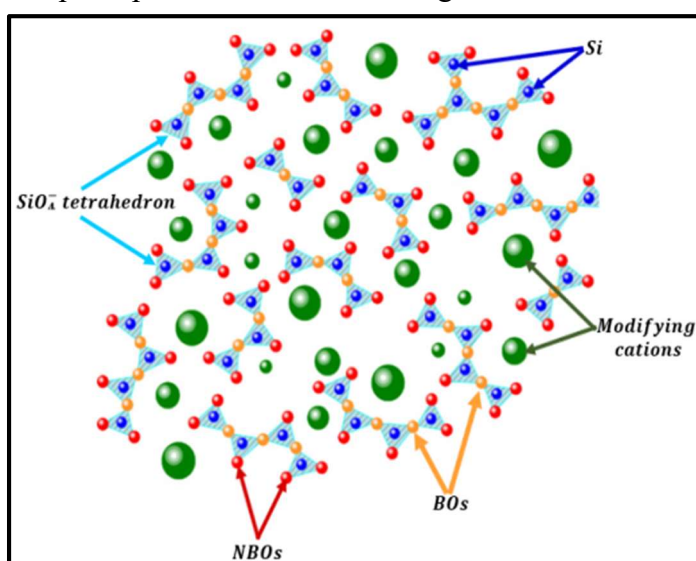# CHAPTER 2

Model for Ion Transport in Glasses

2.1 Introduction

Amorphous solid electrolytes or fast ion conducting glasses have attracted significant attention due to their potential applications in various electrochemical devices, such as batteries, fuel cells, and sensors. Understanding the ion conduction mechanism in these materials is essential for designing and optimizing their performance. Charge transport in glasses is primarily governed by the movement of ions, defects, and polarons. The ions can either hop between neighbouring sites or move through the free volume of the glass network. Defects, such as oxygen vacancies, can act as charge carriers and contribute to the conductivity. Polarons, which are electrons bound to a localized distortion in the lattice, can also move through the glass and contribute to the conductivity. Several theoretical models have been proposed to explain the ion conduction mechanism in glasses. The most prominent ones are the random barrier model, the percolation model, and the tunnelling model. The random barrier model assumes that the ions move through the glass network by overcoming randomly distributed energy barriers. The barrier height distribution is typically assumed to follow an exponential or Gaussian distribution. This model can explain the temperature dependence of the conductivity and the effect of dopants on the conductivity. The percolation model assumes that the ions move through a percolation network of conducting sites. The conductivity is determined by the fraction of conducting sites and the connectivity of the network. This model can explain the dependence of the conductivity on the concentration of dopants and the structural features of the glass. The tunnelling model assumes that the ions tunnel through the potential barriers created by the glass network. The barrier height distribution is assumed to follow a power-law distribution. This model can explain the low-temperature conductivity and the frequency dependence of the conductivity.

Superionic conduction in glasses

Glassy or amorphous materials are excellent candidates for studying fast ion conduction due to their unique properties. In the amorphous state, these materials lack long-range order, which eliminates the presence of grain boundaries that can impede ion transport. This results in isotropic charge transfer, allowing for efficient ion conduction. Warburg was one of the pioneers in the study of ion conduction in glassy materials, demonstrating the electrolytic behaviour of ordinary glass over a century ago. Since then, significant progress has been made in understanding the mechanisms of ion conduction in glassy materials, including the role of defects, structural relaxation, and chemical composition [1].

The framework of the glasses mostly determined by the silicate (glass former) network that has been partially broken or altered (by glass modifier). In the glass skeleton, the cations are placed in "holes" as shown in Fig. 2.1. The fast-ion conductors like $\beta - alumina$ and $\alpha - AgI$, which have a unit cationic transport number, are also important solid electrolytes. Additionally, the transportation of the same kind of charge $(t_+ \cong 1)$ is also observed in a wide variety of borate, phosphate, silicate, and molybdate glasses with varying compositions and stoichiometry [2]–[5]. Numerous studies have been conducted to analyze the properties of FIC glasses, including their ionic conductivity, thermal stability, and structural properties. Computational modelling has also been used to analyze the fast ion transport phenomenon in FIC glasses. Molecular dynamics simulations and other techniques have been used to study the structure and dynamics of ions in FIC glasses, providing insights into the mechanisms that govern ion transport [6]–[15]. Below are the major theoretical models of transport and conduction mechanisms in glassy FICs that are proximately relevant to the subject matter of the thesis.

Figure 2.1: *Warren-Biscoe model for the formation of glass structure in the alkali silicate glass system.*

2.2 Ion transport mechanism in solid state material

Ionic conductivity in solids is indeed connected with the movement of ions between low-energy sites in the structure, and in crystalline materials, this occurs via vacancies and Frenkel defects [16]. However, the lack of three-dimensional periodicity in glasses makes it difficult to apply this concept to understand ionic conduction in these materials. As a result, researchers have developed new concepts to aid in the understanding of ion transport in glasses. One of these concepts is the idea of "fast ion hopping," which suggests that ions move rapidly through a disordered network of low-energy sites in glasses. Another concept is the "percolation model," which proposes that the movement of ions occurs via a network of interconnected pathways in the glass structure.

In addition to these models, direct current (dc) conductivity has been used to study ion transport in glasses. This type of conductivity is due to the movement of electrons in the material, rather than the movement of ions. The sum of the conductivities of all the charge carriers present in a glass sample equals the total conductivity of the glass.

$$\sigma = \sum t_i \sigma_i \quad \ldots \ldots (2.1)$$

where t_i denotes the transport number and σ_i denotes the conductivity of the ith charge carrier species. The conductivity can be given as in the case of a glass when conduction is primarily owing to a single ionic species.

$$\sigma = \sigma_i = n(Ze)\mu \quad \ldots \ldots (2.2)$$

where n is the carrier concentration, Ze is the charge of the carrier and μ is its mobility. When an external field, E, is supplied, a force called ZeE causes the ion to diffuse-migrate within the glass. The produced motion results in a concentration gradient for the relevant ion, which acts as an opposing force. The force (ZeE) due to a concentration gradient is defined as $\left(\frac{kT}{n}\right)\nabla n$, where n and ∇n denote the concentration and its gradient, respectively, T denotes the temperature, and k denotes the Boltzmann constant. Thus, the application of the field creates a dynamic equilibrium in which the fluxes produced by the opposing forces are balanced. The condition for flux balance can be stated as follows (Eq. 2.3), wherein the diffusion coefficient is D, and the drift velocity is v_d.

$$D\nabla n = n v_d \quad \ldots \ldots (2.3)$$

To get the expression for the diffusion coefficient D, the mathematical simplification is shown below.

