CHAPTER 2

Theoretical Aspects

This chapter deals with the various theoretical models and mechanisms invoked to elucidate the charge conduction in disordered organic semiconductors. The theories and mechanisms employed to explain the different experimental results involved in the present thesis have also been discussed. A brief discussion on different models proposed to explicate the heat transport in amorphous metallic glasses has been included.

2.1 Charge conduction mechanism in disordered organic semiconductors

A crystal has a three-dimensional translational symmetry which is constituted by infinite repetition of identical structural units. The structure of a crystal is described as a lattice which is characterized by long-range order and strongly coupled atoms [100]. For inorganic semiconductors such as silicon or germanium, the strong coupling between the atoms leads to the formation of long-range delocalized energy bands which is separated by a forbidden energy gap [100]. Charge carriers in the semiconductor can move in these energy bands with a relatively large mean-free path, and their transport is explained by the band theory of solids. In contrast, conducting polymers lack a well-ordered structural configuration as in inorganic crystals. The conjugation of the polymer backbone is disturbed by the presence of chemical or structural defects, such as chain kinks or twists. Over the past decades, intensive research has been carried out by the scientific community to explain the transport of charge carriers in
these materials; the charge transport of which is strongly influenced by disorder. Several transport models have also been proposed which show good agreement with the electrical measurements for several systems; however no complete explanation has been attained due to the diversity and complexity of these systems [101]. The following subsections include a concise discussion on several models proposed to explain the different electrical characterizations, namely, temperature dependence of conductivity, current-voltage characteristics and magnetoresistance, which have been carried out in the present study to understand the nature of charge transport in these polymers.

2.1.1 Temperature dependence of conductivity

Conducting polymers do not exactly behave as metals, although they are regarded as synthetic metals. The conductivity generally decreases as the temperature is decreased, despite the relatively high conductivity at room temperature. However, there are exceptions when these materials undergo a transition from metallic to insulating behavior. The temperature dependence of conductivity provides valuable information regarding the microscopic charge transport, since direct measurement at the molecular level is not possible. Various models put forward to explain the conductivity behavior of disordered solids usually accounts for the charge transport in conducting polymers. In the following sections, the primary features of some of the theoretical models have been highlighted.

2.1.1.1 Hopping models

For a variety of disordered semiconductors including conducting polymers, the temperature dependence of conductivity is best described by the Mott's variable-range hopping model (VRH) [38]. Disorder results in the formation of localized electronic states in the band gap and conduction occurs by hopping i.e., phonon-assisted tunneling between localized states randomly located within the energy gap. The Mott hopping transport occurs in a constant
density-of-states (DOS), where he proposes that the hopping over long
distances and hopping to high energies are equally important. The term
'variable-range' refers to the change in the average hopping distance of the
moving electron with temperature. As the temperature decreases, the thermal
energy $k_B T$ decreases which in turn decreases the number of nearby states with
accessible energies, and the electron hops to long range hopping sites. This
increases the mean range of hopping. With increasing temperature, $k_B T$
increases and hence the hopping range decreases. Figure 2.1 represents the
schematic of VRH process in the low temperature regime.

$$Figure 2.1: Schematic illustration of variable-range hopping behavior in the low
temperature regime [102].$$

Let us consider two localized states with an energy separation $\Delta E$ at a
distance $r$ apart. An electron can hop from one site to the other by the
absorption of a phonon of energy $\Delta E$. The hopping probability depends upon
two factors: (i) the tunneling decay factor $\exp(-r/L_c)$, here $r$ signifies the distance
between two hopping sites and will be denoted as $R_{hop}$ in the later chapters, and
$L_c$ is the localization length, and (ii) the Boltzmann factor $\exp(-\Delta E/k_B T)$, $k_B$ is the
Boltzmann constant. The overall conductivity is determined by optimizing the
competition between $\exp(-r/L_c)$ and $\exp(-\Delta E/k_B T)$, which can be written as:

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^N\right] \quad (2.1)$$
$n = 1/4, 1/3$ and $1/2$ for three-, two- and one-dimensional hopping of the electrons. The constant $T_0$ is given approximately by $k_B T_0 = 16/[N(E_F)L_c^2]$, where $N(E_F)$ is the density of localized states at the Fermi level.

However, in the VRH model proposed by Mott, the effect of electron-electron interactions was not considered. Efros and Shklovskii pointed out that the Coulomb interaction between localized electrons creates a soft gap known as the 'Coulomb gap' in the DOS near the vicinity of the Fermi level \[103\]. This assumption leads to a situation where the conductivity is found to be proportional to $T^{-1/2}$ regardless of the dimensionality of the hopping process. The expression for conductivity is given as follows:

$$\sigma(T) \propto \exp\left[-\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$$ (2.2)

where $T_{ES}$ is the characteristic Efros–Shklovskii temperature.

