by sublimation or evaporation, conjugated polymers can only be processed from solution, e.g., by spin-coating or printing techniques. Additionally, a number of low-molecular weight materials can be grown as single crystals allowing intrinsic electronic properties to be studied on such model systems. The controlled growth of highly ordered thin films either by vacuum deposition or solution processing is still a subject of on going research, but will be crucial for many applications.

2.2 Charge Transport in Disordered materials

Charge transport in organic materials is described as hopping between localized states. Charge carrier can then occupy the localized states, which are essentially just orbitals. Transport is then described as hopping between these states. If fluctuations in the intermolecular distances and orientations give rise to a large variation in the site energy and transition probability amplitude compared to the other terms, the static disorder dominates the charge transport [16]. A charge carrier moves by uncorrelated hops in a broad density of states. Thermal activation is required to overcome the energy differences between different sites. Charge transport in conjugated molecules cannot be described by band transport. Localized electronic states frequently dominate the transport in disordered semiconductors. The hopping transitions between localized states and the exchange of electrons between localized and extended states form a variety of complex phenomena that determine the carrier transport mechanisms [2].

The polymer chain exhibits much disorder, caused by kinks and other kinds of defects. The disorder breaks the delocalization of the charge carriers, preventing band transport between different parts of the molecule. Also, inter-chain transport cannot be described using the band model. Instead, charge transport is characterized by hopping: a process in which charge carriers move from an occupied state to an empty state by thermally activated tunneling [17]. In conjugated polymers,hopping is the slowest transport mechanism and therefore the rate determining step. The disordered nature of organic semiconductors also causes the conjugated parts to differ slightly in energy. This can be seen in the broadening of the density of states for the HOMO and LUMO. The density of states for the HOMO and the LUMO are usually approximated by a Gaussian distribution of states for the HOMO. Inside the HOMO/LUMO the charges move by hopping transport [18, 19].

An analytically derived solution for the carrier mobility is not available for hopping based transport. However, Pasveer *et al.* [20] formulated a phenomenological equation to describe the mobility in energetically disordered systems. This equation is based on a numerical solution of the master equation for hopping transport. For conjugated systems it was found that the mobility depends on the electric field strength, the charge carrier densities and the temperature.

2.3 Hopping Transport

The transport in a disordered organic semiconductor occurs by hopping of charge carriers between localized states. It has been applied to amorphous inorganic semiconductors such as amorphous silicon and also to organic semiconductors such as π-conjugated polymers. Electrons and holes are accelerated by the electric fields, but lose momentum as a result of various scattering processes. These scattering mechanisms include deflection by lattice vibrations (phonons), impurity ions, other carriers, surfaces, and other material imperfections. Mobility modeling is normally divided into: (i) low field behavior, (ii) high field behavior, (iii) bulk semiconductor regions and (iv) inversion layers. The low electric field behavior has carriers almost in equilibrium with the lattice and the mobility has a characteristic low-field value that is commonly denoted by the symbol μ_{n_0,p_0} . The value of this mobility is dependent upon phonon and impurity scattering, both of which act to decrease the low field mobility. The high electric field behavior shows that the carrier mobility declines with electric field because the carriers that gain energy can take part in a wider range of scattering processes. The mean drift velocity no longer increases linearly with increasing electric field, but rises more slowly.

For a material to be conductive, it must contain some mobile (free) charge carriers. In our materials, they are electrons or holes. We are interested in the movement of these charge carriers, typically in response to an electric field. The main quantity of interest is the charge carrier mobility μ, defined as the ratio of the average carrier velocity to the electric field F :

$$\mu = \frac{< v >}{F}. \tag{2.3.1}$$

The mobility measures the packets average velocity:

$$\mu = \frac{x}{Ft}. \tag{2.3.2}$$

Frequently, one is interested in how the mobility depends on the electric field F and the temperature T. Sometimes also the dependence on the concentration of charge carriers is studied. The average motion of the charge carriers subjected to an electric field is called drift. The mobility

has a simple relationship to the current density j:

$$j = ne\mu F. \tag{2.3.3}$$

$$\sigma = en\mu \tag{2.3.4}$$

$$\mu = \frac{\sigma}{en} = \frac{1}{\rho en} \tag{2.3.5}$$

$$\mu = \frac{\sigma}{en} = \frac{1}{\rho en} \tag{2.3.6}$$

where n is the concentration of charge carriers, e is their charge, σ is conductivity and ρ is Resistivity. In addition, n and μ are dependent on various parameters such as light intensity, temperature and the band gap in a semiconductor.

2.4 The concept of sites

The defining property for the semiconductor materials we model is that they lack a crystal structure. In these materials, there are localized states for electrons and holes. An electron might be confined to the vicinity of an impurity, to one molecule or to a segment of a conducting polymer,as illustrated in Fig. 2.1. Charge transport in this picture happens when the electrons or holes tunnel from one localized state to another. These tunneling events are the *hops* in hopping transport . The states where electrons or holes can exist are usually said sites. Charge carriers on different sites have slightly different energies, due to differences in their environments. In the case of polymers, the energy is also affected by the length of the polymer segment on which the carrier is localized [21].

2.5 The hopping rate

Hopping transport for disordered organic semi-conductors where the Fermi energy is located with in the mobility gap, 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 transport properties of the material are determined by the rates of the different hopping events.

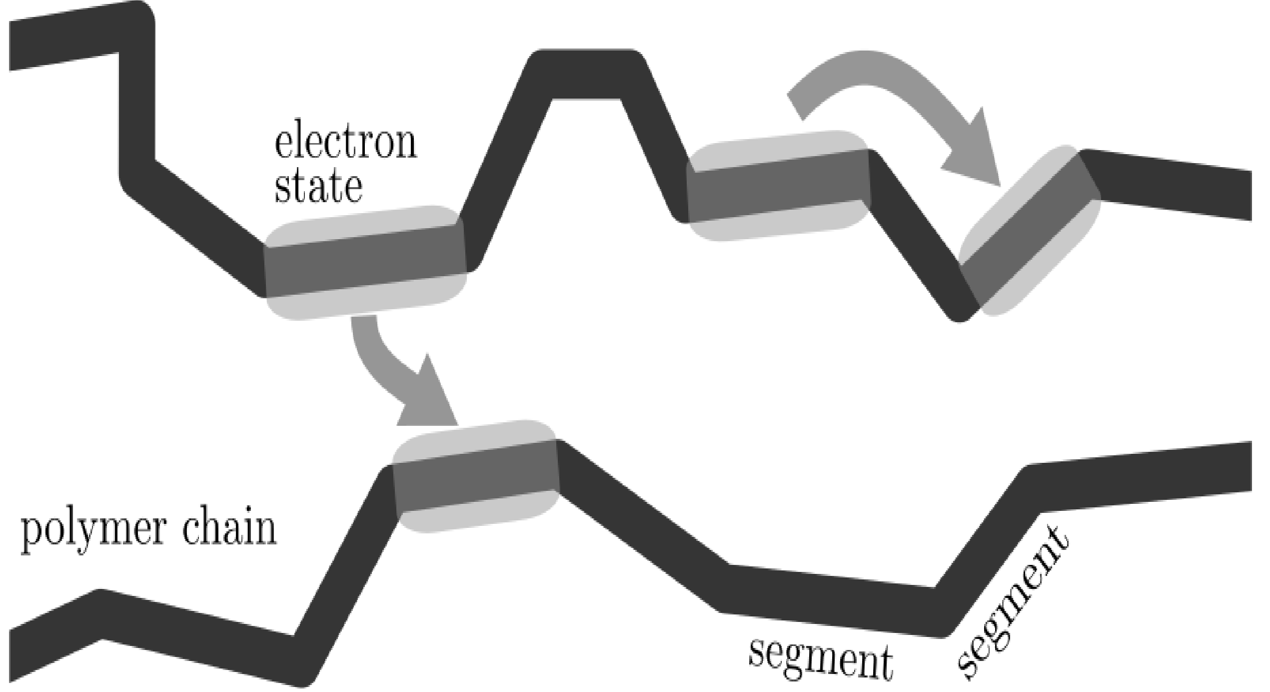

Figure 2.1: Hopping transport in a polymer. A charge carrier is localized to a straight segment of the polymer. It can move by hopping (tunneling) to another segment.

The Gaussian disorder model is the model of thermally-assisted hopping transport within randomly distributed localized states (Fig.2.3). Principal assumptions of the GDM are the Gaussian DOS and the Miller-Abrahams (MA) hopping transition rate.

The MA transition rate is the frequency of charge carrier hopping from an occupied state i to an unoccupied state j, [22].

$$\Gamma_{ij} = \Gamma_0 \exp{(-2\frac{r_{ij}}{\alpha})} \begin{cases} \exp(\frac{-\Delta\varepsilon_{ij}}{KT}) & if \quad \varepsilon_j - \varepsilon_i > 0 \\ 1 & if \quad \varepsilon_j - \varepsilon_i \leq 0 \end{cases} \tag{2.5.1}$$

where T is temperature, k is the Boltzmann constant and Γ_0 is the attempt to escape frequency, typically in the range of 10^{12} to 10^{13} s^{-1} [23, 24], α is localization length of a charge carrier, r_{ij} is the distance between sites i and j. The localization length α describes the spatial size of the electron wave functions of the localized states, while $\Delta\varepsilon_{ij} = \varepsilon_j$ - ε_i is the difference in energy between sites i and j. We see that the hopping rate between sites i and j depends exponentially on both their energy difference and on the distance between them. The factor $exp(-\frac{\Delta\varepsilon_{ij}}{kT})$ for jumps to a higher energy describes the probability of absorbing a phonon with the required

energy.

For hopping in an electric field F as illustrated in Fig. 2.2, the field is taken into account in the energy difference. The energy difference between the sites i and j is then

$$\Delta\varepsilon_{ij} = \varepsilon_j - \varepsilon_i - Fe(x_j - xi), \tag{2.5.2}$$

The general expression formula,

$$U_j - U_i = -eF \mid \overrightarrow{r_j} - \overrightarrow{r_i} \mid \tag{2.5.3}$$

where ε_i is the energy of a charge carrier at site i, e is the elementary charge, and F is the magnitude of the electric field (which is assumed to be directed along the x axis). The electric

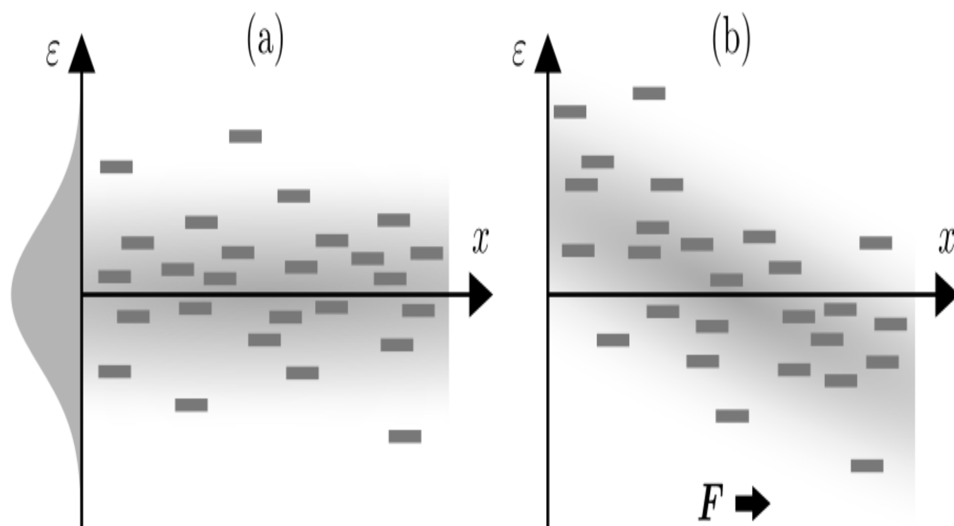

Figure 2.2: Distribution of sites in energy and one spatial coordinate. Figure (a) shows the case without an electric field. In Figure (b) an electric field is applied along the x direction, introducing a slope in the energy landscape.

field, which we just introduced, creates a slope in the energy landscape. As the hopping rate Eq.(2.5.1) favors jumps to lower energies, the charge carriers will on average move along or against the field, depending on their charge. The mobility, introduced above, is a measure of the average drift speed.

In using the MillerAbrahams rate, we assume that the sites have no structure. The hopping rate depends only on the distance between the sites. For a polymer such as the one illustrated

in Fig.2.1. this seems to be a very crude approximation, and it is known that the tunneling rate between organic molecules can be very sensitive to the relative orientation of the molecules [25]. However, in this way, one avoids the need for a detailed model of the polymer structure and the need to compute accurate hopping rates for different orientations, both of which are complicated tasks. It has been shown that already the simple model with the MillerAbrahams hopping rate captures many of the features experimentally observed in conductive polymers and other disordered semiconductors [26, 11]. Another approximation is made in replacing the quantum-mechanical tunneling process by a classical random walk. This is justified when the tunnel- ing rate is small, i.e. when the sites are far apart compared to the localization length. Further, we assume that no delocalized states, or bands, contribute to the transport. This assumption is generally made for disordered organic semiconductors [26, 11, 27]. In contrast, disordered inorganic semiconductors typically have conduction and valence bands, energetically above and below the localized states. In these systems, our assumption is valid if the temperature is so low, that the amount of charge carriers excited to the bands is negligible.Then neling between the localized states dominates the transport, and the hopping transport model described here is applicable. On the other hand, when the bands are important, the multiple-trapping model [28] is more appropriate. To be specific I will assume that the charge carriers are electrons in all cases where only one species of charge carriers are present. Holes behave in the same way as far as the hopping transport model is concerned, except for the sign of the charge.