$$\frac{D}{v_d} = \frac{n}{\nabla n} = \frac{kT}{ZeE} \quad \ldots \ldots (2.4)$$

$$D = \left(\frac{kT}{Ze}\right)\mu \quad \ldots \ldots (2.5) \quad \left(\because \mu = \frac{v_d}{E}\right)$$

The diffusion co-efficient also can be written in terms of conductivity which is known as Nernst-Einstein relation.

$$D = \left(\frac{kT}{n(Ze)^2}\right) n(Ze)\mu = \sigma \left(\frac{kT}{n(Ze)^2}\right) \quad \ldots \ldots (2.6)$$

In the case of the ionic conductor, a random walk computation is used to determine the relationship between the diffusion coefficient D, and jump frequency Γ, and the distance between two adjacent sites λ, is determined by redirecting to the random walk calculation [17], [18].

$$D = \frac{1}{6}\lambda^2\Gamma \;\; \ldots.. (2.7)$$

$$\sigma = \left[\frac{n(Ze)^2\lambda^2}{6kT}\right]\Gamma \;\; \ldots.. (2.8)$$

Jump frequency, Γ, is related to the cation vibrational frequency v_0 in thermally activated processes. If $\Delta G_m = \Delta H_m - T\Delta S_m$ is the migration free energy barrier, then the jump frequency Γ can be rewritten in terms of entropy (S_m) and enthalpy (H_m) as given in the equation.

$$\Gamma = v_0 \exp\left(\frac{\Delta S_m}{k}\right) exp\left(-\frac{\Delta H_m}{kT}\right) \;\; \ldots.. (2.9)$$

Hence, the conductivity term can be modified as

$$\sigma = \left[\frac{n(Ze)^2\lambda^2 v_0}{6kT}\right] \exp\left(\frac{\Delta S_m}{k}\right) exp\left(-\frac{\Delta H_m}{kT}\right) \;\; \ldots.. (2.10)$$

Now if we consider the temperature independent term then σ_0' is presented as

$$\sigma_0' = \left[\frac{n(Ze)^2\lambda^2 v_0}{6k}\right] \exp\left(\frac{\Delta S_m}{k}\right) \;\; \ldots.. (2.11)$$

By considering the $\Delta H_m = P\Delta V_m + \Delta E_m$ where the component $P\Delta V_m$ is insignificant and $\Delta E_m (\equiv E_a)$

$$\sigma = \frac{\sigma_0'}{T} exp\left(-\frac{E_a}{kT}\right) \;\; \ldots.. (2.12)$$

where E_a denotes the energy of activation. E_a is calculated from logarithmic conductivity vs. reciprocal temperature plots. Again, T has a much smaller effect on the pre-exponential part of Eq. 2.12 than on the exponential part. As a result, Eq. 2.12 is frequently expressed in the more familiar Arrhenius form as

$$\sigma = \sigma_0 \, exp\left(-\frac{E_a}{kT}\right) \;\; \ldots.. (2.13)$$

The activation energy barrier plays a crucial role in determining the transport properties of ions or defects in glasses, and the type of conductivity observed depends on the magnitude of the activation energy barrier and the temperature of the system. In the context of glasses, the activation barrier, denoted by the letter E_a, refers to the minimum energy required for

an ion or a molecule to overcome a potential energy barrier and move from one site to another within the glassy structure [19].

Some of the models are discussed in greater depth below.

- DC conductivity, also known as bulk conductivity, refers to the movement of ions over long distances in response to an applied electric field. In glasses, the DC conductivity is mainly attributed to the migration of mobile ions or defects, such as oxygen vacancies or interstitial ions. The DC conductivity is typically observed at high temperatures, where the activation energy barrier is relatively low, and the ions can move freely in response to the applied electric field. At high temperatures, the activation energy barrier is reduced, and the charge carriers have enough thermal energy to overcome the barrier and move more freely through the material, resulting in a higher conductivity.

- On the other hand, AC conductivity, also known as localized conductivity or hopping conductivity, refers to the movement of ions or defects between equivalent energy sites by hopping or jumping mechanisms. The hopping mechanism involves the transfer of ions or defects from one site to another by overcoming an energy barrier of lower magnitude compared to the DC conductivity. AC conductivity is typically observed at low temperatures.

Table 2.1: *List of Theoretical Models for carrier transport for DC and AC conductivity*

Theoretical Models for carrier transport	
D.C. Conductivity $\omega\tau < 1$ *Ions travel long distances*	**A.C. Conductivity** $\omega\tau > 1$ *Ions hop and relax between equivalent energy sites*
Charles– Polarization/ Diffusion	**Jonscher** - Universal Response
Anderson & Stuart - Coulomb & Strain Energies	**Ngai** - Coupling Theory
Moynihan & Macedo - Debye & Faulkenhagen	**Moynihan**– Modulus
Ravaine & Souquet - Weak Electrolyte	**Dyre** - Power Law
Malugani- *AgI* Micro domains	**Funke** - Jump Relaxation
Ingram - Cluster Pathways	**Dieterich & Bunde** -Coulomb Interaction
Elliott - Local Structure/ Diffusion Controlled Relaxation	**Elliott** - Diffusion-Pathways

(a) DC Conductivity models

Numerous theoretical models have been developed to describe the ion conduction pathways in such materials. These models were developed using the thermal, structural, and transport properties of mobile ions. Nevertheless, no model exists today that fully explains the ion which travel long distances resulting into dc conductivity mechanism in glasses. A brief discussion of a few of the models follows.

(i) The Anderson-Stuart model (A-S model)

The Anderson-Stuart (A-S) model, developed in 1954, is a model used to calculate the activation energy required for cationic transport in glasses, specifically silicate glasses like $Na_2O - SiO_2$ and $PbO - SiO_2$ [20]. This model breaks down the activation energy for conduction into two components: the electrostatic binding energy of the initial site (E_B) and the strain energy (E_s). The first component, E_B, represents the Coulombic forces acting on the ion as it moves away from the charge-compensating site. This component is related to the strength of the bond between the ion and the neighbouring atoms in the glass structure. The second component, E_s, represents the mechanical forces acting on the ion as the structure expands to allow the ion to move between sites. This component is related to the strain energy of the glass structure.