Deutscher and his co-workers \[104\] presented a new mechanism where the parameter $n$ equals to $3/7$ for a VRH among superlocalized states without Coulomb interactions in fractal structures. The wavefunctions in a fractal structure varies with distance $r$ as $\psi(r) \propto \exp\left[-(r/L_c)^\xi\right] \[36\]$, where $\xi > 1$, is the superlocalization exponent which is unity in case of Anderson (disorder-induced) localization. The conductivity relation for charge transport by VRH among superlocalized states is given as \[104\]:

$$\sigma(T) \approx \exp\left[-\left(\frac{T_0}{T}\right)^{\frac{\xi}{d_f+\xi}}\right]$$ (2.3)

where $n = \frac{\xi}{d_f} \approx 3/7$ and $d_f$ is the fractal dimensionality.

Later on, Van der Putten et al. \[37\] generalized the VRH theory among superlocalized states including Coulomb interaction and obtained a value of $n = \frac{\xi}{d_f + 1} \approx 0.66$. 

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2.1.1.2 Tunneling models

As opposed to hopping models where the charge carriers hop between the localized states, the tunneling model proposed by Sheng and Klafter [105] and Sheng [35] assume that electrical conduction is mediated by tunneling between conducting regions. In general, disordered materials are characterized by large conducting regions (or long conducting pathways) which are separated by narrow insulating barriers. This model considers charging of some of these conducting regions that occurs through random thermal motion of charge carriers from neighboring neutral regimes. However, this process requires an energy which depends both on the separation and size of the conducting regimes (inversely proportional to size of the conducting regimes), as well as on the applied voltage. When the size of the conducting regions, for example, is very small like 20 nm or less, a considerable amount of energy is required to remove an electron from an electrically neutral island. If the voltage between adjacent metallic islands is small, the carriers are generated by thermal activation causing the temperature dependence of conductivity. The expression of conductivity is given by:

\[
\sigma(T) = \sigma_0 \exp \left[ -\left( \frac{T_0}{T} \right)^{1/2} \right]
\]

where \( T_0 \) and \( \sigma_0 \) are material constants. Eq. (2.4) is similar to that of one-dimensional VRH.

When the applied voltage is high i.e., when the voltage drop between neighboring grains is much larger than \( k_B T / e \), charge carriers are mostly generated by field-induced tunneling between neutral regimes. In this case, the conductivity varies exponentially with field as:

\[
\sigma = \sigma_0 \exp \left[ -\left( \frac{F_0}{F} \right) \right]
\]

(2.5)
where $F_0$ is a material constant related to the size of the conducting metallic islands and $F$ is the applied field.

On the other hand, when the size of the metallic islands is about 1 $\mu$m or more, conduction happens through fluctuation-induced tunneling between conducting islands. The random thermal motion of the charge carriers within the conducting islands induces a randomly alternating voltage across the gap between the neighboring islands. The temperature dependent conductivity is given as:

$$
\sigma(T) = \sigma_T \exp \left( - \frac{T_T}{T + T_s} \right)
$$

(2.6)

where the parameter $T_T$ represents the temperature at which the thermal voltage fluctuations become large enough to raise the energy of electronic states to the top of the barrier, and the ratio $T_T/T_s$ determines the tunneling in the absence of fluctuations.

### 2.1.1.3 Heterogeneous model

Polymers exhibit only partial crystallinity with the polymer chains aligned only in some crystalline regions of typical dimension 10 - 50 nm [28, 106]. These small crystalline regions are termed as crystallites. Some polymer chains may extend through a number of crystallites or may fold back on themselves within the crystallites. In both the cases, the ordered crystallites are interconnected by disordered amorphous regions. This heterogeneous nature of the polymer chains plays a significant role in conduction. When the conductivity of the ordered crystalline regions is high, the total resistance is dominated by the disordered regions, through which the current must pass [83]. For a fibrillar polymer, the expression for resistivity in a heterogeneous model with high and low conductivity sections in series is given by Kaiser [107] as:

$$
\sigma(T)^{-1} = \rho(T) = \sum_i f_i \rho_i(T)
$$

(2.7)
where $f_i$ are geometric factors defined as $f_i = \frac{L_i A_i}{L A_i}$. Here $L$ and $A$ signifies the effective total length and cross-sectional area of the sample, $L_i$ is the length of the path consisting of material $i$ with intrinsic resistivity $\rho$ and $A_i$ is the effective cross-sectional area for conduction in each type of material. For a fibrillar polymer where the fibers have similar properties and the nature of the electronic states does not change with temperature, the temperature dependence of the geometric factors will be small [107].