2.6 Diffusion in the hopping transport

Besides the drift motion of the charge carriers, measured by the drift mobility, one can also measure their random motion, diffusion [29]. The mobility is calculated as

$$\mu = \frac{x}{F t_s} \tag{2.6.1}$$

The diffusion coefficient D measures how quickly a packet of charge carriers broadens:

$$D_{\backslash\backslash} = \frac{< x^2 > - < x >^2}{2t_s}, D_{\perp} = \frac{< y^2 > + < z >^2}{4t_s} \tag{2.6.2}$$

where the averages are taken over different electrons starting from the same position after they have moved for the time t_s. For a two or three-dimensional system in an electric field, the directions along the field and perpendicular to it are not equivalent. In this case, one can define separate diffusion coefficients for the two directions assuming a three-dimensional system with the electric field in the x-direction.

The diffusion coefficient D depends on the temperature T and the electric field F for electrons under going hopping transport. In the limit of small electric field, the diffusion coefficient D and the mobility for electrons and holes are related by the Einstein relation [30] derived below:

$$n = N_c e^{-\frac{E_c - E}{kT}} and \tag{2.6.3}$$

$$p = p_c e^{-\frac{E_c - E}{kT}} \tag{2.6.4}$$

$$J_n = en\mu_n F + eD_n \frac{dn}{dx} \tag{2.6.5}$$

Consider a non-uniformly doped semiconductor. Since the electrons(or holes) are free to move any where in the material, the average energy of the electrons can not change, E_f must be constant when no net current flows and carrier concentration gradients that result in a diffusion current component. Then both electron and hole components must sum to zero.

$$en\mu_n F + eD_n \frac{dn}{dx} = 0 \tag{2.6.6}$$

where

$$\frac{dn}{dx} = \frac{-neF}{kT} \tag{2.6.7}$$

$$en\mu_n F + eD_n(-\frac{neE}{kT}) = 0 \tag{2.6.8}$$

$$0 = \mu_n F - \frac{DeF}{kT} \tag{2.6.9}$$

$$\mu_n = \frac{De}{kT} \tag{2.6.10}$$

then

$$\frac{\mu_n}{D_n} = \frac{e}{kT} \tag{2.6.11}$$

finaly,

$$\frac{\mu_n}{D_n} = \frac{\mu_p}{D_p} = \frac{e}{kT} \tag{2.6.12}$$

As the diffusion coefficient depends on the electric field, we have to ask if the relation is applicable for finite fields. The mobility also depends on the electric field, but the dependence turns out to be much weaker than for the diffusion coefficient.

2.7 Gaussian density of states

The concept of transport energy is the most transparent theoretical approach to describe hopping transport in disordered systems with steeply energy dependent density of states (DOS), in particular in organic semiconductors with Gaussian DOS. It is the number of states that are to be filled by the charge carriers, i.e., electrons and/or holes, at a particular energy. This DOS structure depends on the material properties such as crystallinity. In this section, we will cover several DOS concept that are commonly adopted in the solid state physics. Particularly, Gaussian DOS for organic disordered semiconductors will be highlighted. It 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. The energy distribution of the sites for amorphous materials are assumed to be the exponential and the Gaussian distribution. In inorganic amorphous materials the DOS is described by an exponential distribution

$$g(\varepsilon) = \frac{N}{\varepsilon_0} exp(\frac{\varepsilon}{\varepsilon_0}). \tag{2.7.1}$$

where N is the spatial density of sites (the number of sites per cm^3), ε is the energy of each site while ε_0 is the energy scale of the distribution.

For organic disordered materials the density of states is described by a Gaussian distribution

$$g(\varepsilon) = \frac{N}{\sqrt{2\pi\sigma^2}} exp(-\frac{\varepsilon^2}{2\sigma^2}). \tag{2.7.2}$$

where σ is the width of the energy distribution whose value for disordered organic semiconductors is in the range between 0.05 eV up to 0.15 eV depending on the material [31]. Various universal parameters associated with the Gaussian density of states [32] are the average distance between sites ($a = (N)^{-\frac{1}{3}}$), the normalized carrier density (n= $\frac{N_p}{N}$), the normalized standard deviation of the Gaussian ($\hat{\sigma} = \frac{\sigma}{kT}$), a characteristic electric field ($F_0 = \frac{\sigma}{ea}$), the normalized electric field ($\hat{F} = \frac{F}{F_0}$).

In addition to a Gaussian energy distribution the energies ε_i of different sites are assumed to be independent of each other, or, uncorrelated [33]. The assumption of a Gaussian density of states is supported by measurements of the absorption bands of organic semiconductors, where a Gaussian shape is seen, and by the agreement of the predictions of the hopping transport model with experimental results for organic materials. A Gaussian distribution of site energies is also to be expected if the energy of one site is determined by many independent random contributions [26, 11, 27].

At equilibrium in the zero temperature limit, only the energetically lowest states (states of energy less than or equal to the Fermi energy) are occupied. For the electronic system in a semiconductor, this means that the energetically lowest-lying states are occupied by electrons, i.e., all states below the Fermi level are occupied. All higher states above the Fermi energy are unoccupied. The Fermi energy is the upper energy states occupied at absolute zero temperature. For intrinsic semiconductors it is in the middle of the energy gap. At increasing temperature thermal fluctuations lead to electronic excitations and for intrinsic semiconductor the probability for electrons to occupy states above the energy gap and create holes below the gap increases. The occupation probability for states can be expressed by the Fermi-Dirac distribution function

$$f(E) = \frac{1}{\exp(\frac{E-E_F}{kT}) + 1} \quad when\ T > 0 \tag{2.7.3}$$

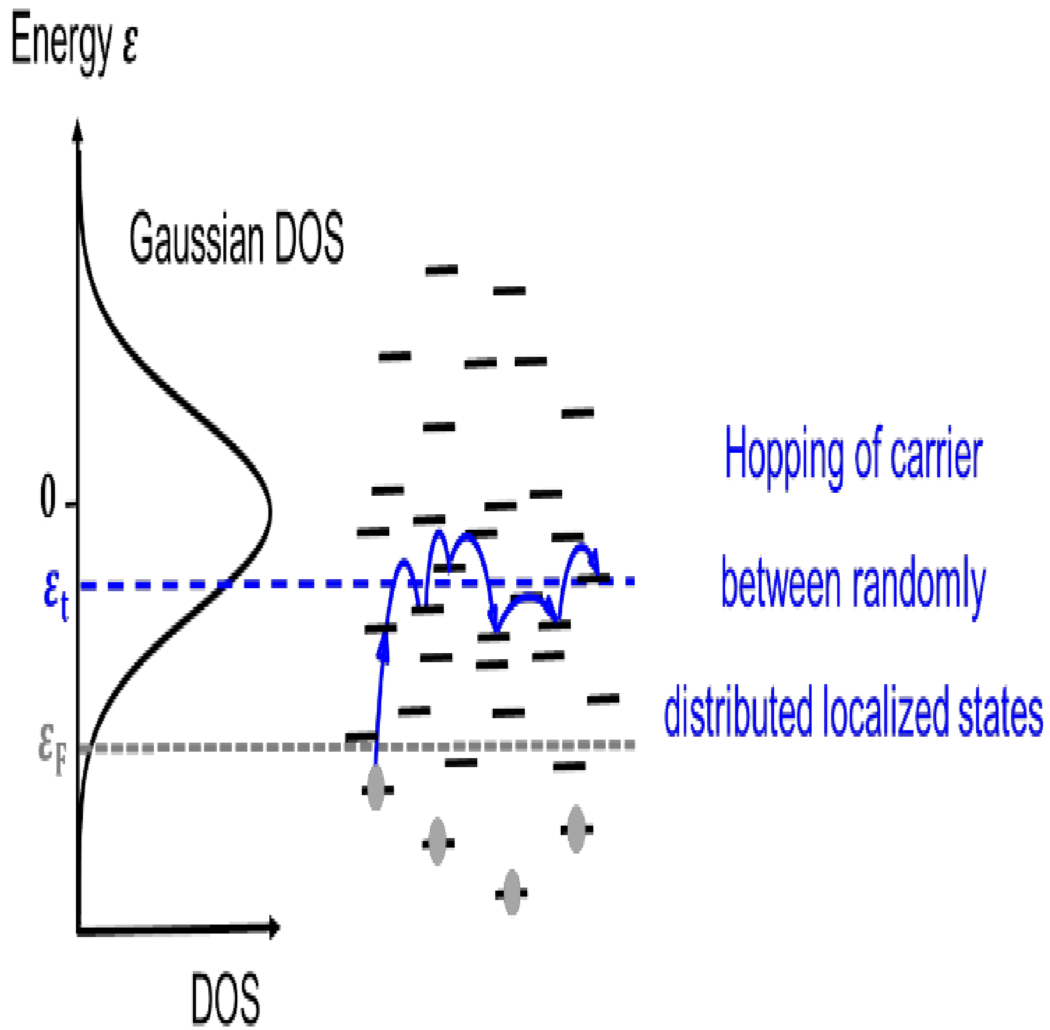

Figure 2.3: Schematic of the Gaussian disorder model in the Gaussian DOS. Charge carriers hop adjacent to the so-called transport energy ε_t.

At absolute zero temperature

$$f(E) = 1 \; when \; E \leq E_F \tag{2.7.4}$$

and

$$f(E) = 0 \; when \; E > E_F. \tag{2.7.5}$$

where E_F is the Fermi level. The value of E_F is determined by the neutrality of the material, i. e., the number of occupied states at finite temperature must equal the number of occupied states at zero temperature limit. In a semiconductor, this means that the number of holes below the band gap equals the number of free electrons above the band gap. At increasing temperature

E_F is shifted towards the energy where the DOS near the gap is smaller [34]. In semiconductors, we usually have $\frac{(E-E_F)}{kT}$ >> 1 and then $exp\frac{(E-E_F)}{k_BT}$ becomes much greater than 1. Therefore, eliminating one we have

$$f(E) = exp(-\frac{E - E_F}{kT}) \tag{2.7.6}$$

2.8 Parameters in the model

The disorder strength, or disorder amplitude, is commonly specified by the standard deviation σ of the energy distribution. It is convenient to express temperature and electric fields compared to the disorder strength, using the dimensionless quantities $\frac{kT}{\sigma}$ and $\frac{eFd}{\sigma}$, where a = $N^{-1/3}$. In the case of a lattice of sites, a gives the lattice constant, while d for randomly placed sites serves as a typical distance from a site to its closest neighbors. The localization length α can also be expressed as the dimensionless quantity α/a. For studying the dependence of the transport parameters on the amount of charge carriers present, one needs the additional parameter n, the (spatial) concentration of charge carriers. With the definitions above, the task in the hopping transport model can be stated more exactly: find the mobility and the diffusion coefficient D of charge carriers, as functions of $\frac{kT}{\sigma}$, $\frac{eFd}{\sigma}$, $\frac{\alpha}{a}$ and $\frac{N_p}{N}$.

The hopping rate (2.5.1) contains the constant ν_0, the frequency of jump attempts. This frequency is commonly assumed to be of the same order of magnitude as the phonon frequency of the material, around 10^{12} to 10^{14} s^{-1} . For simplicity, we will frequently state the results in units where ν_0 = 1 and a = 1.

2.9 Applying the model analytical and numerical

The hopping transport process is controlled by both the energies of the sites and their placement in space. There is a trade-off between short jumps to the nearest neighbors and longer jumps to sites with lower energy. The length of the typical hops is determined by the parameters; a low temperature (in relation to the energetic disorder) and a long localization length (in relation to the site concentration) both make long jumps more favorable. This regime, where the hopping length varies with the temperature and localization length is called variable range hopping [35].

A different behavior appears when the temperature is high and the localization length is short. These conditions favor short jumps, and lead to hopping between nearest neighbors. The typical hopping length is then determined not by the temperature and localization length, but by the distances between the sites. This regime is called nearest-neighbor hopping. A full analytical treatment of the hopping transport process has not been done. Particularly the case with a Gaussian density of states has resisted an analytical treatment. However, several important aspects of the model have been treated analytically. The case of hopping transport in a system of sites with equal energy in a small electric field, has successfully been analyzed with percolation theory. The mobility is seen to depend exponentially on the concentration of sites [35].