The basic concept is that an ion simply jumps from one site to the another and transits by an "opening doorway" that only opens as ion passes through it. For this to occur, the presence of non-bridging oxygen at cation sites is required. As a result, the model calculates the activation barrier (E_a) as the total of the two variables in the equation.

$$E_a = E_B + E_S \ \ldots\ldots (2.14)$$

The activation energy E_a corresponds to the energy barrier for cation migration. Whereas, E_B is the electrostatic binding energy between the mobile ion and the host network as given as Eq. (2.15) and E_S represents the elastic component of mechanical strain energy.

$$E_B = -\left(1 - \frac{1}{m}\right) M E_c \ \ldots\ldots (2.15)$$

The binding energy E_B is assigned to the difference in the columbic energy,

$$E_c(x) = \left(\frac{Z_1 Z_2 e^2}{\varepsilon_\infty x}\right) \ \ldots\ldots (2.16)$$

Which acts at a distance x between two point charges, $Z_1 e$ and $Z_2 e$, across a dielectric medium with the permittivity of dielectric medium, ε_∞, while it is at an equilibrium site and when it is midway between equilibrium sites for all ion pairs. M in Eq. 2.15 is referred

to as the Madelung constant for the specific glass structure and represents the sum of the impacts of other charges (ions) in the network. By taking $\left(1 - \frac{1}{m}\right) M \approx 1$, the Eq. 2.15 can be simplified [21].
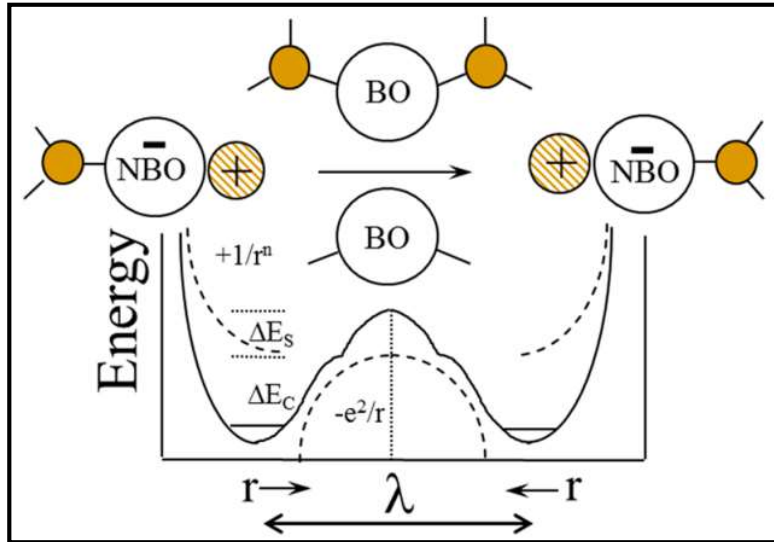
The mathematically the A-S model can be represented as:

$$E_a = \frac{\beta_M}{\gamma}\left[\frac{zz_0e^2}{\delta + \delta_0} - \frac{zz_0e^2}{a/2}\right] + 4\pi G \delta_D(\delta - \delta_D)^2 \quad ..... (2.17)$$

When the jump distance a tends to the limit ∞, the Eq. 2.17 can be simplified as

$$E_a = \frac{\beta_M}{\gamma}\left(\frac{zz_0e^2}{\delta + \delta_0}\right) + 4\pi G \delta_D(\delta - \delta_D)^2 \quad ..... (2.18)$$

The terms δ and δ_D are corresponding radius of the cation and the "opening doorway" respectively. Anderson and Stuart assert that the covalence parameter, γ, indicates the deformability of the electron cloud on oxygen atoms, which is arbitrarily chosen in the equation corresponding to the relative permittivity ε_r of the atoms. Depending upon the spatial arrangement of ions in the matrix, the Madelung constant β_M can be defined.

Figure 2.2: A-S model for Alkali Oxide glasses: Schematic potential energy landscape of an alkali ion.

The charge and the radius of the O^{2-} are denoted as z_0 and δ_0 respectively and the charge of the cation is given by z. The modulus of elasticity is described by the parameter G. The doorway radius δ_D is estimated using the diffusion data of uncharged noble gases such as He, Ne, and Ar. During its motion, the ion must first overcome the coulombic interactions that bind it to its site. Following that, it must cross a narrow passage known as a doorway. The term "doorway" refers to the opening between two anions that are normally linked with one another. When three ions are mutually connected, the doorway can be a triangular opening. It is observed in alkali silicate-like oxide glasses, where the doorway is formed by the bridging (BO) and non-bridging oxygens (NBO).

The A-S model (also known as the "two-site model") refers to the process of ion conduction in solid electrolytes. The model proposes that the ion conduction occurs through a series of well-defined sites, or "doorways," that are separated by regions that are impermeable to ions. According to the A-S model, each doorway consists of two equivalent and well-separated ion sites, which can accommodate one ion each. To allow ion passage, the doorway must be opened, which requires pushing oxygen atoms outward. This process causes atom compression, which also contributes to the activation energy required for ion conduction. The activation barrier E_a is consequently estimated as the sum of two factors in this model as shown in Fig. 2.2.

(ii) The weak electrolyte model

The weak electrolyte model is a theoretical framework used to describe the behaviour of electrolyte solutions that contain a low concentration of ions. In such solutions, only a fraction of the solute molecules dissociates into ions, resulting in a low conductivity. This model is applicable to liquids and glasses where the actual stoichiometric concentration of ions is greater than the concentration of mobile ions in solution [22]. When a foreign ion is added to a weak electrolyte solution, its effect on the conductivity depends on whether it increases or decreases the concentration of mobile ions in solution. If the foreign ion increases the concentration of mobile ions, then the conductivity of the electrolyte will increase. On the other hand, if the foreign ion decreases the concentration of mobile ions, then the conductivity of the electrolyte wi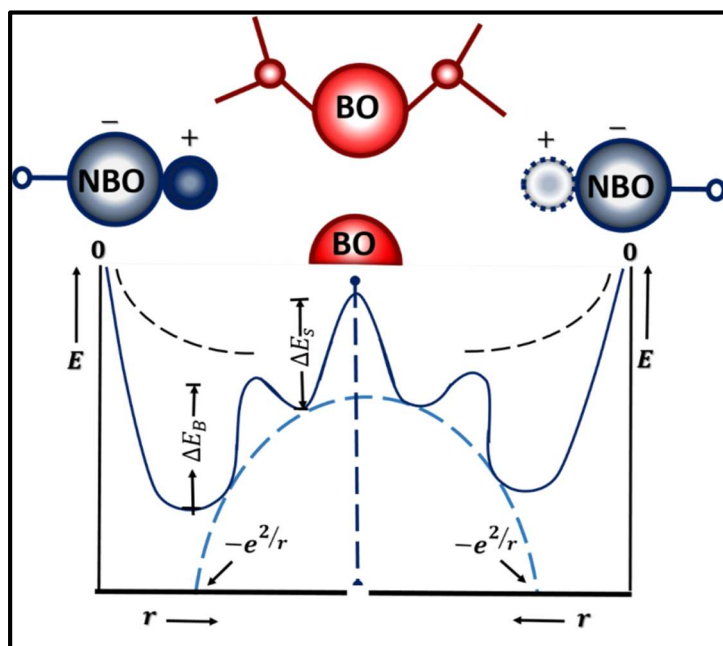ll decrease [23]. Ravaine and Souquet have found out that the square root of the M_2O interaction in glasses such as $Na_2O - SiO_2$ and $K_2O - SiO_2$ is related to the ionic conductivity by using the measurement of O_2 to O^{2-} ratio. According to the theory the charge carriers, M^+, come from a dissociation equilibrium like $M_2O = M^+ + OM^-$.