For non-fibrillar polymers, a more complex series heterogeneous model is proposed where the effect of separating thin barriers is taken into account. When the metallic regions are extended, separated by thin barriers, the overall conductivity is given by a combination of quasi one-dimensional metallic conduction and fluctuation-induced tunneling [108]:

\[
\sigma(T)^{-1} = \rho(T) = f_1 \rho_m \exp\left(-\frac{T_m}{T}\right) + f_2 \rho_0 \exp\left(\frac{T_i}{T+T_s}\right) \tag{2.8}
\]

As the tunneling conductivity increases with temperature and the metallic conductivity decreases, Eq. (2.8) gives rise to a peak in the conductivity at a crossover temperature, when the temperature coefficient of conductivity changes sign from non-metallic to metallic.

For smaller metallic regions, the fluctuation-induced tunneling is replaced by the expression for tunneling between mesoscopic islands limited by their charging energies [109]:

\[
\sigma(T)^{-1} = \rho(T) = f_1 \rho_m \exp\left(-\frac{T_m}{T}\right) + f_2 \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^{1/2}\right] \tag{2.9}
\]

Eq. (2.9) is also applicable when the conduction through the barrier is by quasi one-dimensional VRH [108].
2.1.1.4 Metal-insulator transition and localization-interaction model

High degree of structural disorder prevented the conducting polymers of first generation to exhibit metallic features. Considerable progress achieved in recent years in synthesis and improvement of the structure, reduced the degree of disorder making it possible to identify and study the mechanisms of charge carrier transport in doped conducting polymers, including those on the metal side of the metal-insulator transition (MIT) [110, 111]. The degree of disorder significantly affects the conductivity $\sigma(T)$ at low temperatures [47, 112].

Ioffe and Regel [113] argued that in a disordered metallic system, the metallic behavior is limited by the extent of disorder present. When the mean-free path becomes less than the inter-atomic spacing, coherent metallic transport is not possible. The Ioffe-Regel criterion is defined as $k_F l_m \sim 1$, where $k_F$ is the Fermi wave vector and $l_m$ is the mean-free path. The metallic regime corresponds to $k_F l_m >> 1$. Considering the Ioffe-Regel criterion, Mott [38, 112] anticipated that a MIT must occur when the disorder is sufficiently large such that $k_F l < 1$. This MIT is called the 'Anderson's transition' (disorder-induced transition) [43]. In the limit when $k_F l \ll 1$ i.e., when the strength of the random disorder potential is large compared to the bandwidth, all the electronic states become localized and the conductor becomes a 'Fermi glass' [114]. Although there is no gap in a Fermi glass, it still behaves as an insulator because the states at the Fermi level are spatially localized.

According to Mott, the states in the band tails are more susceptible to localization and hence there exists a critical energy separating the localized from the delocalized states which is called the mobility edge ($E_c$) [38, 112]. A transition from a metal to a Fermi glass insulator occurs when the Fermi energy falls in the region of localized states. The scaling theory of localization established that the disorder-induced MIT is a true phase transition with a well defined critical point [115]. MacMillan [116], and later Larkin and Khmelnitskii
[117] showed that near the critical regime of Anderson localization, a power-law temperature dependence of conductivity is expected.

The metallic and insulating regimes can be discriminated only by the zero temperature limit of conductivity ($\sigma$) [118]. The basic property of the metallic behavior is the existence of a finite conductivity when $T \to 0$ K. This indicates the presence of delocalized states at the Fermi level. On the other hand, if $\sigma \to 0$ as $T \to 0$ K, the sample is an insulator. This simple definition cannot be put to practical use for the determination of metallic and insulating samples, since absolute zero is not attainable. Besides, the positive temperature coefficient of resistivity (TCR) shown by metals is also difficult to observe in a disordered metal, although a positive TCR over a specific temperature range can be considered as an indication of metallic transport. However, detailed studies of disordered metals have shown that systems with weak negative TCR can also be metallic [119]. Zabrodskii and Zeninova [120] have shown that the temperature dependence of conductivity is better understood by using the reduced activation energy ($W$) which is defined as:

$$W = \frac{d(\ln\sigma)}{d(\ln T)} = \frac{T}{\sigma} \frac{d\sigma}{dT}$$  \hspace{1cm} (2.10)

According to Eq. (2.10), $W(T)$ vanishes as $T \to 0$ for a metallic sample. The reduced activation energy $W$ is more sensitive than conductivity [121]; hence it is used to analyze the temperature dependence of conductivity showing a weak negative TCR. The characteristic transport regimes near a MIT can be identified by different temperature dependences of $W(T)$ in the following way [119]:

1. If $W(T)$ has a positive temperature coefficient at low temperatures, then the system is on the metallic side of the MIT.
2. If $W(T)$ is temperature independent for a wide range of temperatures, then the system is on the critical regime of the MIT.
3. If $W(T)$ has a negative temperature coefficient at low temperatures, the system is on the insulating side of the MIT.
In the insulating regime, the conductivity is well described by the Mott's VRH model as given by the Eq. (2.1). The conductivity in the critical regime follows a power-law dependence of the form [116, 117]:

\[
\sigma(T) = \left( \frac{\hbar^2}{4\pi^2 e^2 p_F} \left( \frac{k_B T}{E_F} \right) \right)^{1/\delta} = A T^\delta
\]  

(2.11)

where the predicted range of validity for \( \delta \) is 0.3 < \( \delta \) < 1. \( p_F \) is the Fermi momentum, \( \hbar \) is Planck's constant, and \( e \) is the electronic charge. A value of \( \delta \approx 1/3 \) indicates that the system is just on the metallic side of MIT. It has to be emphasized that besides disorder-induced MIT, Coulomb correlation in an ordered system may also lead to similar metal-insulator transition [122]. The conductivity on the metallic side of MIT at low temperatures is thus described by the localization-interaction model, which is based on weak localization (disorder) and electron-electron interactions. The conductivity relationship is given as [47]:

\[
\sigma(T) = \sigma(0) + m T^{1/2} + B T^{p/2}
\]  

(2.12)

where the second term is determined by the influence of the electron-electron interactions and the third term is determined by the corrections to zero temperature conductivity due to weak localization effects. The value of \( p \) is determined by the temperature dependence of the scattering rate, \( \tau_m = T^{-p} \) of the dominant dephasing mechanism. For electron-phonon scattering, \( p = 2.5-3 \); for inelastic electron-electron scattering, \( p = 2 \) and 1.5 in the clean and dirty limits, respectively [123]. However, Belitz and Wysokinski [124] have shown that very near the MIT, electron-electron scattering also leads to \( p = 1 \). According to this model, the electron-electron interaction affects the transport at low temperatures, whereas the weak localization effects are dominant at higher temperatures.
2.1.2 Current-voltage characteristics

Some macroscopic models for current flow as a function of applied voltage are discussed in the following sections. In general, these models can be combined together to completely describe the measured current-voltage curve and to determine the material parameters.

2.1.2.1 Ohmic conduction

In organic semiconductors, Ohmic conduction is observed when the density of injected charges is lower than the density of thermally excited charges. In this case current density \( J \) varies linearly with applied voltage \( V \) and is described as:

\[
J = \frac{e\mu n_c V}{d}
\]  

(2.13)

where \( e \) is the charge of the carrier, \( n_c \) is the density of carriers, \( \mu \) is the mobility of carriers and \( d \) is the thickness of the sample.

2.1.2.2 Space-charge-limited conduction

When carriers injected through an Ohmic contact exceed the concentration of intrinsic carriers, the current is limited by space-charge. Space-charge means a region where there is a large concentration of charges in the form of electrons, holes or ions (the charges depend upon the material). These charges may be mobile or localized, but constitute a localized non-uniform electric field. The transport of charges under the influence of this non-uniform field is called space-charge-limited conduction (SCLC), and is widely observed in organic semiconductors. SCLC methods provide useful information regarding the charge carrier mobility, concentration and energy distribution of localized defects or charge trapping states [125].

The basic requirement to achieve SCLC regime is bulk-limited transport which is acquired by using an injecting Ohmic contact. When charge carriers
are injected by applying an electric field, the injected space-charge decreases the electric field at the injecting surface and gives rise to a space-charge-limited current.

Mott and Gurney [126, 127] proposed an approximate theory of SCLC in a trap-free solid. In this case, current varies as square of the applied voltage and is expressed as:

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \]  

(2.14)

where \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon_r \) is the relative permittivity. This equation is known as the Mott-Gurney law which describes the nature of current in a trap-free material. This behavior can be observed either in trap-free materials, or when all available traps are filled with charges. This is also observed when the concentration of traps is less than the free carrier concentration [128, 129].

Trapping sites, especially in disordered organic semiconductors are expected to be distributed in energy starting from the HOMO or the LUMO level. These traps can arise from disorder, dangling bonds or impurities. Mark and Helfrich [125] studied the SCLC in the presence of exponentially distributed trap states. They assumed that the free carrier concentration is much less than the trapped carrier concentration, and that the traps are exponentially distributed in the band gap. If the trap energies are continuously distributed with an exponential function, the density of trap states as a function of the energy level \( E \) above the HOMO level \( (E_{HOMO}) \) can be expressed as:

\[ N(E) = \frac{N_t}{l_k B T} \exp \left( -\frac{E}{l_k B T} \right) \]  

(2.15)

The integration from \( E = 0 \) to \( \infty \) then gives the total trap density \( N_t \) [130]. When \( E = l_k B T \), the exponential term has the value \( 1/e \); therefore, \( l_k B T \) is regarded as
the 'characteristic width' of the exponential distribution. This relation leads to
the following power-law dependence of $J$ on $V$,

$$J = e^{l-1} \mu N_{\text{HOMO}} \left( \frac{1 + l}{1 + 1} \right)^{l+1} \left( \frac{1}{l + 1} \frac{\varepsilon \epsilon_0}{N_t} \right)^{l} \frac{V^{l+1}}{d^{2l+1}} \quad (2.16)$$

where $l$ is an energy parameter given by $l = T_c/T$, $T_c$ is the characteristic
temperature of traps, $N_{\text{HOMO}}$ is the effective DOS of the HOMO level.