The temperature dependence of the mobility in the low-field limit has been understood in Vissenberg and Matters extension of the percolation approach [36]. The temperature dependence of the mobility has also been analyzed using the concept of transport energy [37, 38]. With the transport energy approach, it has been shown that the low-field mobility depends on temperature according to

$$\ln(\mu) \propto \frac{1}{T^2}, \tag{2.9.1}$$

for a Gaussian density of states, when the concentration of charge carriers is negligible. The transport energy treatment has recently been extended to account for the dependence of the transport energy level on the electron concentration [39]. The field and temperature-dependence of the mobility, however, is not easily obtained. In studying charge transport in a material, we are interested in finding the electron flow in response to an electric field F . This flow is known to depend on the temperature T of the material. We are always interested in making the model as simple as possible. Therefore, we investigate if it is possible to express the combined effect of the temperature and the electric field using some combination of T and F . Such a combination of temperature and electric field is called the effective temperature, $T_{eff(T,F)}$. While general analytical solutions to the hopping transport problem are difficult to obtain, the problem is well suited for numerical solutions. Two popular numerical techniques are Monte Carlo simulation of the hopping process and solving balance equations relating the occupation probabilities of the sites and the flow of charge carriers between them. These methods are the topics of the two following chapters.

2.10 Variable range hopping

Variable range hopping (VRH) theory has been applied successfully to describe the temperature dependence of conductivity in organic materials. However, the experimentally observed electric field dependence has been verified only in a small range in high electric field region. In this work, we show numerically using Monte Carlo (MC) simulation methods that the VRH theory can verify the temperature and electric field dependent of conductivity that similar to that verified experimentally.

For a disordered organic semiconductor we assumed that localized states are randomly distributed in both energy and space coordinates, and that they form a discrete array of sites. The presented theoretical calculations are applied to explain recent experiment. A good agreement between theory and experiment is observed. The hopping model mimics the the charge carriers conduction based on the hopping of a charge carrier between different sites separated by randomly distributed distances at different energies. These types of models consider that the hopping from a particular site takes place over a variable distance to the most favorable energy site. Variable range hopping is a model used to describe a carrier transport in a disordered semiconductor or in amorphous solids by hopping in an extended temperature range. It is widely accepted that a charge carrier transport in disordered semiconductors is governed by variable range VRH among the system of localized states. As it was put forward by Mott [40], 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 semiconductors. Whereas at low temperature the probability of NNH decreases. In this situation between two sites whose transfer integral is smaller leads the activation energy to be small and hopping is most probable over a long distance known as variable range hopping. The VRH model 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 [2].

2.11 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 [41] 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. As suggested recently [42] a computer algorithm 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 [43].

2.12 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 [44]. The time required to reach this equilibrium distribution (called the relaxation time) τ_r is of key importance for the analysis of experimental results [45]. Indeed, at time scales shorter than 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_r , 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 other words, at ($t = \tau_r$) 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.

2.13 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 (2.11) 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 $\frac{-\sigma^2}{kT}$.

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 ($\frac{N}{n} << 1$) [28]. 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. From Eq.(2.7.3) which means

$$f(\varepsilon, \varepsilon_f) = [exp(\frac{\varepsilon - \varepsilon_f}{kT}) + 1]^{-1} \approx exp - (\frac{\varepsilon - \varepsilon_f}{kT}) \tag{2.13.1}$$

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

$$g(\varepsilon)f(\varepsilon, \varepsilon_f) \approx g(\varepsilon)exp(\frac{-\varepsilon}{kT})exp(\frac{\varepsilon_f}{kT}) \tag{2.13.2}$$

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 $g(\varepsilon)exp(\frac{-\varepsilon}{kT})$. It is therefore calculated as

$$\langle \varepsilon_\infty \rangle = \frac{\int_{-\infty}^{\infty} \varepsilon g(\varepsilon)f(\varepsilon)d(\varepsilon)}{\int_{-\infty}^{\infty} g(\varepsilon)f(\varepsilon)d(\varepsilon)} \tag{2.13.3}$$

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.(2.13.3), by their values from Eq.(2.7.2) and Eq.(2.13.1) an expression for ε_∞ becomes

$$\langle \varepsilon_\infty \rangle = \frac{\int_{-\infty}^{\infty} \varepsilon exp(\frac{-\varepsilon^2}{2\sigma^2})exp(\frac{-\varepsilon}{kT})d(\varepsilon)}{\int_{-\infty}^{\infty} exp(\frac{-\varepsilon^2}{2\sigma^2})exp(\frac{-\varepsilon}{kT})d(\varepsilon)} \tag{2.13.4}$$

The constant term of Eq.(2.7.2), $\frac{N}{\sqrt{2\pi\sigma^2}}$, in the above equation is already taken out from both the integrals and canceled each other. So now Eq.(2.13.4) can be evaluated by using the integration by parts method.
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= $\int_{-\infty}^{\infty} exp(\frac{-\varepsilon}{kT})d(\varepsilon)$, and v = $-kTexp(\frac{-\varepsilon}{kT})$,
so applying the formula of integration by parts, the equation becomes

$$-kTexp(\frac{-\varepsilon}{kT})exp(\frac{-\varepsilon^2}{2\sigma^2}) \mid_{-\infty}^{\infty} - \frac{kT}{-\sigma^2}\int_{-\infty}^{\infty} \varepsilon exp(\frac{-\varepsilon^2}{2\sigma^2})exp(-\frac{\varepsilon}{kT})d(\varepsilon) \tag{2.13.5}$$

$$0 - \frac{kT}{-\sigma^2}\int_{-\infty}^{\infty} \varepsilon exp(\frac{-\varepsilon^2}{2\sigma^2})exp(-\frac{\varepsilon}{kT})d(\varepsilon) \tag{2.13.6}$$

The first term of the equation vanishes when it is evaluated from $(-\infty)$ to (∞) , and the remaining term (second term) of Eq.(2.13.5) is replaced for the denominator of Eq.(2.13.3) and the final equation can now be written as

$$\langle \varepsilon_\infty \rangle = \frac{-\sigma^2}{kT} \frac{\int_{-\infty}^{\infty} \varepsilon exp(\frac{-\varepsilon^2}{2\sigma^2}) exp(\frac{-\varepsilon}{kT}) d(\varepsilon)}{\int_{-\infty}^{\infty} \varepsilon exp(\frac{-\varepsilon^2}{2\sigma^2}) exp(\frac{-\varepsilon}{kT}) d(\varepsilon)} \tag{2.13.7}$$

From eq.2.13.7

$$\langle \varepsilon_\infty \rangle = \frac{-\sigma^2}{kT}, \tag{2.13.8}$$

and this equals to

$\langle \varepsilon_\infty \rangle = \hat{\sigma}\sigma$ where $\hat{\sigma} = \frac{\sigma}{kT}$

Using the formula we got in Eq.(2.13.8), the equilibration energy can be calculated for different values of $(\frac{\sigma}{kT})$ as shown below. We keep the same parameter of $(\frac{\sigma}{kT})$ and calculate $\mu \propto \frac{100}{T}$ and $(\frac{100}{T})^2$ using kMC simulation method. The disorder parameter in our case is taken 0.15eV, since the energy disorder of most organic semi-conductors ranges from 0.05eV to 0.15eV.

Chapter 3

Methodology

3.1 Monte Carlo Simulation Method

Monte Carlo Simulation, also known as the Monte Carlo Method or a multiple probability simulation is a mathematical technique which is used to estimate the possible outcomes of an uncertain event. The Monte Carlo Method was first used by John von Neumann and Stanislaw Ulam during World War II to improve decision making under uncertain conditions. It was named after a well known casino town, called Monaco, since the element of chance is core to the modeling approach, similar to a game of roulette. They are a broad class of computational algorithms that rely 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 first Monte Carlo methods were developed during the 1940s within the Manhattan project to study diffusion of coefficient in materials, and the Metropolis algorithm was originated during that time. Since then until today this algorithm is a convenient technique to study equilibrium properties of physical systems. However, the Metropolis algorithm is not capable of modeling the time-dependent evolution of a system. The Monte Carlo (MC) simulation approach which is used to find charge transport properties in disordered semiconductors is known as kinetic Monte Carlo. It is the most popular and widely used tool in this field of research. Since Monte Carlo methods use random numbers, it is necessary to know how the random numbers are generated. As we mentioned above, there are a number of good methods for generating random numbers [46, 47].

3.1.1 Kentic Monte Calo Algorithm

Monte Carlo (MC) simulations refer to a broad class of numerical algorithms utilizing random numbers to solve real-world problems. The first Monte Carlo methods were developed during the 1940s within the Manhattan project to study neutron diffusion in fissionable materials. During that time, the Metropolis algorithm [48] originated, which is until today a convenient technique to study equilibrium properties of physical systems. However, the Metropolis algorithm is not capable of modeling the time-dependent evolution of a system. The kinetic Monte Carlo method is a specific MC method that allows propagating a physical system from state to state including the corresponding time information of the propagation steps. Therefore, kMC simulations are often termed simulated experiments because they essentially mimic the explicit evolution of a real-world system. The step by step evolution, where each time-step depends only on the previous one, fulfills the properties of a Markov chain and makes the kMC algorithm a sequential algorithm. kMC methods have gained large popularity in a variety of fields due to their ease of implementation and the increasing computational power of modern computers. The modern version of the kMC method is based on the work of Gillespie [49] and Bortz et al. [50]. For further information for the reader, an illustrative description of the method was provided by Voter [51]. In the kMC calculation, a certain number of carriers are allowed to jump between neighboring traps. In this work, we study the influence of temperature on mobility and diffusivity of charge carriers using kMC simulation method. We consider holes or electrons as charge carriers and limit the study to the low charge carriers density keeping the electric field constant so that the interactions between charge carriers in the simulations is neglected.

The hopping rate of each charge carrier is found in a simulation, and only one charge carrier that can transit the system to neighboring state is given a chance to hop to a position which 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 given by Eq.(2.5.1). The total rate of hopping of all charge carriers is used to randomly choose the carrier dwell time on each site. During the simulation the distance that the carriers travel in each state transition and the simulation time is stored. The transport coefficient such like the mobility can hence be evaluated from the ratio of the average velocity of a charge carrier and F.

3.1.2 Model of the simulation

The sample material is modeled as a simple cubic lattice of L_x, L_y, L_z sites where L_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 constant applied electric field applied along the dimension of the system.

Low charge carrier mobility is one key factor limiting the performance and applicability of devices based on organic semiconductors. Theoretical studies on mobility using the kinetic Monte Carlo or master equation are mainly based on a Gaussian energetic disorder and regular cubic lattices. In this work, we investigate the influence of spatially correlated site energies and spatial disorder in the lattice sites on the mobility using kinetic Monte Carlo simulations [52]. The simulation is performed on a regularly arranged three dimensional lattice sites, with the assumption that the hopping among the lattice sites is governed by the Miller-Abrahams rate equation in which the jump rate Γ_{ij} of the charge carrier from site i to site j is given by Eq. (2.5.1). We only consider the situation of uncorrelated Gaussian disorder model. The energies ε_i and ε_j are randomly drawn from the Gaussian density of states given by Eq.(2.7.2). These disordered energies are uncorrelated. Each simulation step starts with a random distribution of a certain number (N_p) of charge carriers provided that N_p divided by the total number of sites ($L_x \times L_y \times L_z$) 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 charge carrier density, we neglect the effect of electrostatic interactions. The number of charge carriers we considered are 5, 10, 50 and 100, and the total number of sites is $N = Lx \times L_y \times L_z = 100 \times 100 \times 100$ or expressed in terms of density as $\frac{N_p}{N} = \frac{5}{100\times100\times100a^3} = \frac{5}{10^6a^3} = 5 \times 10^{-6}a^-3$,
$\frac{N_p}{N} = \frac{10}{100\times100\times100a^3} = \frac{10}{10^6a^3} = 1 \times 10^{-5}a^-3$
$\frac{N_p}{N} = \frac{50}{100\times100\times100a^3} = \frac{50}{10^6a^3}, = 5 \times 10^{-5}a^{-3}$
and
$\frac{N_p}{N} = \frac{100}{100\times100\times100a^3} = \frac{100}{10^6a^3} = 1 \times 10^{-4}a^{-3}$
where a is a lattice parameter which is about 1 nm for disordered organic semiconducter.