Figure 2.3: *The dissociated ions are available for conduction: Schematic of weak electrolyte model.*

The statement that the concentration of "free" M^+ ions, not the mobility, causes the strong dependence of conductivity on the mole fraction of M_2O suggests that the presence of these ions in the material is crucial for efficient conduction. The "weak electrolyte" idea states that only dissociated cations are easy to get to for conduction further supports this notion, as it implies that the ions need to be in a certain state (dissociated) in order to contribute to conductivity. The concept of "interstitial pair – non bridging oxygen compounds" may be related to the structure of the material, and they may play a role in the formation or presence of the M^+ ions [24], [25]. Following this concept, the ionic conductivity can be stated mathematically as the following expression:

$$\sigma = n\,(zq)\,\mu \quad \ldots\ldots(2.19)$$

$$\sigma = constant \; x \; [Na^+] \quad \ldots\ldots(2.20)$$

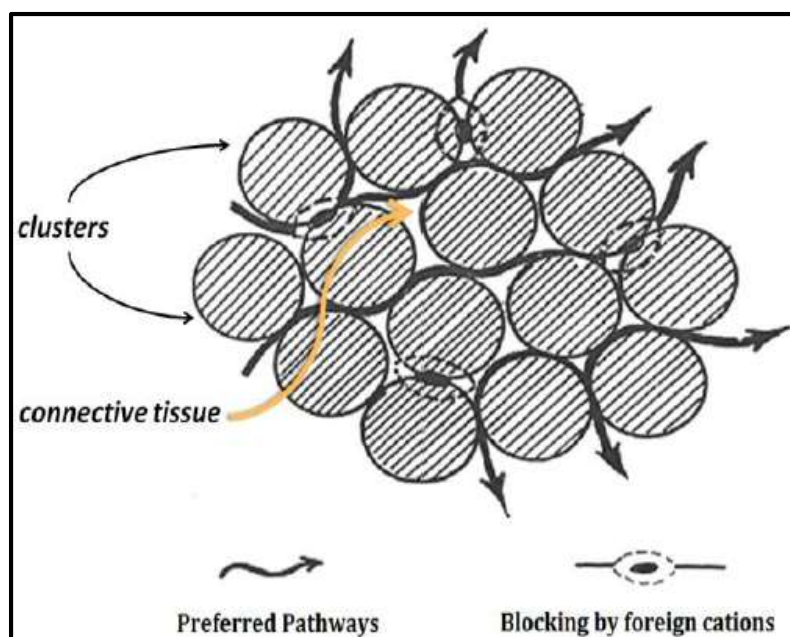$$Na_2O \leftrightarrow Na^+ + NaO^- \quad \ldots\ldots(2.21)$$
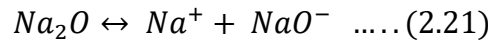
Where, n is the mobile ion concentration with the charge (zq) and (μ) is the mobility of this ion type.

This model can be used to describe the conductivity of $Na_2O - SiO_2$ glass [7], [22], [26], [27], where SiO_2 acts as the solvent and Na_2O acts as the solute. In the weak electrolyte idea, the solvent is seen as a dielectric continuum. The ionic conductivity and thermodynamic activity of the Na^+ (from Na_2O) cation are shown to be correlated in the following equilibrium reaction Eq. 2.21. Choosing a glass network with highly polarizable atoms increases the dielectric constant and thus the conductivity.

(iii) The cluster bypass model

Ingram's hypothesis proposes that the ionic conductivity in glasses arises from small regions that remain in the liquid phase even when the temperature is below the glass transition temperature (T_g) [28], [29]. These regions create pathways that allow the diffusion of cations through the glass via a percolation process. As the residual liquid phase solidifies, the number of pathways decreases, resulting in a decrease in glass conductivity with increasing temperature. The cluster bypass model demonstrates the increase in activation energy due to the presence of "mixed mobile ions". Foreign cations accumulate in the liquid phase regions and restrict the most favourable pathways, leading the mobile host cations to take less favourable paths through the glass clusters. This effect is known as the "mixed ion effect". Burton et al,; [30], [31] defined glass as having a cluster-tissue texture, and vitrification was thought to be the congelation of orderly micro domains or clusters contained in a really amorphous, low density "tissue" material. It is known that the

Goodman model [32] was used by Ingram et al. [28] to explain the behaviour of inter-cluster spaces in a particular system. The Goodman model proposes that the spaces between clusters are filled with a residual liquid that solidifies into a "connective tissue" when cooled below T_g. This connective tissue acts as a pathway for ion migration in the system. Fig. 2.4 likely shows a visual representation of this concept.

Figure 2.4: Clustering in glass shows ion migration pathways.

The Goodman model is a theoretical model that describes the electrical conductivity of glasses, specifically those containing ionic conductors. It is based on the idea that the ionic conductivity in glasses is primarily determined by the diffusion of ions through a network of channels formed by the glass structure. These channels are not completely open, but instead are partially closed by other ions or structural defects.

The Arrhenius trend refers to the relationship between the temperature and the electrical conductivity of glasses. According to the Arrhenius equation, the electrical conductivity of a material increases exponentially with temperature. In some AgI-rich glasses, this trend can be explained by the continuous exchange of matter between the "tissue" and "cluster" regions in the glass. The tissue region is where the glass structure is more open, allowing for the movement of ions, while the cluster region is where the structure is more ordered and the movement of ions is restricted. The exchange of matter between these regions can enhance the mobility of ions and increase the electrical conductivity of the glass.

In alkali silicate glasses, the Goodman model can be used to explain the significant dielectric loss observed in these materials. The mobility of ions in the partially closed channels of the glass structure can result in significant dielectric loss, as the ions interact with the electric field and dissipate energy as heat. The addition of halide dopants to glasses can also affect the conductivity of the material. Halide ions can occupy some of the partially

closed channels in the glass structure, which can increase the mobility of ions and enhance the electrical conductivity of the material. The Goodman model can be used to explain these effects and provide insights into the behavior of ionic conductors in glasses.

(b) AC Conductivity models

Models of conductivity that have been presented previously by researchers all over the world are essentially random potential energy models [33],[34]. As a result of the presence of a random structure, the ions in this model are assumed to have a randomly varying potential energy.