### 2.1.2.3 Poole-Frenkel mobility

Poole-Frenkel (PF) mobility was first predicted by Frenkel [131] to explain the
increase in conductivity of insulators and semiconductors when high electric
field is applied. It is defined as:

$$\mu = \mu_0 \exp(\gamma \sqrt{F}) \quad (2.17)$$

where $\mu_0$ is the zero-field mobility, $\gamma$ is the field activation parameter and $F$ is
the applied electric field. $\mu_0$ and $\gamma$ depend on the considered system. In
conventional semiconductors, charges trapped at a charged defect can be
detrapped by applying an electric field, which lowers the barrier for the carrier
to thermally escape the Coulombic potential. This gives rise to a PF field
dependence of mobility. The physical effect of an electric field is then to
effectively reduce the hopping barrier. Assuming a Coulomb potential for
hopping barrier, the mobility will have an electric field dependence of the PF
type as given in Eq. (2.17) with the zero-field mobility $\mu_0$ given by [132]:

$$\mu_0 = \mu_i \exp \left( -\frac{E_b}{k_BT} \right) \quad (2.18)$$

where $\mu_i$ is the intrinsic mobility at zero hopping barrier and $E_b$ is the zero-field
hopping barrier, also known as low-field activation energy. Eq. (2.17) can be
rewritten as:
Eq. (2.19) has been modified by Gill [39] to increase agreement with experimental data by substituting $T$ with an effective temperature $T_{\text{eff}}$, such that

$$\frac{1}{T_{\text{eff}}} = \frac{1}{T} - \frac{1}{T_0}$$

(2.20)

where $T_0$ is the characteristic temperature of the material.

The empirical form of charge carrier mobility then becomes:

$$\mu = \mu_0 \exp\left(\frac{\gamma \sqrt{F} - E_b}{k_B T}\right)$$

(2.19)

$$\mu = \mu_0 \exp\left(-\frac{E_b}{k_B T}\right) \exp\left[\frac{\gamma}{k_B} \left(\frac{1}{T} - \frac{1}{T_0}\right) \sqrt{F}\right]$$

(2.21)

### 2.1.2.4 Gaussian disorder model

A semiconducting polymer is not a perfect conjugated system. The twisted and kinked chains, and chemical defects in a semiconducting polymer chain cause conjugation breaks. The variation in the conjugation length and interaction energies causes the semiconductor to have an energetic spread of charge transport sites approximated by a Gaussian DOS, instead of having two delocalized energy bands separated by an energy gap. Therefore, the charge carriers are transported via hopping between sites with randomly varying energy levels and inter-site distances as depicted in Figure 2.2.
Figure 2.2: Charge hopping process between localized states in a Gaussian DOS of width $\sigma'$. A charge hops between two localized sites with an energy difference $\Delta E$ separated by a distance $r$ [133].

Bässler and co-workers [40, 134] proposed a charge transport model for disordered organic semiconductors to explain the field and temperature dependence of mobility of carriers. They assumed a Gaussian DOS with a width $\sigma'$. In this model, the carrier transport is described as a biased random walk among the hopping sites with Gaussian-distributed random site-energies. In this way, both positional disorder (fluctuation in inter-site distance) and energetic disorder (fluctuation in site-energy) are introduced. Based on this assumption and performing Monte-Carlo simulations, they were able to reproduce Eq. (2.21) for temperatures around room temperature, but only for a very narrow field range, and at relatively high electric fields ($> 10^6$ V/cm) as compared to the experimental regime. The temperature and field dependence of mobility according to the Gaussian disorder model (GDM) is given as:

$$\mu_{UGDM} = \mu_\infty \exp \left[ - \left( \frac{2\sigma'}{3k_B T} \right)^2 + C' \left( \frac{\sigma'}{k_B T} \right)^2 - \Sigma^2 \right] \sqrt{F} \text{ for } \Sigma \geq 1.5 \quad (2.22)$$
where $\mu_\infty$ is the mobility in the limit $T \to \infty$, $C'$ is a constant that depends on the site spacing and $\Sigma$ is the degree of positional disorder. A consequence of hopping in a Gaussian DOS is the non-Arrhenius behavior of the mobility in contrast to that observed in Eqs. (2.19) and (2.21). The Gaussian disorder model is also known as the uncorrelated Gaussian disorder model (UGDM) as it does not take into account the correlation between site-energies as discussed below.