3.1.3 Simulation procedure

The kinetic Monte Carlo (kMC) method is a Monte Carlo method computer simulation intended to simulate the time evolution of some processes occurring in nature. Having laid the conceptual foundation, it is now straightforward to design a stochastic algorithm that will propagate the system from state to state correctly. Our simulation procedures begin by the formation of the three dimensional lattice of $100 \times 100 \times 100$ 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 nearest neigbouring sites. 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 to choose the charge carrier with a large probability of hopping. 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 [43]

$$p_{i,j} = \frac{\Gamma_{i,j}}{\sum_{l}^{N_p} \sum_{j}^{26} \Gamma_{i,j}} \tag{3.1.1}$$

where i = 1,2,3,...,N_p,   j=1,2,3,...,26

and j counts the possible nearest neighboring sites for each charge carrier from one to, say, 26 and i counts the number of charge carriers from one to the last, say N_p . Equation (3.1.1) ensures that a detailed balance condition is satisfied in the steady state condition. This is the probability of hopping for particle i from site i to site j. Obviously

$$\sum_{i}^{N_p} \sum_{j}^{26} p_{i,j} = 1 \tag{3.1.2}$$

and, therefore, these probabilities generate a sequence of length intervals between 0 and 1, and the transition from one configuration to another takes place by one of the N_p charge carriers along one path. This means that we use the probability length for each path and realize a transition of a system of charge carriers from one configuration to another by moving one of the charge carriers based on a stochastic approach, i.e., the summation is done over all possible hops of all the particles and the total probabilities are normalized to 1. To decide for a particular hop, we generate a random number R from a uniform distribution in the interval between 0 and 1, which points at a particular interval and consequently at a particular destination site to which one of the charge carriers jumps with the scheme [53], in general balance equation

$$\sum_{i=0}^{N_p-1} \sum_{j}^{l-1} p_{i,j} \leq R < \sum_{i}^{N_p} \sum_{j}^{l} p_{i,j} \tag{3.1.3}$$

where we have defined P 00 = 0. We have restricted the possible destination sites j in Eq.(3.1.1) to the 26 nearest neighbor sites in an average volume of 3 x 3 x 3 lattice sites. Even if more number of possible destinations is involved, a vast majority of the hopping events occur to the nearest neighbor sites, and the effect of this restriction is negligible. This step is repeated for a certain number of MCTSs until enough data are recorded. One MCTS corresponds to moving one charge carrier after choosing from all charge carriers, according to the procedure described above. The mean dwelling time τ_{av} at site i is given by

$$\tau_{av} = \frac{1}{\sum_{i}^{N_p} \sum_{j}^{26} \Gamma_{i,j}}, \tag{3.1.4}$$

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

$$\tau = \tau_{av}[ln(1-r)], \tag{3.1.5}$$

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 5.5×10^6 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. The process is repeated in such a way that for each transition state the carrier that happens to have a minimum hopping time moves and the time is advanced by time intervals of variable size τ. The displacement of the charge carriers along the length in the direction of F per unit time gives velocity, and the mobility of the charge carriers is obtained from the ratio of the velocity to applied electric field. This means that we obtain detailed information regarding the transport properties of charge carriers. Finally, the simulation data are collected as a function of the charge carrier density, electric field F, and temperature T for different localization length. Our simulation procedure is repeated for different values of temperature or $(\frac{\sigma}{kT})$.

Chapter 4

Results and Discussions

In our simulation results we mainly discuss the influence of the disordered energetic parameter on the temperature dependence of a charge carrier mobility for different values of the localization length and electric field F. The temperature dependence of the mobility has also been analyzed using the concept of the hopping transport in disorder organic semiconductor materials. The mobility is expressed mostly in terms of lattice parameter a, disorder energy parameter σ, a unit charge on electron e, and phonon frequency ν_0 (or in units of $\frac{ea^2\nu_0}{\sigma}$). When these parameters are known explicitly, the mobility is also expressed explicitly. The range of the magnitudes of electric field used for our calculations is chosen to highlight regimes of different transport behaviors. The charge carrier hopping rarely occurs when the localization length is small (or the state is strongly localized) at a relatively high in a lower electric field region.

It has been shown that for disordered organic semiconductors whose density of is Gaussian the mobility depends on temperature according to $ln(\mu) \propto T^{-1}$ when the charge carriers density is high and $ln(\mu) \propto T^{-2}$ for low charge carriers density. We considered a disordered material of Gaussian DOS with a Gaussian width σ. We calculated the mean energy and mobility of charge carriers in disordered organic semiconductors in three dimensional system for different values of $\frac{\sigma}{kT}$. The results of our kMC calculations are shown by the plots in Figs. (4.1 to 4.12). Hopping transport for disordered organic semiconductors where the Fermi energy is located with in the mobility gap, the charge transport is taking place in the localized states. For hopping transport increasing the temperature of the system increases the number of available phonon and charge

carriers become more energetic. In the contrary reducing the temperature reduces the number of available phonon and their respective mean energy of charge carrier.

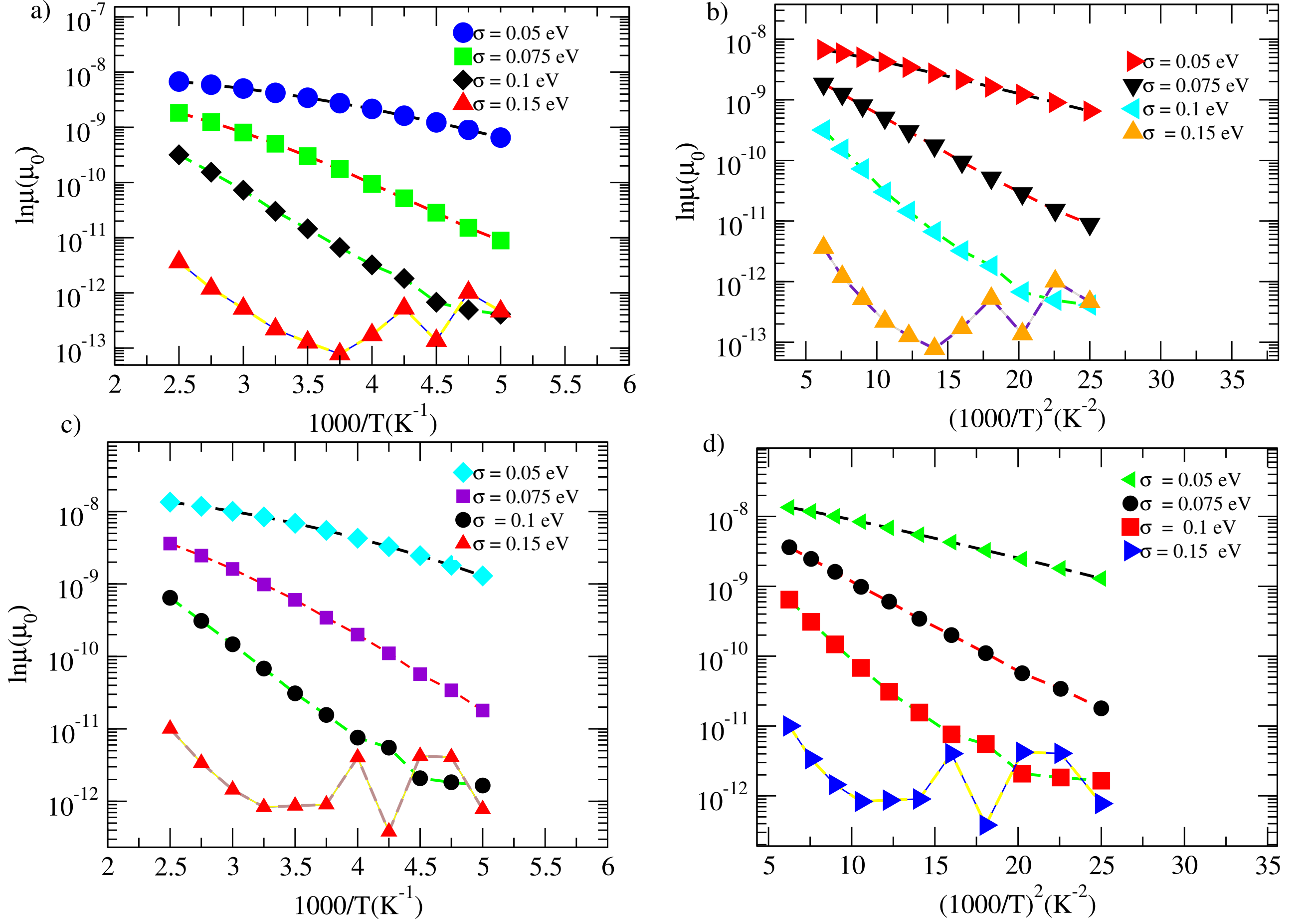

Figure 4.1: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for the same $\alpha = 0.1a$, for different values of electric field $\mathrm{F} = 0.08(\frac{\sigma}{ea})$ and different values of Gaussian width ($\sigma = 0.05$ eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5 \times 10^{15} cm^{-3}$ and that in c) and d) is $n = 1 \times 10^{16} cm^{-3}$, where $\mu_0 = \frac{ea^2\nu_0}{\sigma}$.

From the plots shown in Figs. (4.1) to (4.6) we observe that the energy distribution width sigma (σ) characterizes the the dependence of mobility on temperature. For all the values of σ we considered we see that the mobility increases with the increase of temperature. But, the change of mobility with temperature is more pronounced when σ gets larger. Apart from this we also see the decrease of mobility with the increase of σ. The increase of mobility with temperature has been rationalized for disordered organic semiconductors in the earlier studies [11, 40].

The simulation results for a charge carrier mobility versus T^{-1} and T^{-2} respectively, for fixed electric fields at F $=0.08 \times \frac{\sigma}{ea}$ are presented in all Figures. The mobility as well as the charge carriers densities and temperature are expressed (on a logarithmic scale) in units of $\mu_0 = \frac{ea^2\nu_0}{\sigma}$

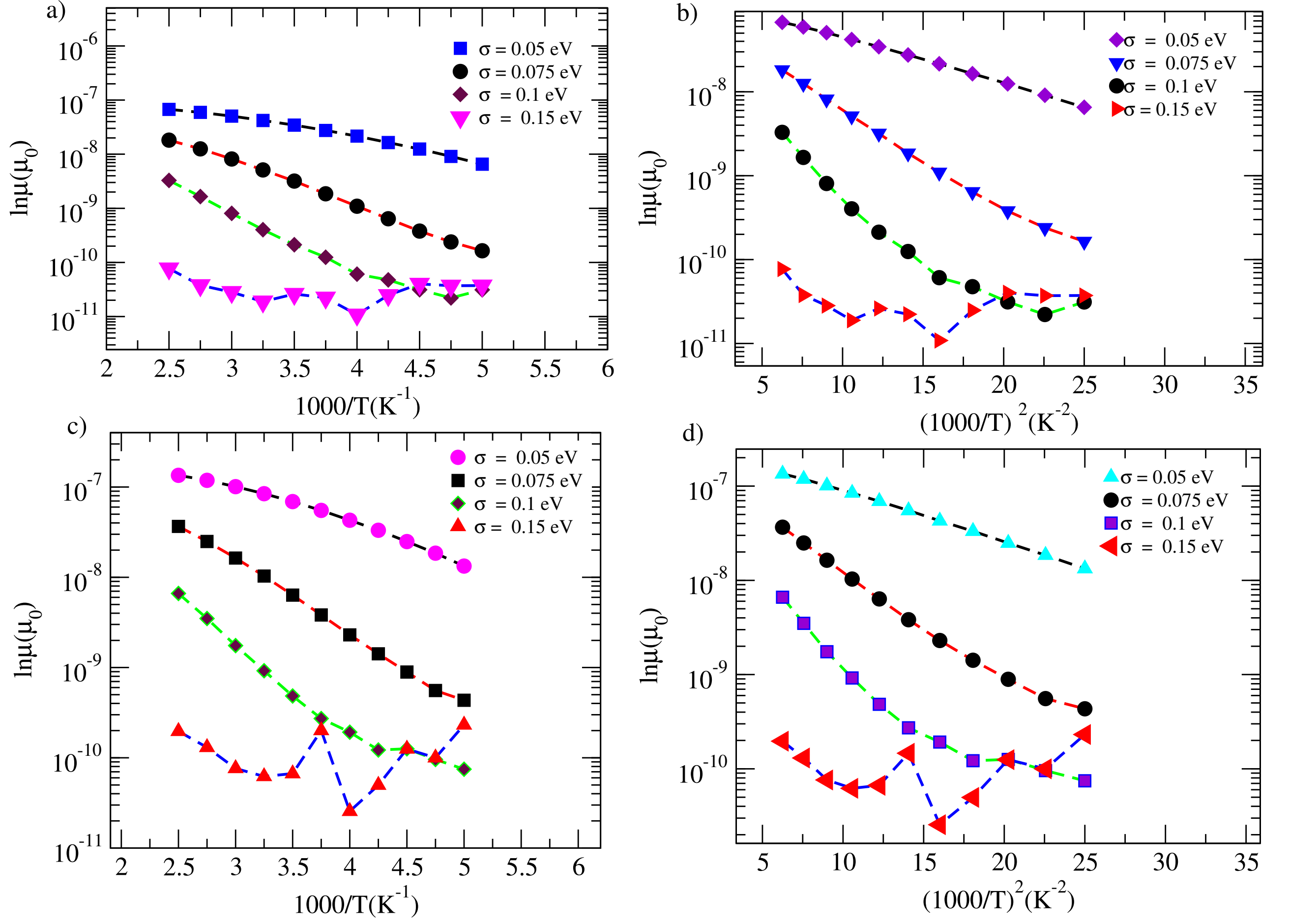

Figure 4.2: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for the same $\alpha = 0.1a$, different value of $F = 0.08[\frac{\sigma}{ea}]$ and different values of Gaussian width (σ = 0.05 eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5 \times 10^{16} cm^{-3}$ and that in c) and d) is $n = 1 \times 10^{17} cm^{-3}$.

and cm^{-3} for two different values of localization length $=$ 0.1a, 0.2a, 0.3a and different energetic disorder

In all the figures where are broken curves, the broken curves represent the mobility calculated for the hopping on randomly distributed states, and ones represent the mobility calculated for the hopping on regularly distributed states excluding the spatial disorder. Our discussion will be based on the results temperature dependence of charge carrier mobility when we compare the results represented by broken curve in panels.