In ac conductivity measurements, the dc conductivity is signified by the σ_{dc} or $\sigma(0)$. While the value of $\sigma(0)$ typically varies by several orders of magnitude between different solid substances, the value of $\sigma(\omega)$ fluctuates substantially less when the value of ω is relatively high. This can be interpreted in terms of Dyre's (1993) formula for alternating current conductivity, which is as follows:

$$\sigma(\omega) = \sigma(0)\left(\frac{i\omega\tau}{\ln(1 + i\omega\tau)}\right) \quad \dots \dots (2.22)$$

At a higher frequency when ω tends to ∞, then the conductivity comparison for two different solids can be given as,

$$\frac{\sigma_1(\omega)}{\sigma_2(\omega)} = \frac{\sigma_1(0)\tau_1}{\sigma_2(0)\tau_2} = \frac{\Delta\varepsilon_1}{\Delta\varepsilon_2} \quad \dots \dots (2.23)$$

Because the relation for the dielectric strength can be given as,

$$\Delta\varepsilon = \frac{\sigma(0)\tau}{2\varepsilon_0} \quad \dots \dots (2.24)$$

Due to the very minute difference in $\Delta\varepsilon$ amongst solids, the ac conductivities of the majority of materials fluctuate very little at high frequencies.

Jonscher formulates the first attempt to develop a general model for ac conductivity in glasses. The equation $\sigma(\omega) = \sigma(0) + A\omega^n$, where $0 < n < 1$, represents the variation of ac conductivity with frequency. The log-log plot of conductivity vs. frequency permits visualisation of a variety of well-known phenomena, ranging from long-range displacement to resonant vibration. From $n = 0$ to $n = 0.6$ to 1, the power law area and law behaviours (plot trend) can be identified as the frequency increases. The power law area and the dc plateau should be viewed as a single unit. According to Funke, both regions collectively represent 'successful' and 'unsuccessful' mobile ion hopping [35].

In dc conduction, the charge carrier must overcome the largest barrier to hop to another site, but in ac conduction, the charge carrier must hop across a much smaller barrier, resulting in a very little distance travelled. Because charge carrier jump probabilities are believed to be time-independent, whenever the process re-enters state, the Markovian property forces it to resume, as explained in hopping models. As a result, rate theory provides an adequate description of hopping conductivity. The following are some of the fundamental theories that describe charge carriers hopping across a small and random potential barrier. Here are a few of them:

1. Mott's Variable Range Hopping: This theory applies to materials where the hopping occurs through localized states. According to this theory, the probability of a charge carrier hopping to a nearby site depends on the distance between the sites and the energy required to overcome the potential barrier.

2. Efros-Shklovskii Hopping: This theory applies to materials where the hopping occurs through Coulombic states. According to Efros-Shklovskii variable range hopping (ES-VRH) $R \sim exp[(T_{ES}/T)^{1/2}]$, the hopping rate depends on the density of states, the distance between the sites, and the energy required to overcome the potential barrier.

3. Marcus Theory of Electron Transfer: This theory applies to materials where the hopping occurs through molecules or ions. According to this theory, the hopping rate depends on the reorganization energy, the electronic coupling between the sites, and the energy required to overcome the potential barrier.

Numerous theories have been presented to explain ac conduction in amorphous systems. The pair approximation is frequently assumed to hold true, implying that dielectric loss happens as a result of carrier motion being regarded to be concentrated inside pairs of sites [36].

(i) The Random site model

The random site model proposed by Nassau [37] is a model that can be applied to binary glass systems, specifically those that contain lithium ions and network modifier dopant salts such as $Li_2O - B_2O_3, Li_2O - Ga_2O, Li_2O - Al_2O_3$. In this model, the dopant salt is uniformly distributed throughout the glass, which helps to enhance ion conduction by reducing the potential barrier height within the glass structure. The model considers all ions of a particular type as potential carriers, and assumes that their activation energy is distributed according to a Gaussian distribution.
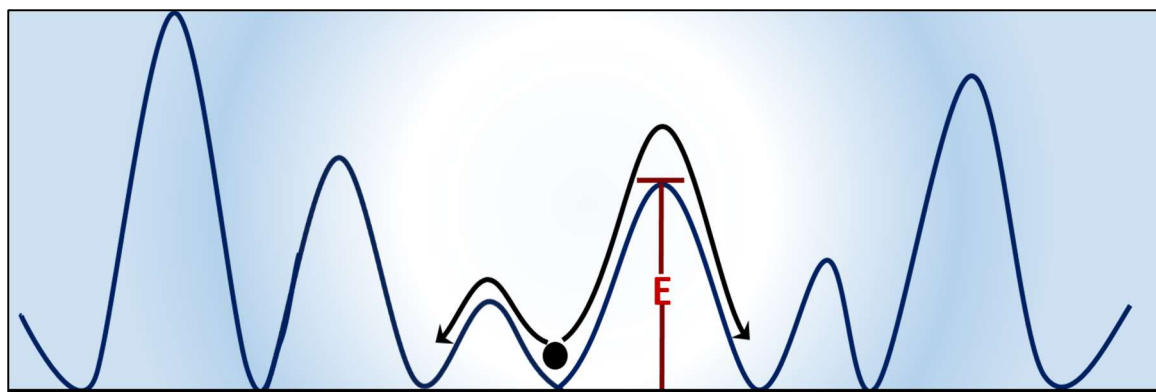
Figure 2.5*: Random barrier/site model. Typical potential for a system described by the RBM, shown here in one dimension. The barriers are assumed to vary randomly according to some probability distribution. The arrows indicate the two possible jumps for the charge.*

The mobility of the charge carrier changes with the distribution of activation energy and thus with the glass composition. The variation in conductivity with composition is mainly determined by the variation in mobility because the variation in carrier concentration is often small. Fig. 2.5 shows how the mobility changes with the distribution of activation energy and hence with the glass composition. The random site model provides a useful framework for understanding the ion transport behavior in binary glass systems containing lithium ions and dopant salts, and can be used to predict the conductivity of these materials under different conditions. Thus, the glass composition is the critical parameter for determining the average ion mobility, which changes with the activation energy distribution [38]. This model is distinct from the weak electrolyte model in that it assumes that the mobility of cation increase as the modifier or dopant salt concentration increases, whereas in the weak electrolyte model, only a fraction of the cations is mobile and their mobility is assumed to be constant.
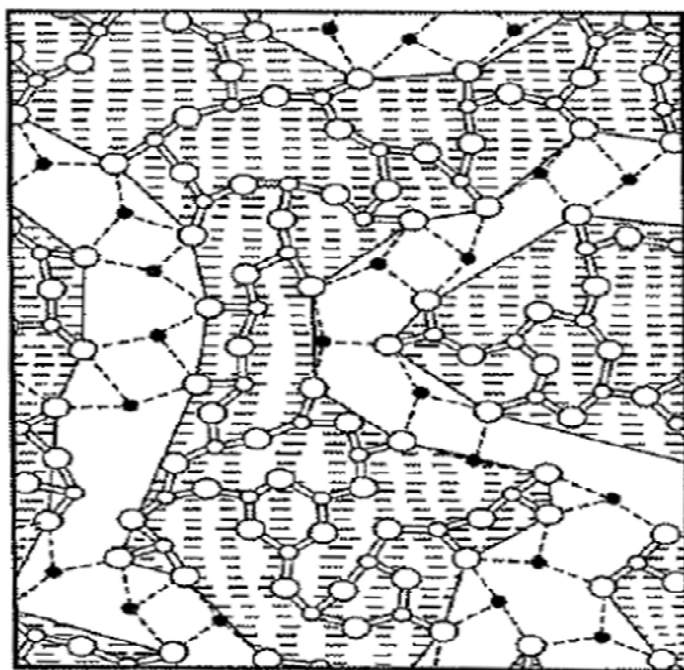
(ii) The Diffusion Pathway model