To improve the validity regime of the field dependence of mobility, Gartstein and Conwell [135] took into account spatial correlations between the energies of neighboring sites, which successfully extended the PF behavior to lower electric fields in accordance with the experimentally observed results. A spatially correlated site-energy means that the energies are correlated over a greater length than the distance between hopping sites. Due to the correlation of energies of adjacent sites, the field dependence of the mobility extends to lower electric fields. The spatial correlations in site-energy arise from the long-range charge-dipole interactions in the material, where the disorder is determined by the random orientations of dipole moments of nearby molecules. According to this correlated Gaussian disorder model (CGDM), the empirical expression for mobility is given by [41, 136]:

$$\mu_{\text{CGDM}} = \mu_\infty \exp \left[ - \frac{\left( \frac{3\sigma'}{5k_BT} \right)^2 + C_0 \left( \frac{\sigma'}{k_BT} \right)^{3/2} - 2.5 \sqrt{F} }{\sqrt{\sigma'}} \right] \text{ for } \Sigma \leq 1.5$$  

(2.24)

where $C_0 = 0.78$, $a$ is the inter-site separation and $\Gamma = 2$ for organic materials. The main difference between CGDM and UGDM is the predicted temperature dependence of field activation parameter $\gamma$. 

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2.1.3 Magnetoresistance

Conducting polymers generally exhibit a transition from positive to negative magnetoresistance (MR) with increase in temperature, and is explained using different theories [137, 138] which are discussed in the following sections. The bipolaron model used to explain the observed MR behavior in the present study is also elaborated.

2.1.3.1 Positive magnetoresistance

A positive MR is generally expected for strongly localized carriers exhibiting VRH under the application of a magnetic field. When a magnetic field is applied, there is shrinkage in the overlap of the localized state wavefunctions leading to a decrease in the tunneling probability and a corresponding increase of the average hopping length [34, 38, 139]. This leads to a large positive MR at sufficiently low temperatures. The VRH resistivity is strongly dependent on temperature and magnetic field. The weak-field MR can be expressed as [34, 139]:

\[
\ln\left(\frac{\rho(H)}{\rho(0)}\right) = t_1 \left(\frac{L_c}{L_H}\right)^4 \left(\frac{T_0}{T}\right)^\gamma \propto H^2 . T^{-\gamma}
\]  \hspace{1cm} (2.25)

where \( t_1 \) is a constant, \( L_H = (\hbar/eH)^{1/2} \) is the magnetic length, \( L_c \) is the localization length, \( \hbar (= h/2\pi) \) is the Planck’s constant. For three-dimensional Mott VRH, \( t = 5/2016 \) and \( \gamma = 3/4 \); for one-dimensional VRH, \( t = 0.0015 \) and \( \gamma = 3/2 \). In case of strong magnetic field, there is a deviation from \( H^2 \) dependence with lowering temperature. According to VRH theory, the high-field MR can be written as [34, 139]:

\[
\ln\left(\frac{\rho(H)}{\rho(0)}\right) = t_2 \left(\frac{L_c}{L_H}\right)^{2/3} \left(\frac{T_0}{T}\right)^{1/3} \propto H^{1/3} . T^{-1/3}
\]  \hspace{1cm} (2.26)

where \( t_2 \) is a constant. When the applied field is sufficiently high, a transition from the \( H^2 \) dependence to \( H^{1/3} \) dependence of \( \ln(\rho(H)/\rho(0)) \) occurs at the characteristic field \( H_c \), which decreases with lowering temperature.
2.1.3.2 Negative magnetoresistance

The negative $MR$ in the hopping regime is caused by the dephasing effect of magnetic field on the quantum interference of many possible hopping paths. The orbital magnetoresistance in the VRH regime was studied by Nuugen et al. [140, 141] and Sivan et al. [142]. Nuugen et al. considered the effect of magnetic field on the hopping probability between two sites separated by a distance $r$ ($r$ is the hopping length), where the hopping probability is determined by the interference of many possible paths connecting the two sites. On averaging the logarithm of conductivity over many random impurity realizations in a macroscopic sample, they obtained a net decrease in resistivity with field i.e., negative $MR$ [143-145]. On the other hand, Sivan et al. applied critical path analysis and obtained the same results but the field dependence of $MR$ was found to be quadratic at small fields. The field dependence of resistivity in both the models is determined by the flux threading an area over which phase coherence is maintained, and the area of such a coherent loop is that of an ellipse of length $r$ and area $(ram)^{1/2}$ ($am$ is microscopic length). The $MR$ is expected to approach a constant negative value at high magnetic fields when the flux $\phi_M$ threading a coherent loop becomes comparable to or greater than one quantum flux $\phi_0$. According to Sivan et al. [142, 146], at small magnetic fields (such that $\phi_M < \phi_0$), the $MR$ is proportional to the square of the flux threading the loop. A common form of equation combining both the models can be written as:

$$MR = (\rho(H) - \rho(0))/\rho(0) \propto -H^x . T^{-y}$$

(2.27)

where $x = 1$ [140] or 2 [142] and $y = 3/4$ for three-dimensional VRH and $y = 3/2$ for one-dimensional VRH.
2.1.3.3 Bipolaron model