We first presents charge carrier mobility as a function of electric field for different values of $\hat{\sigma}$ $= \frac{\sigma}{kT}$ and also three different values of localization length(α). Mobility is plotted on a logarithmic scale and the electric field is expressed in units of $\frac{\sigma}{ea}$ for $\hat{\sigma}$ in the range from 2.5 to 5 for different values of localization length, α = 0.1a, 0.2a, 0.3a and for the same density as shown in Figures

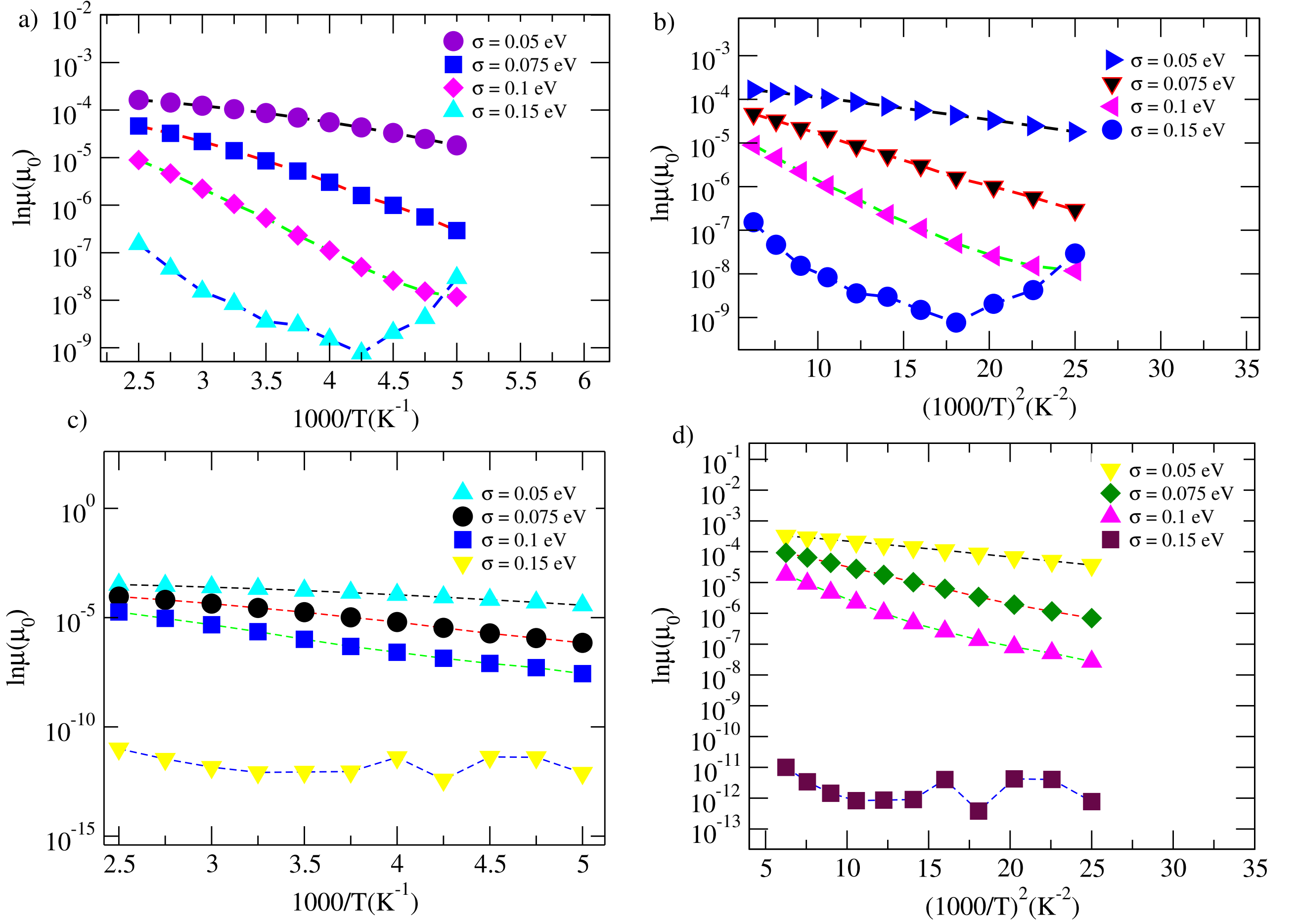

Figure 4.3: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for the same $\alpha = 0.2a$, different value of F $= (0.08)[\frac{\sigma}{ea}]$ and different values of Gaussian width ($\sigma = 0.05$ eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5{\times}10^{15}cm^{-3}$ and that in c) and d) is $n = 1 \times 10^{16}cm^{-3}$.

4.1(a,(b),4.3(c, d) and 4.5(a,d). The plots in the figures indicate that increasing the disorder energy decreases the mobility, but the temperature dependence of the mobility increases with the increase energy distribution width. For smaller σ the charge carrier mobility increases very slowly or remains stationary with temperature for the same electric field, whereas at a higher value of σ the charge carrier mobility increases increases relatively sharply.

The difference is that apart from the shift (increase) in values with the decrease in σ the mobility increases with the electric field and saturates at nearly the same value of the electric field for all values of n. An increase in electric field is seen to increase mobility in disordered materials for the low field region, but a decrease in mobility is observed at high fields. The field dependence in the range $10^4 - 10^6$ $\frac{V}{cm}$ nearly shows $\mu(F) = \mu_0 e^{\gamma}\sqrt{F}$ a Poole-Frenkel behavior.

The curves in panels of Figure 4.1 to 4.12 show that the mobility in the lower electric field

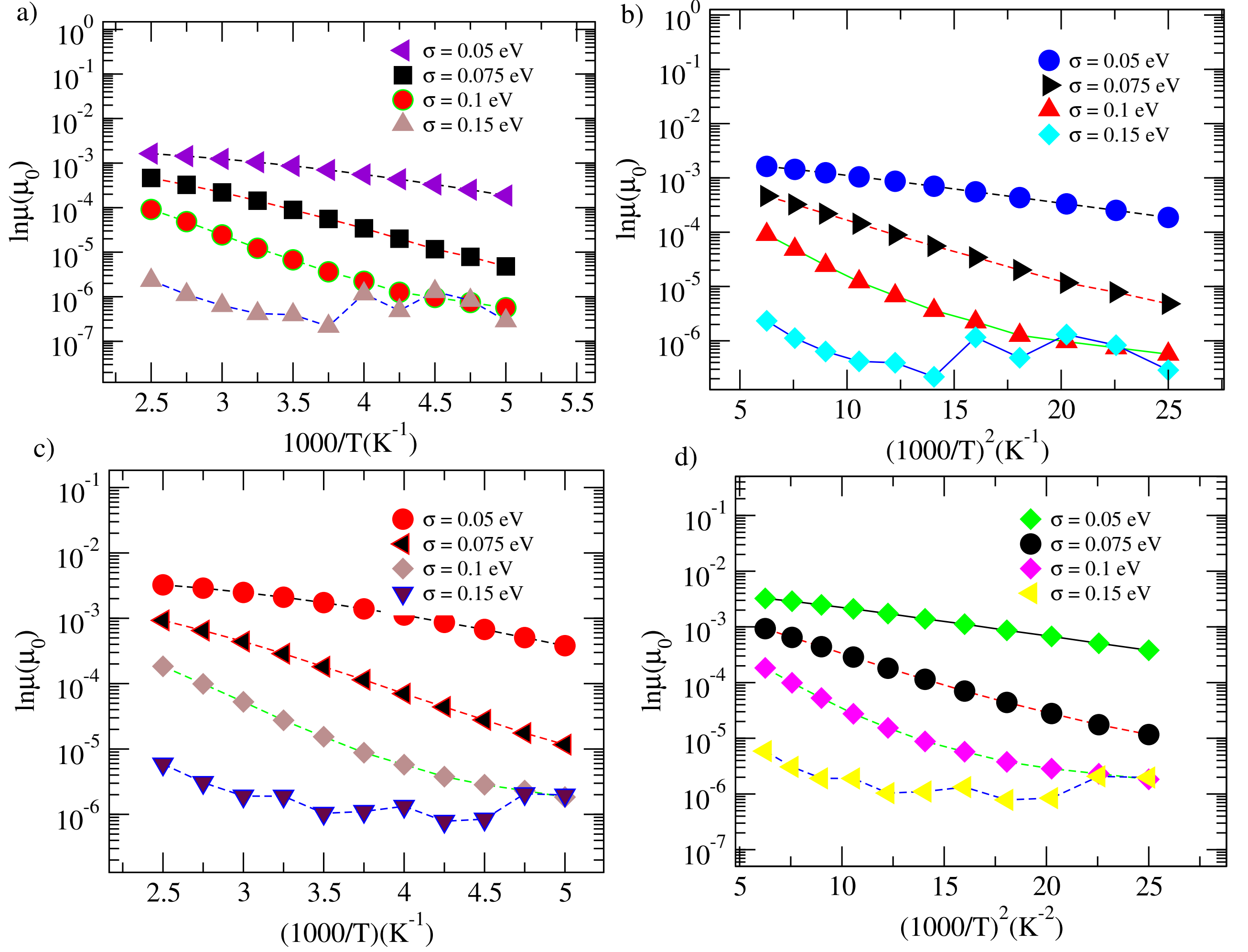

Figure 4.4: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for $\alpha = 0.2a$,for different values of F $= (0.1)\frac{\sigma}{ea}$ and different values of Gaussian width ($\sigma = 0.05$ eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5 \times 10^{16} cm^{-3}$, and that in c) and d) is $n = 1 \times 10^{17} cm^{-3}$.

region decreases with the increase of $\hat{\sigma}$ as verified and justified in the previous section. In the lower electric field region the mobility is more influenced by temperature than electric field, the transport mainly occurs due to diffusion and the mobility remains almost constant. At an electric field larger than $\frac{\sigma}{ea}$ the impact of activation barriers on a charge carrier hopping decreases with the increase of the electric field and the conduction is dominantly caused by the drift due to the field, and the mobility increases with the electric field until a saturation value is attained corresponding to each greater than 2.5. Whereas, for the lower value of localization length, = 0.1a, mobility increases with the electric field until it reaches saturation. The change becomes significant when $\hat{\sigma}$ gets larger. The saturated mobility values for different $\hat{\sigma}$ are nearly the same and reach at nearly the same electric field provided that is the same. The reason for the

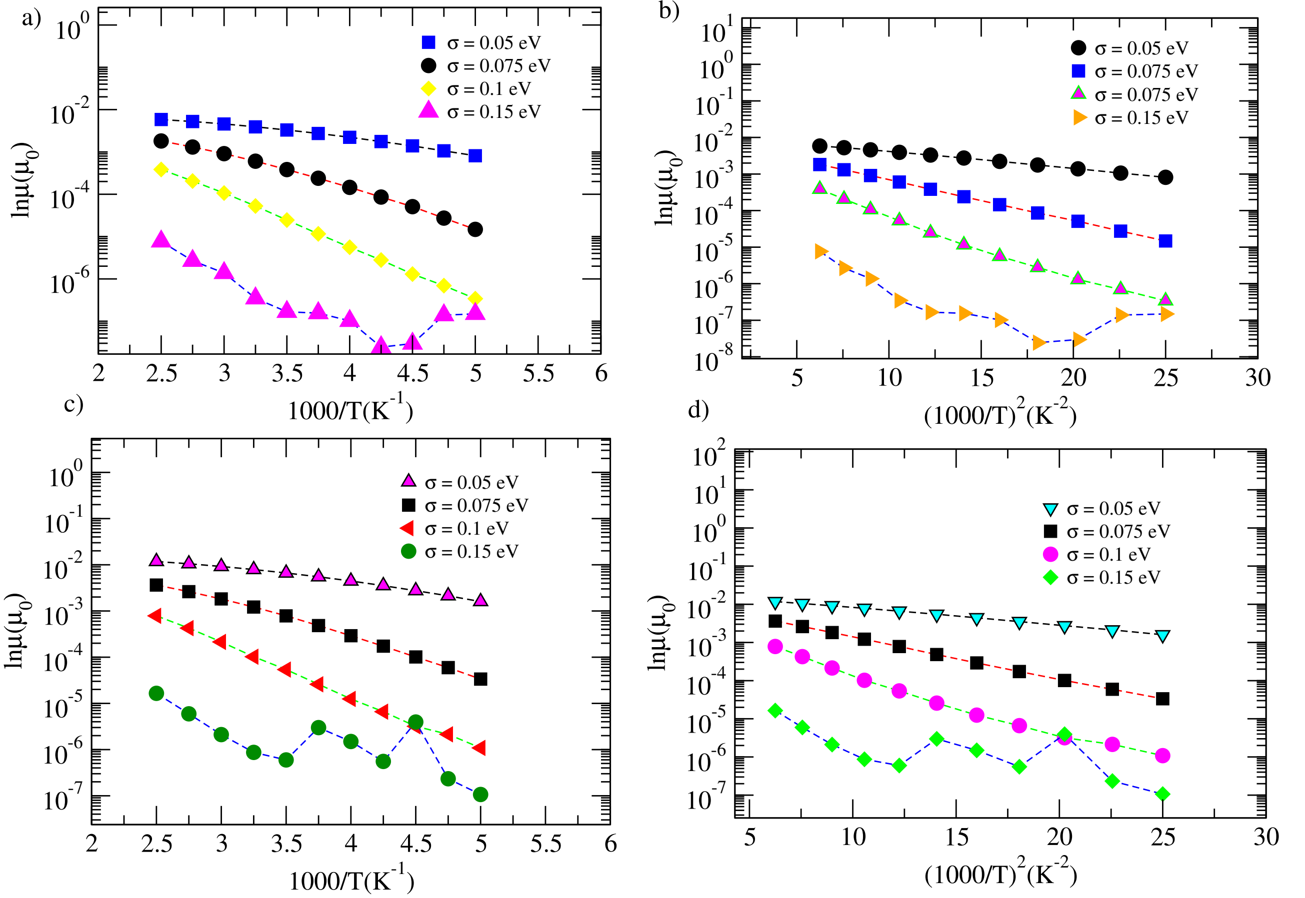

Figure 4.5: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for same value $\alpha = 0.3a$, for different value of F $= (0.1)[\frac{\sigma}{ea}]$ and different values of Gaussian width (σ = 0.05 eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5 \times 10^{15} cm^{-3}$ and that in c) and d) is $n = 1 \times 10^{16} cm^{-3}$.