T. Minami (1985) proposed the diffusion pathway model, which considers both the mobility and concentration of mobile ions in $AgI - Ag_2O - M_xO_y$; ($M_xO_y = P_2O_5, B_2O_3$ and V_2O_5) glasses [38]. According to this hypothesis, the metal halide (dopant) is present in small clusters or micro domains in the vitreous glassy network, which are connected pathways that enable the ions to diffuse through the glass easily and effectively. A significant potential energy difference caused by the co-existence of two different types of anions, iodide and oxide, may explain the facts that all silver ions in a glass do not contribute to conduction and that the mobility factor varies depending on the composition of the glass.

There are three types of potential energy combinations present in the glass structure:

1. The first type of interaction occurs between iodide ions themselves, which leads to shallow-shallow potential wells. This means that the energy required for the ions to move is relatively low, resulting in a high level of ion mobility.

2. The second type of interaction occurs between iodide and oxide ions, resulting in deep-shallow potential wells. In this case, the iodide ions are more strongly attracted to the oxide ions, which creates a deeper potential well for the iodide ions. This makes it more difficult for the iodide ions to move, leading to lower ion mobility.

3. The third type of interaction occurs between oxide ions themselves, resulting in deep-deep potential wells. In this case, both the oxide ions are strongly attracted to each other, creating a deep potential well. This makes it extremely difficult for ions to move, resulting in very low ion mobility.

The formation of potential wells can be described when Ag^+ interact with different types of ions, such as iodide ions and oxide ions. A broad shallow potential well is formed when silver ions interact with iodide ions, while a narrow deep potential well is formed when silver ions interact with oxide ions. The framework oxyanion also interacts with iodide ions, leading to a significant potential energy difference. Silver (Ag) ions trapped in deep potential wells have less mobility than those trapped in shallow potential wells.

Figure 2.6: *Modified continuous random network (MCRN) model.*

The carrier concentration, or the number of mobile ions available for conduction, is proportional to the amount of silver ions in the shallow wells, while their mobility is proportional to the time the shallow wells are connected. When shallow wells are connected for an extended period of time, they form a diffusion channel that is favourable for ion transport. This suggests that the shallow wells may play a critical role in facilitating the movement of ions, while the deep wells may hinder ion transport.

In random structures, such as amorphous materials or disordered alloys, the lack of long-range order and symmetry can create a large number of low-energy pathways for ions to move through. This can facilitate diffusion and ion migration, allowing for faster transport of charged species. In particular, halide ions such as iodide or bromide can promote ion migration in random structures by forming low-energy barrier pathways through their interactions with the surrounding host matrix. This behavior has been observed in a range of materials, including perovskite solar cells and solid-state electrolytes. This model can be described using the modified continuous random network (MCRN) model [39] which is depicted in Fig. 2.6. The percolation pathways in the metal oxide modified network glasses are created through the inter-network channels of network modifiers and NBOs, and they serve the same purpose that the halide ions do in the doped glasses in terms of forming percolation pathways.

The diffusion pathway model is similar to the cluster bypass model, except that the interconnected sections in the diffusion pathway model are formed of the dopant site or network modifiers, whereas in the cluster bypass model, they are comprised of residual liquid.

(iii) The Jump Relaxation model

The phenomenon of jump relaxation pathways in solid ionic conductors is characterized by the movement of defects in the material due to repulsive interactions. According to Elliot's model [40], individual defects exhibit correlated forward and backward hopping, as illustrated in Fig. 2.7. The frequency spectrum of the hopping motion can be described by this simple model, which captures the microscopic relaxation dynamics. This function is useful in empirically demonstrating the "universal dynamics response," which is observed in the complex behavior of conductivity, permittivity, and ionic conductivity as a function of frequency. Funke's prediction that all hops are prone to failure is related to the fact that the defects tend to return to their original locations due to attractive interactions. This can result in a phenomenon called "trapping," where defects become immobilized in certain regions of the material. The dynamics of defect motion and trapping have important implications for the performance of solid ionic conductors in applications such as batteries and fuel cells.
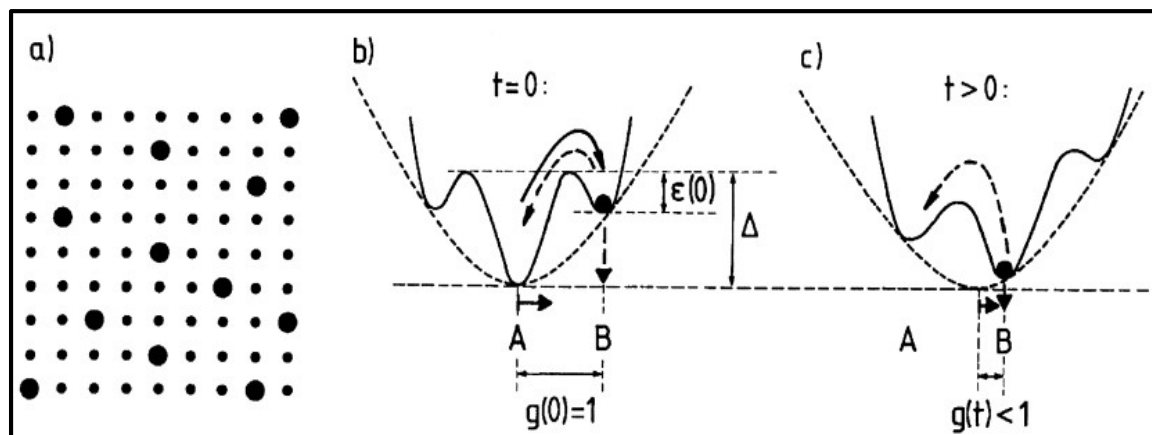
Figure 2.7*: Model for jump relaxation, (a) Ions on a sub lattice, (b) potential cage effect **(--)**, and single-particle potential (solid line) after a hop from A to B at time t=0, (c) building up potential for $t > 0$.*

If the back-hope process is delayed, the target site relaxes, finally resulting in the successful hop [35]. Non-Debye-like relaxation processes are common in glasses. These systems exhibit a non-exponential behaviour, which can be attributed to the inhomogeneous structure of glasses and the numerous body influences on relaxation. In high ion conducting glasses, the many body interactions between mobile ions is strong.