Bipolaron model [147, 148] was proposed to explain the organic magnetoresistance (OMAR) in disordered organic semiconductors. OMAR is a large low-field symmetric magnetoresistance (MR) present in completely non-magnetic organic devices at room temperature. This model considers that bipolarons are formed out of two polarons as an intermediate state in the charge transport process. The charge transport in organic semiconductors takes place via a limited number of percolation paths [149]. On such paths, some low energy sites with quasi-trapped charges in form of polarons might block the passage of other charges. As the common mode of charge conduction in conducting polymers occurs through a hopping of polarons, therefore when these mobile polarons jump on the sites already occupied by other polarons, they form an intermediate bipolaron, before it can move further through the materials. However, intermediate bipolaron state cannot be formed if the spin configuration of polarons are parallel i.e., a triplet configuration; hence the charge cannot pass the site. This phenomenon is called 'spin blocking' and causes a decrease in the mobility resulting in a decrease in current.

Figure 2.3 illustrates the formation of bipolaron and spin blocking. Hyperfine field induced spin mixing [Figure 2.3(c)] eliminates spin blocking by changing the initial triplet configuration of polaron pairs into singlet configuration and thereby, allowing a larger current to pass. On the application of a large external magnetic field, the spins will precess around the sum of the external field and the local hyperfine field [Figure 2.3(d)]. The hyperfine field being almost negligible, the spins experience approximately the same field. As a result, two parallel spins will remain parallel and no mixing occurs. Applying an external magnetic field thus favors spin blocking resulting in a positive MR. A negative MR can also result when the long-range Coulomb repulsion is taken into account. The long-range Coulomb repulsion is expected to enhance the bipolaron formation [147]. When more bipolarons are formed, there are less free
carriers to carry current. By applying an external magnetic field, the number of bipolarons is decreased which gives a negative MR.

![Diagram of bipolaron formation](image)

Figure 2.3: Schematic illustration of (a) bipolaron formation when the polarons are in singlet configuration, (b) spin blocking when the polarons are in triplet configuration, (c) hyperfine precession of the carriers and (d) precession of the carriers under total magnetic field $H_{tot}$, where $H_{tot}$ is the sum of hyperfine field $H_{hf}$ and applied external field $H$ [150].

The bipolaron model has been investigated using a Monte Carlo approach [147], considering a large grid of lattice sites, and also an analytical approach [148], considering two sites and the environment. The Monte Carlo based simulation shows that bipolaron formation is best facilitated when $U \approx \sigma'$, where $U$ is the bipolaron formation energy and $\sigma'$ is the width of Gaussian DOS. OMAR exhibits two characteristic $MR(H)$ line shapes. A Lorentzian,

$$MR(H) = MR_\infty \frac{H^2}{H^2 + H_0^2}$$

(2.28)

and a more slowly saturating empirical non-Lorentzian,
where $MR_\infty$ is the MR value at $H = \infty$ and $H_0$ is the characteristic magnetic field width. $H_0$ is the half-width at half-maximum in the case of Lorentzian and the half-width at quarter-maximum in the case of non-Lorentzian line shape. The bipolaron model proposes that $H_0$ is dependent on the branching ratio $b$. This ratio is defined as $b = r_{\alpha \rightarrow \beta} / r_{\alpha \rightarrow e}$, where $r_{\alpha \rightarrow \beta}$ is the rate at which a carrier from a singly occupied site $\alpha$ hops into a neighboring singly occupied site $\beta$ to form a bipolaron and $r_{\alpha \rightarrow e}$ is the rate at which a carrier from $\alpha$ bypasses $\beta$, by hopping over $\beta$ into unoccupied sites in the environment. Both the Monte-Carlo simulations [147] and the analytical calculations of a two-site model [148] have shown that increasing $b$ results in increasing $H_0$. Therefore, the more a carrier is forced to hop into another occupied site and form a bipolaron, larger is the width of the MR feature. This can explain the temperature induced transition from positive to negative $MR$. At low temperatures, carriers have less energy to hop into sites further away in the environment and hence are more likely to form bipolarons. Therefore, the carriers have to hop into neighboring singly occupied sites creating bipolarons and resulting in the increase of both $b$ and $H_0$. The models predict that upon increasing temperature or decreasing $b$, the linewidth saturates below a certain value, and the empirical non-Lorentzian line shape converges into a Lorentzian one with a width of approximately equal to the hydrogen hyperfine field ($H_{hf} \approx 1$ mT [151]), the relevant field scale in the bipolaron model.