occurrence of saturation is due to the fact that the electric field reduces the barrier height for an energetic uphill jumps from the transport energy level in the field direction and thereby enhances the mobility in the hopping conduction of charge carriers as described in previous. The drift mobility is calculated from the $\mu = \frac{v}{F}$ relation which leads to mobility reduction with the increase of electric field, where v is the drift velocity of a charge carrier due to the electric field (F). This means that increasing the electric field is more effective in reducing the activation barrier, though it also reduces mobility, until the electric potential energy difference between any two sites separated by a distance x along the electric field, eFx, approaches (but does not surpass) the energy scale σ. If eFx is greater than an excess energy from eFx above which is the same as eFx - σ does not have any contribution to speed up hopping conduction but reduces mobility since it appears in the mobility calculation, $\mu = \frac{v}{F}$. We can also interpret eFx as an energy that

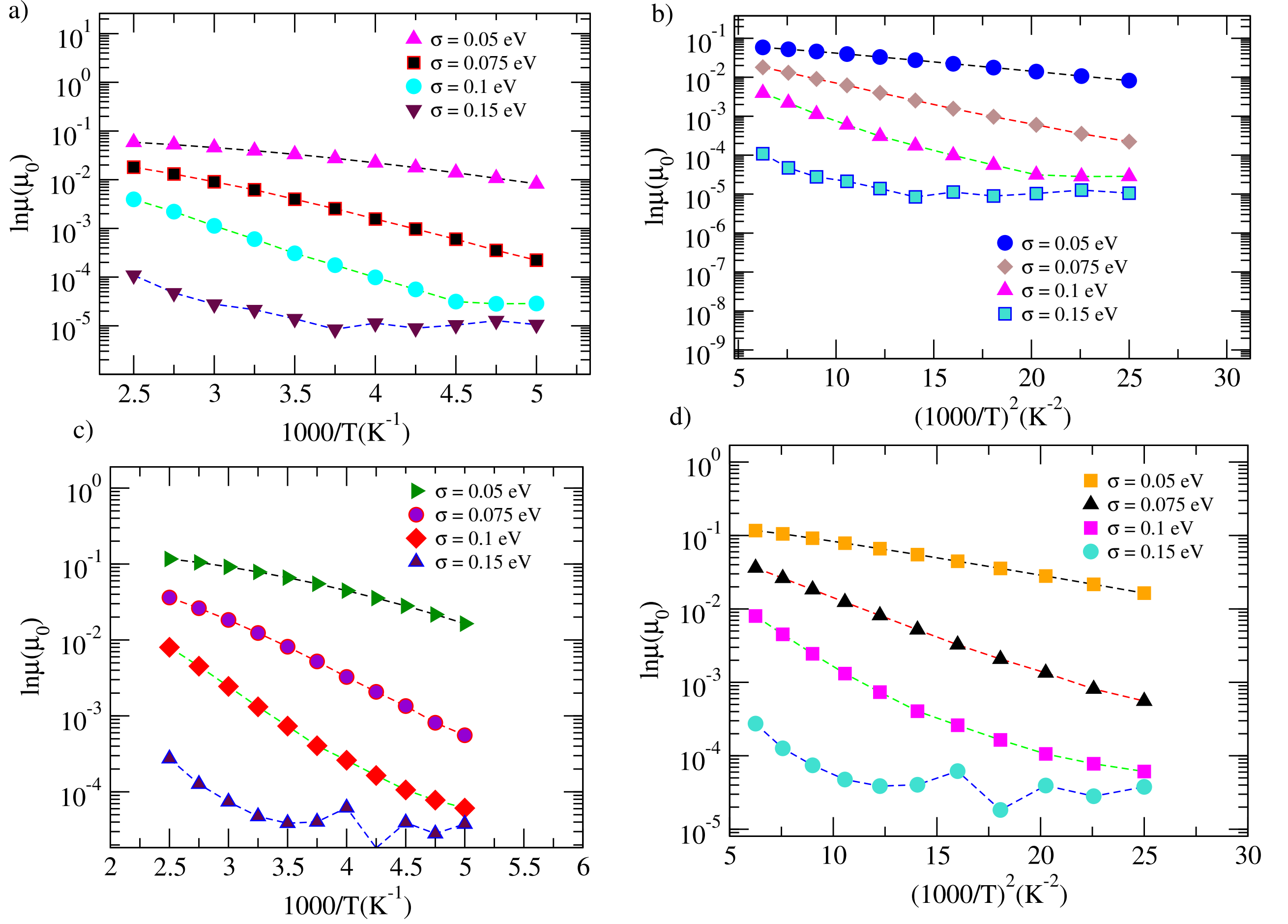

Figure 4.6: Mobility as a function of temperature plotted as $\ln(\mu)$ versus T^{-1} and T^{-2}, respectively, for $\alpha = 0.3a$, F $= (0.08)[\frac{\sigma}{ea}]$ and different values of energy distribution width ($\sigma = 0.05$ eV to 0.15 eV). The charge carriers density in panels a) and b) is $n = 5 \times 10^{16} cm^{-3}$, and that in c) and d) is $n = 1 \times 10^{17} cm^{-3}$.

reduces the activation barrier, and the increase of mobility with electric field is effective provided that the difference between eFx and the average activation barrier height between hopping sites separated by a distance x is significant. The reference energy value we took here, σ, to justify the statement that electric field raises mobility until eFx reaches σ may not be exact and needs experimental verification though it makes sense and seems reasonable.

Due to this reason the effect of electric field in increasing the mobility is more significant for the larger . Similarly, temperature plays a crucial role in reducing the difference between the energies at the transport level and that of the hopping particle at the equilibrium level as discussed previous. Most of the broken curves in all Figure show an overall similar behavior except that there is an increase of mobility with the increase of localization length. We also observe that the mobility saturates at a lower electric field in the case of a larger localization

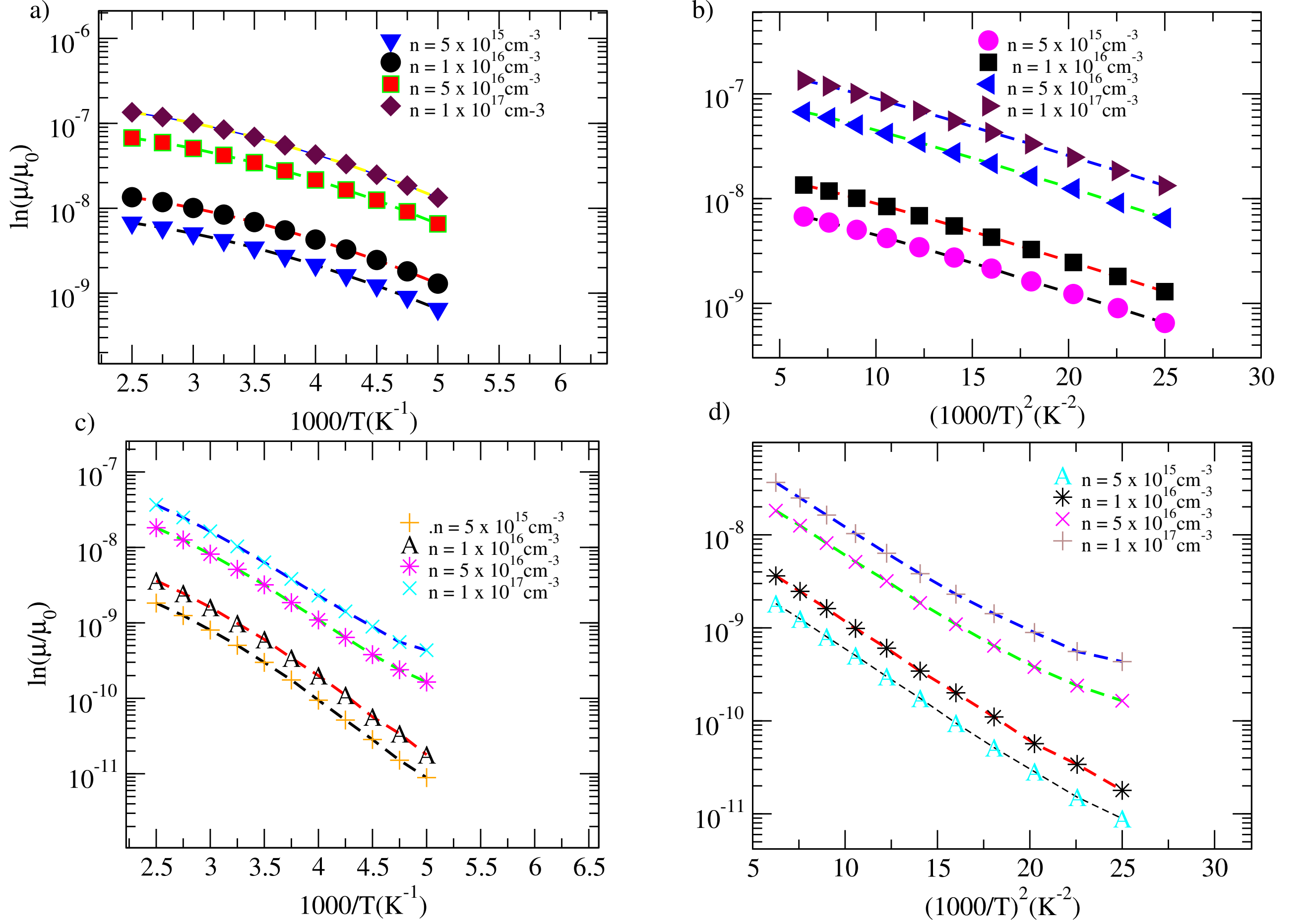

Figure 4.7: The data for temperature dependence of a charge carrier mobility are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} for $\alpha = 0.1a$, and for different values of charge carriers density and electric field of F $= (0.08)[\frac{\sigma}{ea}]$: a) and b) $\sigma = 0.05$ eV, $\frac{V}{cm}$ that in c) and d) $\sigma = 0.075$ eV, $\frac{V}{cm}$ where $\mu_0 = \frac{a^2\nu_0 e}{\sigma}$.

length. This indicates that a charge carrier conduction increases with the localization length and the effect of the electric field on mobility decreases with the increase of localization length. The possible justification for this is that whenα increases the probability for a charge carrier hopping to a site at a larger distance increases.This gives rise to the increment of eFx, which will, consequently, increase the role of electric field to reduce the barrier height between hopping sites separated by a distance x. This can be the reason for the mobility saturation observed at relatively lower electric field than when the localization length is smaller. The charge carrier hopping rarely occurs when the localization length is small (or the state is strongly localized) at a relatively high σ in a lower electric field region. Another important point that we can infer from our simulation results is that the possible value of the localization length is closer to 0.3a than to 0.2a and 0.1a. The argument here for this suggestion, though it needs experimental verification,