Kohlrausch, William, and Watt (KWW) were among the first researchers to study the behavior of electrical conductivity relaxation in electrolytes. They observed that the relaxation process did not follow a simple exponential decay but instead exhibited a stretched exponential behavior. As you mentioned, this stretched exponential behavior can be quantified using the Kohlrausch constant, β. When $\beta = 1$, the relaxation behavior is known as Debye relaxation, and it occurs when all the ions in the electrolyte have the same relaxation time. However, when $\beta < 1$, it suggests that the relaxation behavior is due to a distribution of relaxation times, which could arise from the different structural parts of the system. Alternatively, the stretched exponential behavior could also be attributed to the cooperative motion of charge carriers in the electrolyte. In this case, a lower β value could indicate that there are different structural parts of the system that contribute to the relaxation process, leading to a slower and more complex relaxation behavior. Overall, the stretched exponential behavior of conductivity relaxation in electrolytes is a complex phenomenon that can be attributed to various factors, including the distribution of relaxation times and cooperative motion of charge carriers. Numerous attempts have been made to link β with a variety of factors such as inter-cationic distance and conduction activation barriers. The temperature dependence of the frequency exponent, $n(T)$, is often used to understand the

conduction mechanism of a material. The value of $n(T)$ can vary with temperature and frequency, and it is typically obtained from fitting experimental data of the complex impedance or admittance of a material. The value of $n(T)$ is related to the distribution of relaxation times in the material, which is related to the mobility of charge carriers and the density of states in the material. Different theoretical models have been proposed to explain the behavior of $n(T)$ for different conduction mechanisms. By analyzing the temperature dependence of $n(T)$ and comparing it with theoretical models, we can recommend an acceptable model for the conduction mechanism to determine the primary conduction mechanism of the sample.

(iv) Correlated Barrier Hopping model (CBH)

The Correlated Barrier Hopping (CBH) model is a theoretical framework used to describe the electrical conductivity of materials with localized states in their bandgap. The model proposes that the conduction mechanism occurs via hopping of charge carriers between localized states separated by a Coulombic barrier. In this model, the charge carriers are either polarons or bi-polarons, which are 'quasiparticles' formed by the interaction of an electron with the surrounding lattice.
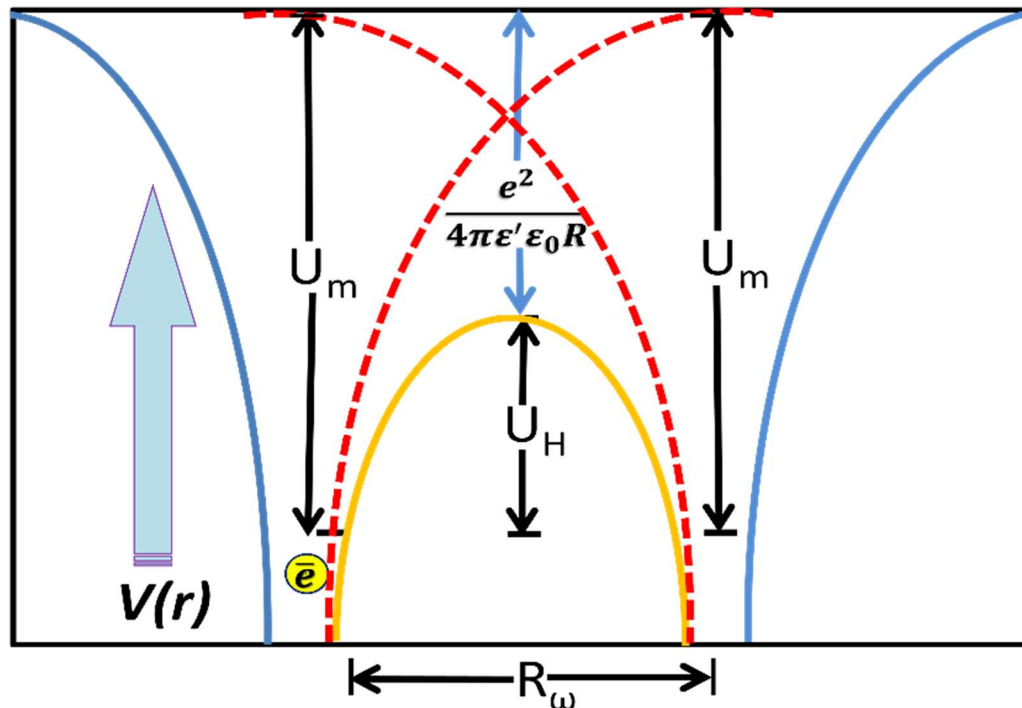
Figure 2.8: *Correlated barrier hopping (CBH) model for charge carrier transfer.*

The CBH model also assumes that the Coulombic barrier between the localized states decreases with increasing temperature, leading to an increase in the hopping probability and, consequently, an increase in the conductivity. The frequency dependence of the

conductivity is described by a power-law relationship, where the frequency exponent $n(T)$ decreases as the temperature increases. This behavior is attributed to the temperature dependence of the Coulombic barrier and the correlation between the charge carriers. Pike (1972) [41] used the CBH model to calculate the frequency-dependent conductivity of Scandium oxide films, while Elliott (1978) [42] extended the model to study chalcogenide glasses.

Theoretically, this model is based on the assumption that charge carrier hopping is frequency independent, as indicated by the fact that the relaxation variable U_M is found to be independent of the distance between two sites separated by R. The mathematical expressions that will be used to demonstrate the model are listed below.

$$n(T) = 1 - \frac{6kT}{U_M + kT\ln(\omega\tau_0)} \quad \ldots\ldots (2.25)$$

If the maximum barrier height at a certain temperature is specified as $U_M \gg kT$, $\omega\tau_0 \sim 1$ where τ_0 is the time constant for downhill jump. When the field is applied, the revised values of the frequency dependent power exponent $n(T)$ and frequency dependent hopping distance (R_{min} in Å) can be written as follows:

$$n(T) = 1 - \frac{6kT}{U_M} \quad \ldots\ldots (2.26), \quad and \quad R_{min} = \frac{e^2}{\pi\varepsilon'\varepsilon_0 U_M} \quad \ldots\ldots (2.27)$$

Charge carriers (e.g. electrons or ions) are moving between two sites, and the energy required for them to move from one site to the other depends on the Coulombic potential of each site and the distance between them. When the two sites are close together, the Coulombic potentials overlap, which reduces the effective energy barrier that the charge carriers have to overcome to move from one site to the other i.e., from (infinitely separated) U_M to U_H. The higher the barrier, the less likely it is for the charge carriers to move, and the lower the temperature, the less thermal energy the charge carriers have, which also reduces the likelihood of movement. This can be expressed as the following equation.