2.2 Heat transport mechanism in amorphous materials

The nature of heat transport in disordered organic semiconductors is not understood and hence no model has yet been proposed to elucidate the mechanism of heat transfer. In this thesis, the models proposed to explain the heat transport in amorphous materials have been borrowed for qualitative
description of the observed results. The following subsections include a brief discussion on the different theories proposed to explain the thermal conductivity of amorphous solids.

2.2.1 Thermal conductivity

The thermal conductivity $\kappa$ of amorphous solids shows, in general, three regions of different behavior: (i) at very low temperatures ($< 1$ K), it behaves approximately as $\kappa \propto T^2$; (ii) for $T \approx 10$ K there is a plateau independent of temperature; and (iii) at higher temperatures $\kappa$ increases often linearly with $T$ and mostly reaches a saturated value.

The behavior at and below the plateau can be explained by the widely accepted soft-potential model [152]. However, the behavior of $\kappa$ above the plateau in the high temperature regime is quite intriguing. Some widely differing scenarios have been proposed by different researchers to explain such monotonic increase in $\kappa$ with $T$. A completely harmonic model was proposed that assumes heat transport by diffusive motion of delocalized, but non-propagating vibrational modes [153]. The model based on fracton hopping requires anharmonicity to make energy transport possible [154, 155]. In the fracton hopping model, it is considered that localized fracton states are anharmonically coupled to long-wavelength phonons and the dependence, $\kappa \propto T$ above the plateau is due to phonon-assisted fracton hopping. Böttger et al. [156] studied the heat transport in a simple model system of Anderson localized optical carrier phonons which perform thermally activated hopping due to anharmonic interaction with delocalized acoustic phonons. The hopping contribution to thermal conductivity exhibits a linear increase with temperature at lower temperatures and finally reaches a saturated value at higher temperatures.
2.2.2 Thermally activated hopping model

Thermally activated hopping (TAH) model [157] is an extension of the fracton hopping model initially developed by Alexander and co-workers [154, 158, 159] to explain the $\kappa(T)$ behavior of amorphous metallic glasses. The TAH model is different from the fracton hopping model as it does not consider the phonons to be fractons, since the mesoscale structure of the metallic glasses is not known. There are two basic features of the TAH model. The first is a phonon spectrum containing both low-frequency extended phonons and localized phonons above a minimum frequency $\omega_c$, the phonon mobility edge. Phonons with frequency $\omega < \omega_c$ are extended while that for $\omega > \omega_c$ are localized. The second criterion is the presence of significant anharmonic forces to provide thermal activation to the localized phonons.

![Figure 2.4: Schematic representation of hopping of localized phonons. A localized phonon with frequency $\omega'_{\text{loc}}$ hops to another site with frequency $\omega''_{\text{loc}}$ separated by a distance $r$. This hopping process is facilitated by an extended phonon $\omega_{\text{ext}}$ [160].](image)

A similar hopping model extending the assumptions of TAH, and analogous to Mott VRH for localized electronic states was proposed to explain the heat transport arising from localized vibrational hopping [160]. This model predicts the existence of three types of excitations instead of two in the acoustic band of glasses: extended (or weakly localized), strongly localized (SL) and mesoscopically localized. The model [160], however considers coupling between the extended modes and the SL modes, but not between the SL and the
mesoscopically localized modes. The vibrational hopping of the SL modes depends on the anharmonic coupling between two localized (SL) states at different spatial positions, and a long-wavelength extended mode to make up the energy mismatch between the two localized states [161]. Figure 2.4 presents a schematic of hopping of the localized modes. The thermal conductivity arising from hopping of SL modes is given by [160, 161]:

\[
\kappa_{\text{hop}}(T) = \frac{192C_{\text{eff}}^2 k_B T}{\pi^2 \nu_s^5 \rho d^3 \xi_M^3 l_{ph}^2} T
\]  

(2.30)

where \( C_{\text{eff}} \) is the third-order anharmonic coupling constant, \( G \) is a constant of order unity, \( \rho_d \) is the mass density, \( \nu_s \) is the velocity of sound, \( l_{ph} \) is the localization length of a phonon and \( \xi_M^3 \) is the volume of finding a SL mode.

The relation in Eq. (2.30) has been derived replacing the fractons by SL modes in the expression derived by Alexander et al. [158, 159] and applying Mott's [162] argument of variable-range localized electronic hopping to localized vibrational hopping.