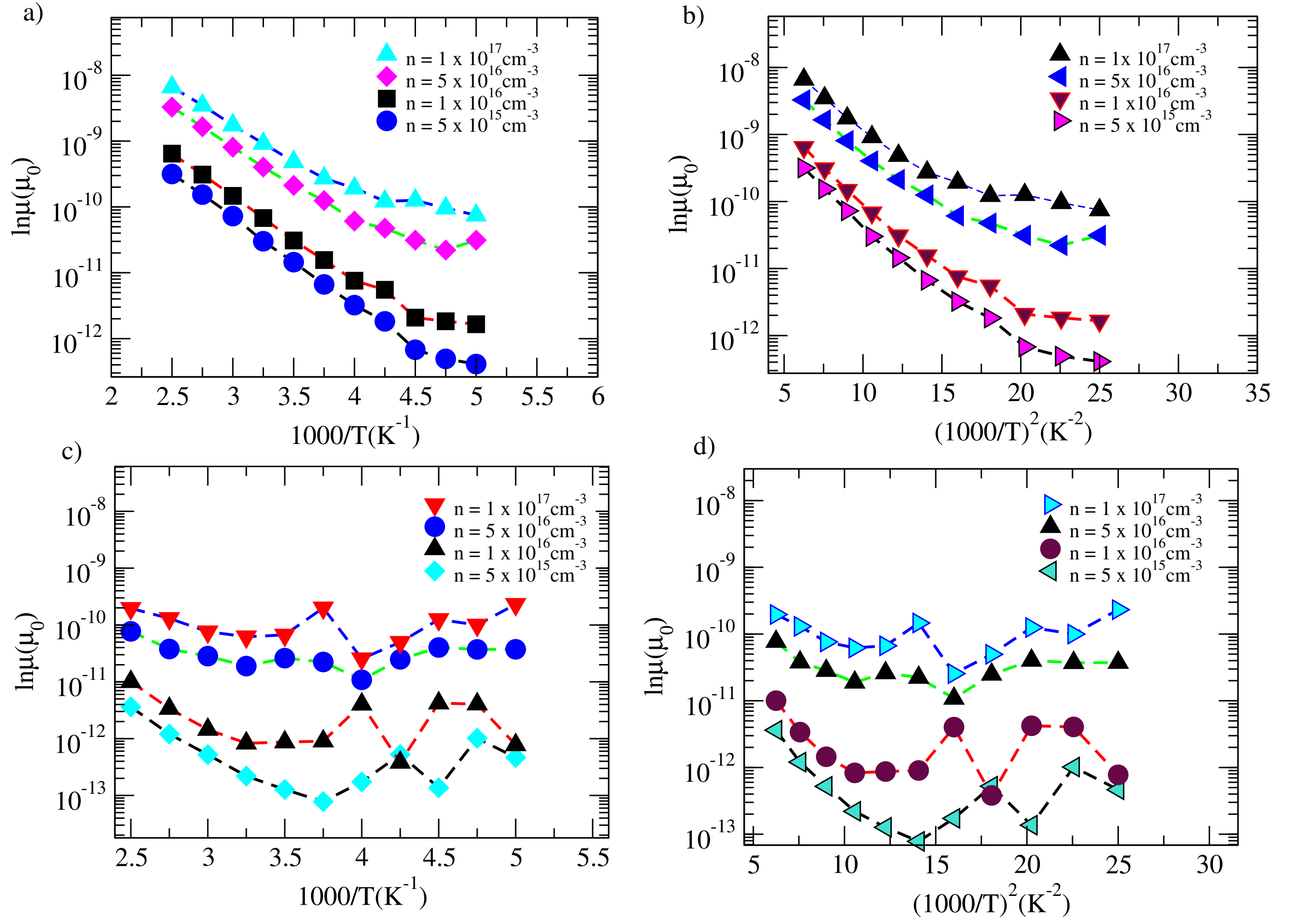

Figure 4.8: Temperature dependence of a charge carrier mobility are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} for the same $\alpha = 0.1a$, and for different charge carriers densities and electric field of F $= (0.08)[\frac{\sigma}{ea}]$: a) and b) $\sigma = 0.1$ eV, that in c) and d) $\sigma = 0.15$ eV, where $\mu_0 = \frac{a^2\nu_0 e}{\sigma}$

is that the mobilities found are in the same order with that demonstrated experimentally in previous when the localization length is 0.3a than that found for $= 0.2$a and 0.1a which is much lower. The curves in Figures 4.7 to 4.12 show the temperature dependences of mobility, plotted

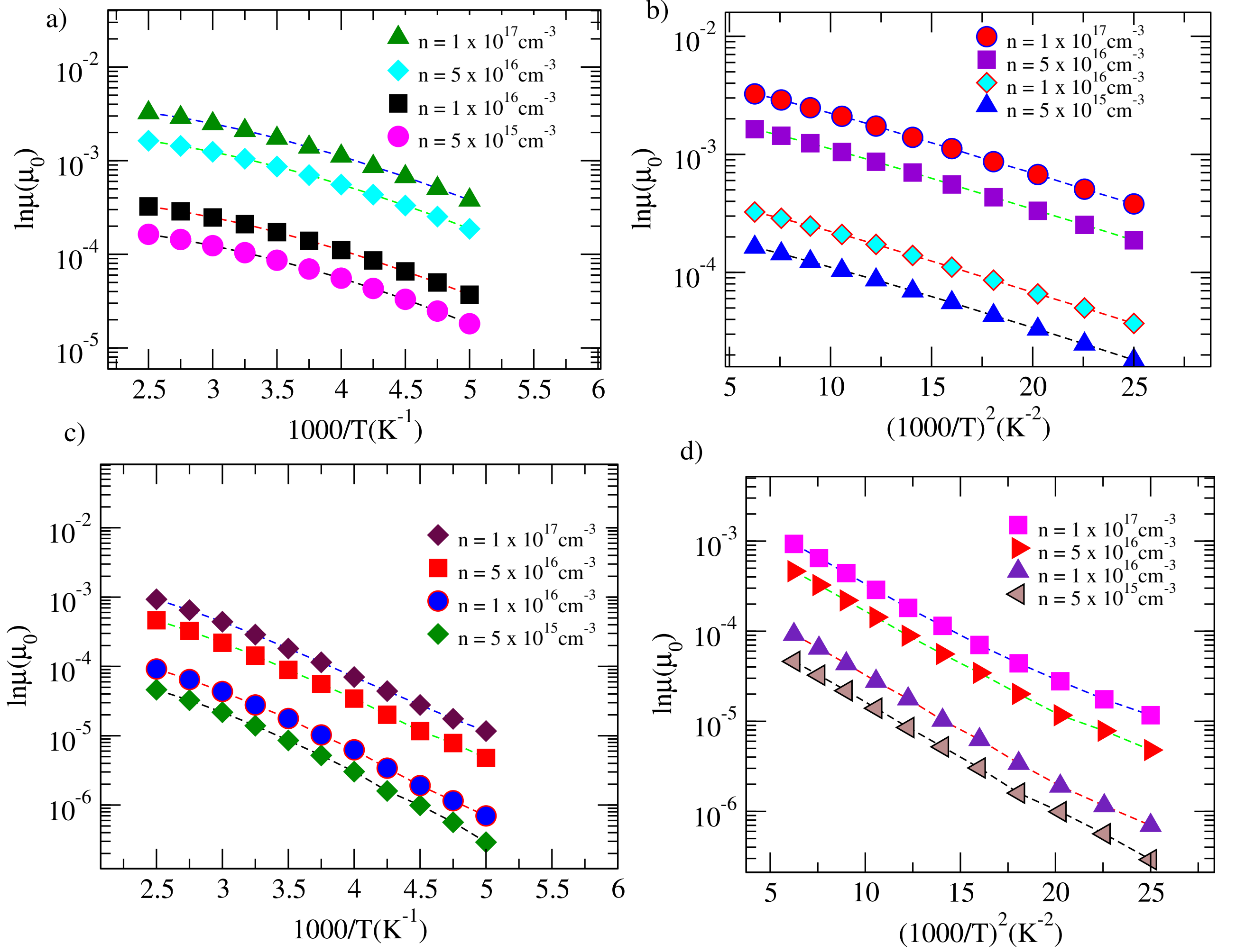

Figure 4.9: Temperature dependence of a charge carrier mobility the data are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} at the same localization length $\alpha = 0.2a$ for different values of charge carriers density and electric field of F $= (0.08)[\frac{\sigma}{ea}]$ a) and b) $\sigma = 0.05$ eV, that in c) and d) $\sigma = 0.075$ eV, where $\mu_0 = \frac{a^2 \nu_0 e}{\sigma}$.

as $ln(\frac{\mu}{\mu_0}) \propto \frac{\sigma}{kT}$, for different charge carrier densities. The plots show that for hopping transport in disordered organic semiconductors, the mobility of charge carriers is strongly dependent also on charge carriers density likewise that on temperature and the electric field. These results are in agreement with that verified experimentally and numerically in the previous works [20] Our numerical study shows that both the energy distribution and the mobility of charge carriers in systems with a Gaussian density of states, such as organic disordered semiconductors, hence

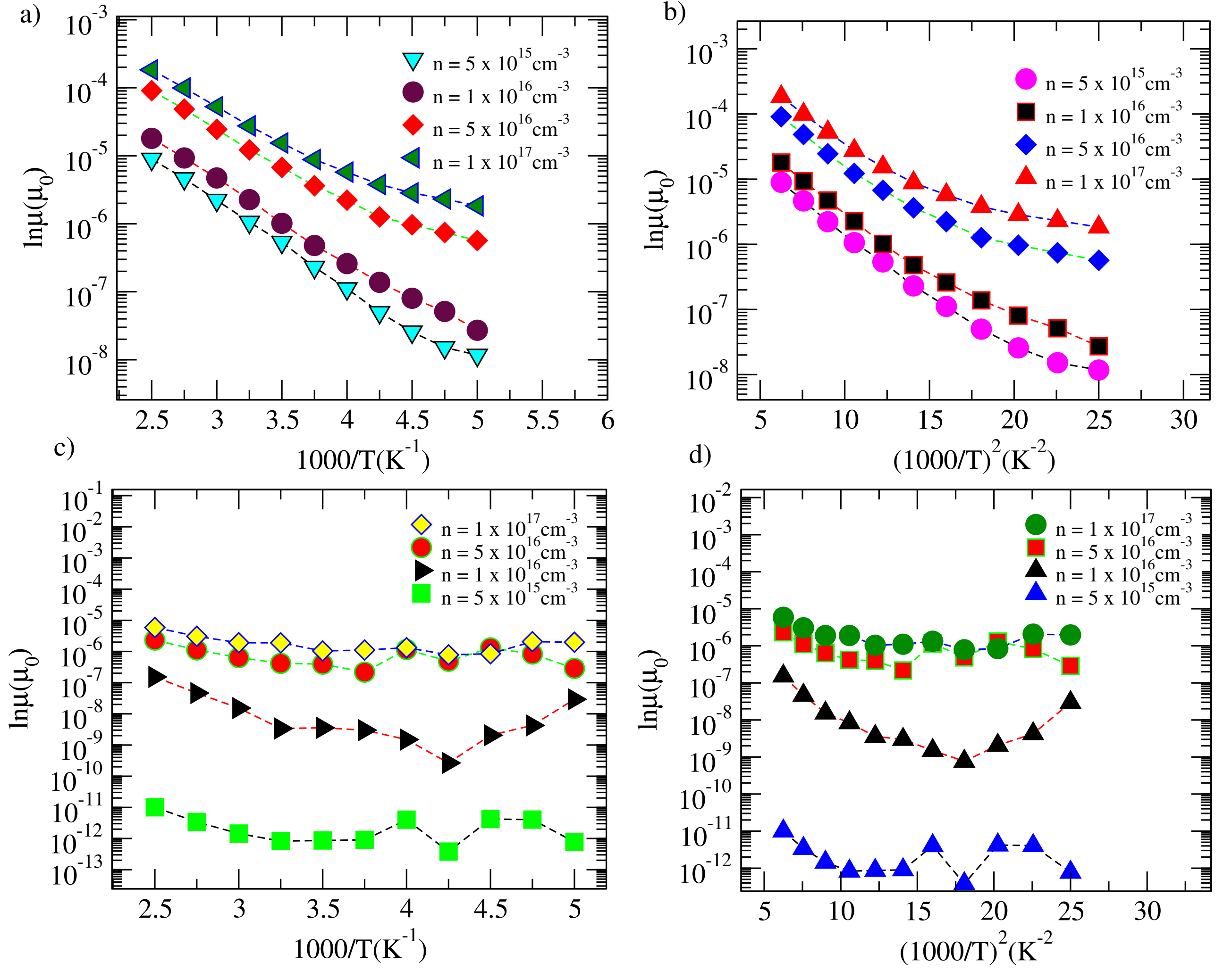

Figure 4.10: Temperature dependence of a charge carrier mobility data are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} for the same $\alpha = 0.2a$, and for different charge carriers densities and electric field F $= (0.08)[\frac{\sigma}{ea}]$: a) and d) $\sigma = 0.1$ eV, that in c) and d) is $\sigma = 0.15$ eV, and where $\frac{a^2\nu_0 e}{\sigma}$

mobility does depend on the charge carrier concentration, energetic disorder and temperature. The difference between the curves in Figs.(4.8 in c and d and 4.12 in c and d) is that apart from the shift (increase) in values with α, the mobility increases faster in the lower electric field region in the case when σ is larger.