$$U_H = U_M - \frac{e^2}{4\pi\varepsilon'\varepsilon_0 R} \quad \ldots\ldots (2.28)$$

where e denotes the charge of the carrier, ε' denotes the dielectric constant of a material, and ε_0 denotes the free space permittivity. The distance between two adjacent hopping sites (R in Å) and τ_0 is the characteristic relaxation time; its usual value τ_0 $(= 10^{-13}s)$ is of the order of vibrational period of an atom. kU_M is the energy necessary to entirely remove

an electron from a site. While N indicates the concentration of a pair of sites and R_ω refers the hopping distance between them at a certain frequency (ω) can be written as,

$$\sigma_{ac} = \frac{\pi^3}{12} N^2 \varepsilon' \varepsilon_0 \omega R_\omega^6 \quad \ldots \ldots (2.29), \text{ and } R_\omega = \frac{2e^2}{\pi \varepsilon' \varepsilon_0 \{U_M + kT \ln(\omega \tau_0)\}} \quad \ldots \ldots (2.30)$$

The models seen in Fig. 2.8, is well explained in bismuth silicate glasses with titanium [43],lithium-bismuth-borate glasses [44], lithium iodide lithium tungsten [45] and $V_2O_5 - MnO - TeO_2$ glass systems [46].

(v) Quantum Mechanical Tunnelling model (QMT)

In a system with oscillating electric fields, ions will experience a potential energy that varies with time. If the frequency of the oscillating field is high enough, the ions will not have enough time to move significantly before the field changes direction. As a result, the ions are unable to diffuse and become trapped in their potential well. This phenomenon is known as ion trapping. The extent to which ions are trapped depends on several factors, including the strength and frequency of the electric field, the mass and charge of the ion, and the temperature. In general, lighter ions with higher charge-to-mass ratios are more easily trapped than heavier ions with lower charge-to-mass ratios. Additionally, it has been discovered experimentally that when the frequency of a system increases, the conductivity increases as well. Based on this theory, Pollak and Geballe (1961) [47] initially explained electron tunnelling in glassy materials; later, Caldeira and Leggett (1981) [48] extended this idea to explain macroscopic tunnelling. QMT, conductivity is often described in terms of the tunnelling of charge carriers, such as electrons or ions, through potential barriers. In materials with frequency-dependent conductivity, the charge carriers can tunnel between unoccupied sites, which leads to a complex response to applied electric fields that depends on the frequency of the field. There are two main mechanisms proposed to explain the relaxation behaviour of such materials: quantum-mechanical tunnelling and classical hopping over a barrier. In many cases, the two mechanisms may coexist, and the carriers may be a combination of electrons, polarons, or ions [36]. The precise mechanism(s) responsible for the frequency-dependent conductivity of a particular material depends on the specific properties of the material. The following Eq. 2.31 gives the characteristic tunnelling distance R_ω at a given frequency ω, where $\omega \tau_0 = 1$.

The exponent n describes the quantum mechanical tunnelling through the potential barrier.

$$R_\omega = \frac{1}{2\alpha} \ln\left(\frac{1}{\omega\tau_0}\right) \quad \dots\dots (2.31)$$

In this model the exponent n is predicted to be independent or weakly dependent of temperature[49].Thus, for the QMT model, the frequency exponent n is temperature independent but frequency dependent, and a value of $n = 0.81$ is determined from Eq. 2.32 for typical values of the parameters, namely $\tau_o \cong 10^{-13}$ s and $\omega = 10^4$ s^{-1} [36].

$$n = 1 - \frac{4}{\ln\left(\frac{1}{\omega\tau_0}\right)} \quad \dots\dots (2.32)$$

For the QMT, the real part of the ac conductivity can be written as follows.

$$\sigma(\omega) = \frac{Ce^2 kT}{\alpha} N^2\left(E_f\right) \omega R_\omega^4 \quad \dots\dots (2.33)$$

where $N\left(E_f\right)$ is the density of states at the fermi energy level, the constant $C = \frac{1}{24}\pi^2$. This model is being used by many researchers for the systems like in silver vanadate glass by Bhattacharya & Ghosh [50] and amorphous semiconducting material, tetrahedral and group V and chalcogenides are reviewed by Long (1982) [51].

(vi) Non-overlapping Small Polaron Theory (NSPT)

A charge carrier (such as an electron or a hole) can interact strongly with the surrounding lattice, leading to the formation of a localized distortion or "polaron cloud" around the charge carrier. This distortion can be significant enough that the total energy of the system (including both electronic and lattice contributions) is lowered by an amount W_P, resulting in the formation of a 'quasi-particle' called a polaron. If the polaron is "small" (i.e., the distortion cloud is localized to a single lattice site), it behaves like a free particle with an effective mass that is increased due to the interaction with the lattice. At low temperatures, the small polaron can move coherently through the lattice by tunnelling between adjacent sites, resulting in a mobility that is typically lower than that of a free particle. At higher temperatures, thermal fluctuations can activate the polaron to hop between sites, resulting in an activated transport mechanism.

 As a result, the activation energy for polaron transfer, $W_H \approx \frac{1}{2}W_P$, is independent of the inter-site spacing. The Non-overlapping small polaron tunnelling (NSPT) model [52] is a theoretical framework used to describe charge transport in disordered systems.

In this model, the charge carriers are assumed to be small polarons that hop between localized states in the material. The NSPT model predicts that the frequency exponent $'n'$ for charge transport in such systems depends on the temperature and the characteristic frequency of the hopping process. The expression for $'n'$ in the NSPT model is given by:

$$n = 1 - \frac{4}{ln\left(\frac{1}{\omega\tau_0}\right) - \frac{W_H}{k_B T}} \quad \ldots\ldots (2.34)$$

where ω is the characteristic frequency of the hopping process, τ_0 is the characteristic hopping time, W_H is the polaron binding energy, k_B is the Boltzmann constant, and T is the temperature. According to the NSPT model, the value of n decreases with increasing temperature. This means that the characteristic hopping time τ_0 decreases with increasing temperature, which in turn leads to an increase in the frequency exponent $n(T)$.

The increase in $'n'$ with temperature is due to the fact that at higher temperatures, the hopping process becomes more thermally activated, and the charge carriers are able to access states that are further away from their initial position. It should be noted that the NSPT model is a simplified description of charge transport in disordered systems, and there are other models that may be more appropriate in certain situations.

However, the NSPT model has been used successfully to explain the behavior of a wide range of materials, and it remains a useful tool for understanding charge transport in disordered systems. This approach is shown to apply to transition metal oxide doped semiconducting glassy systems [53] and bismuth zinc vanadate glass system by R. Punia et al,; [54].

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