Assuming a Gaussian density of states, Eq. (2.7.2), for the on site energy distribution, and using kMC simulation methods the temperature and electric field dependence of hopping mobility was proposed by Bssler that charge transport in disordered organic semiconductors. This density of states reflects the energetic spread in the charge transporting levels of chain segments due to the fluctuation in conjugation lengths and structural disorder. When the energetic disorder increase, then the mobility also decreases at all localization length $\alpha = 0.1$a, 0.2a and 0.3a shows

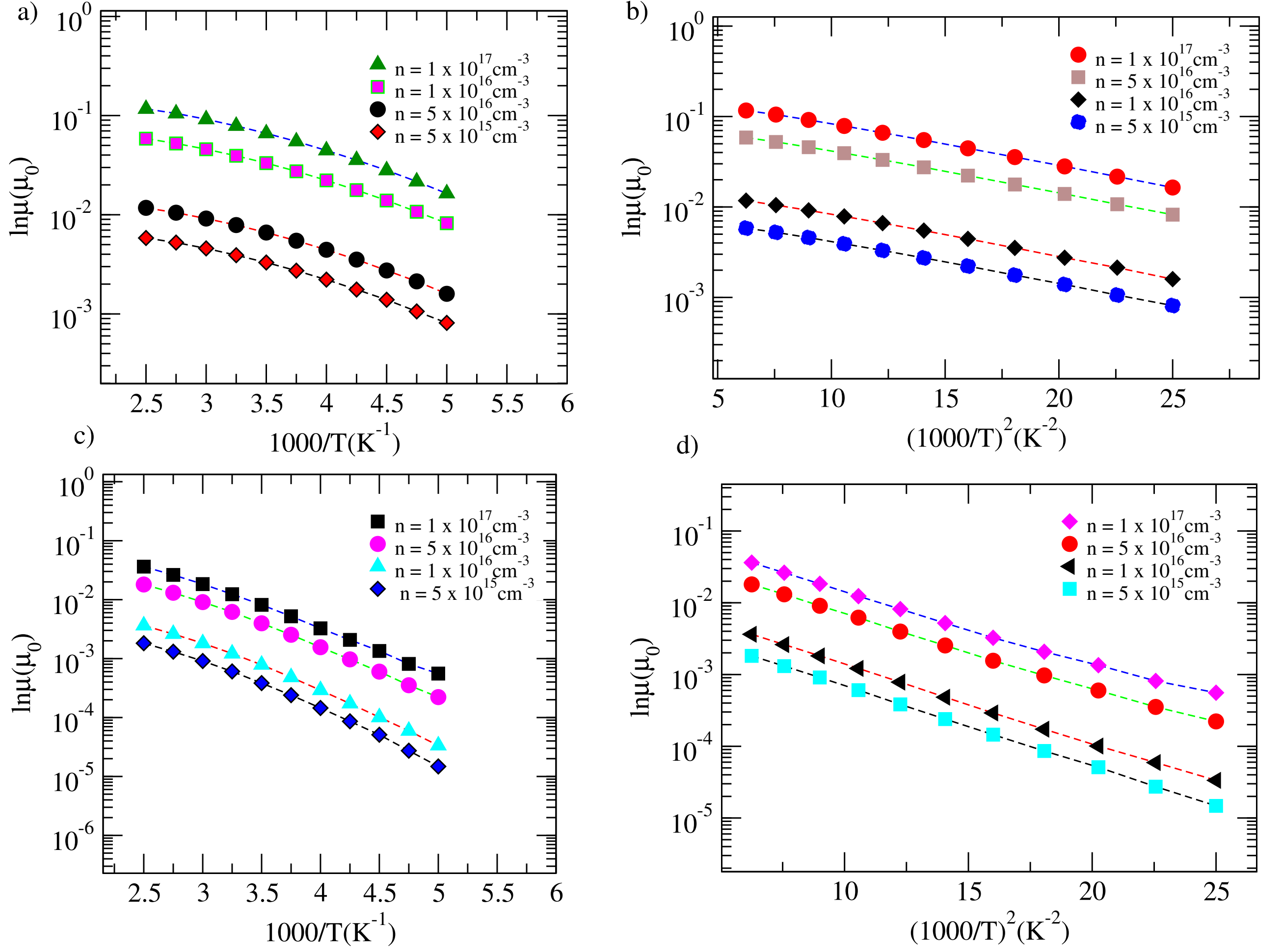

Figure 4.11: Temperature dependence of a charge carrier mobility data are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} for same $\alpha = 0.3a$, and for different values of charge carriers density and electric field F $= (0.08)[\frac{\sigma}{ea}]$: a) and b) is $\sigma = 0.05$ eV, and that in c) and d) is $\sigma = 0.075$ eV, where $\mu_0 = \frac{a^2\nu_0 e}{\sigma}$

in figures 4.1 to 4.12.

In high disordered systems a charge carrier transport generally occurs via hopping and is thermally activated. Higher temperatures improve transport by providing the energy required to overcome the barriers created by energetic disorder. The temperature dependence has been often fitted to an Arrhenius- like behaviour, $\mu = \mu_0 e^{-\frac{\Delta}{kT}}$.

The analyses carried out at low temperature demonstrates the energy activated holes/electrons mobility which brings to an Arrhenius-like plot represented by the law $ln(\mu) \propto \frac{1}{T}$. For low carriers densities, the charge transport is similar to the relation $ln(\mu) \propto \frac{1}{T^2}$ as demonstrated experimentally by Borsenberger *et al* [27].

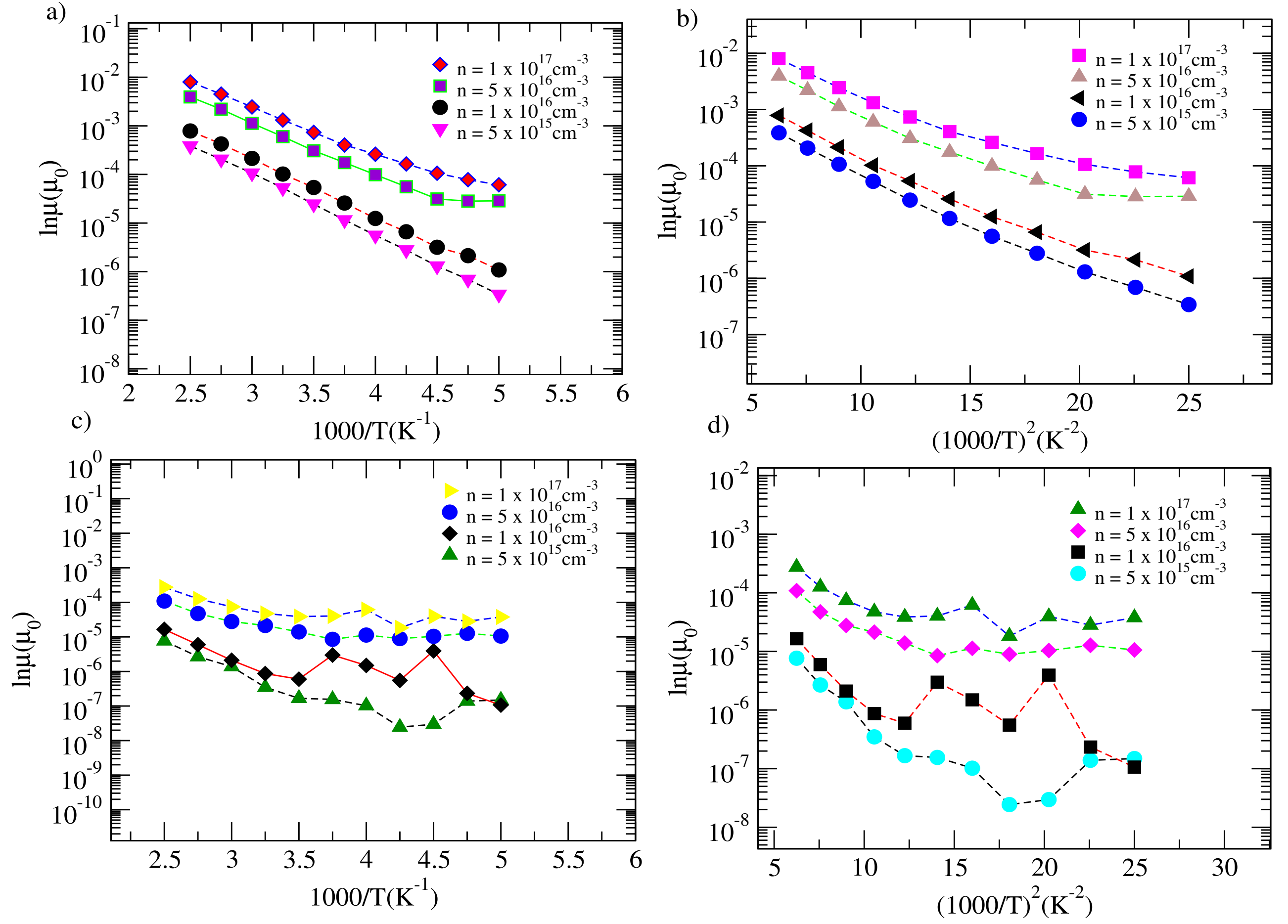

Figure 4.12: Temperature dependence of a charge carrier mobility data are plotted as $ln(\mu)$ versus T^{-1} and T^{-2} respectively for same $\alpha = 0.3a$, and for different charge carriers density and electric field F $= (0.08)[\frac{\sigma}{ea}]$: a) and b) $\sigma = 0.1$ eV, and that in c) and d) is $\sigma = 0.15$ eV.

Chapter 5

summary and conclusions

In this work, we have studied density and temperature dependent of charge carriers mobility in disordered organic semiconductors. The charge carriers in hypothetical energetically disordered organic semi-conducting systems using kMC simulation methods. The main focus was on the effects of the Gaussian disorder parameter that has been considered to have temperature, electric field, localization length and other parameters used to investigate the charge carrier mobility. Particularly, we have calculated charge carrier mobility using a variable range hopping model for regularly spaced lattice sites and also randomly distributed states considering uncorrelated site energies, which have a Gaussian form distribution. The randomly distributed states were formed using computer programs and uniformly distributed random numbers so that the model could include energetic disorder effects.

The data for the mobility were generated, and the dependence of mobility on temperature, applied electric field, and disorder parameters was analyze. The concentration of charge carrier and their energy level in the forbidden band and measuring a semiconductors conductivity, one can determine mobility of free electrons or holes. A new numerical approach is suggested to determine the transport path of hopping charge carriers in a steeply decreasing DOS. The approach is based on simulating the effect of a DOS modification on charge transport properties. The method is applied to the Gaussian DOS relevant for organic disordered semiconductors.

The data we generated for T^{-1} and T^{-2} have shown no variation in charge carrier mobility with the temperature ; however,for $\sigma = 0.15$ eV, the diffusion coefficient was found to increase

with decrease or increase temperature. The strong electrical field dependence of the mobility of the partially conjugated material stems from both the large energetic disorder and large site separation. At a higher $\hat{\sigma}$ for both regularly and randomly distributed sites, mobility increases with the increase of density. Consequently, we concluded that the effect of the disorder parameter ($\hat{\sigma}$) on mobility, in the low density region, is more pronounced than that of the density. Moreover, we observed that mobility is less for hopping on randomly distributed system than for that on regularly distributed system at low energetic disorder and vice versa for the larger energetic disorder. We also found that the dependence of density on mobility is stronger for hopping on randomly distributed states than on regularly distributed states. The generated data also yielded information on the localization length of the wave function of a charge carrier when analyzed in comparison with experimental data. For this parameter, different values have been used in the above discussion. The consistency of our numerical data with the previous MC simulation and experimental results support the assumption we made to model a disordered system for the simulation studies, notably the statistical nature of the irregularly distributed hopping sites. On the basis of this agreement we can conclude that the material parameters that describe the charge carriers properties of the system, that is,the charge carrier localization length, the energetic disorder, and the lattice sites spacing have been given appropriate values. The simulation results of charge carrier mobility vs T^{-1} and T^{-2} respectively,for different values of the charge carrier density and localization length α = 0.1a, 0.2a and 0.3a and for different values of σ = 0.05, 0.075, 0.1 and 0.15 eV are show in figures. We observed that charge carriers density reduces the influence of the electric field on mobility. Similarly, it determines also the dependence of mobility on an energetic disorder parameter or temperature. The graphs show similar behaviors for all charge carriers densities when $\hat{\sigma}$ is in the range between 2.5 to 5. However, for when $\hat{\sigma}$ is greater than 3 the mobility variation with $\hat{\sigma}$ depends on are different for different densities. The mobility decreases more with the increase of $\hat{\sigma}$ in the case of lower charge carriers densities than the higher ones qualitatively similar to that demonstrated in [54]. This reveals that in a hopping transport the role of temperature is more when the charge carriers density is less, and also displays a transition from a nonArrhenius to Arrhenius form of temperature dependence similar to that demonstrated experimentally [34, 55]

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DECLARATION

I, hereby declare that this project is my original work and has not been presented for a degree in any other university, and that all sources of materials have been duly acknowledged.

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This project has been submitted for examination with my approval as University advisor.

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