Chapter III

Theoretical aspects
3.1 Introduction: Much of the increased activities in superionic solids are due to their potential applications in solid state ionic devices. In addition, they are also fascinating for physicists in understanding the conduction process. The fundamental problem of basic research is to establish relationships between ionic transport and local atomic structure. Different classes of fast ion conductors have different structural arrangement and many theoretical models have been proposed to explain their transport properties. Several excellent reviews have been published outlining the theoretical treatment of solid electrolytes [1-12]. The present chapter gives a brick review of various theoretical models proposed and recent developments for cash class of supersonic solids.

The ionic conductivity is due to the movement of ions through the lattice. The direct cation anion exchange is ruled out because of high potential barrier involved. Hence, the ion transport is mediated through defects. The ion transport in general is governed by the jump probability of the ion into a defect. This in turn is proportional to the probability for the ion to jump into the defect in a given direction in unit time, which is called jump frequency "ω" and the probability that a given site has a defect on a nearest neighbor site this is the mole fraction of defect multiplied by the number of nearest neighbor sites. The jump frequency 'ω' depends upon the potential barrier seen by the ions, Fig (3.1a). If the Einstein model is taken, the ions are vibrating harmonically around their equilibrium positions with a vibrational
frequency \( \nu_0 \). The jump frequency \( \nu \) for a point defect in a system is given by (Chandra 1981) [1].

\[
\omega = \nu_0 \exp \left( -\frac{\Delta G}{KT} \right)
\]

(1)

where \( \Delta G \) is the free energy barrier that opposes the migration of the ion and is termed as free energy of migration. \( \Delta G \) can be written as

\[
\Delta G = \Delta H - T\Delta S
\]

(2)

where \( \Delta H \) is the enthalpy of migration, \( \Delta S \) is the entropy of migration.

\[
\omega = \nu_0 \exp \left( \frac{\Delta S}{k} \right) \exp \left( -\frac{\Delta H}{kT} \right)
\]

(3)

This is the expression for the thermodynamic equilibrium where the direction of jump is arbitrary. When an electric field is applied, the ions move in the direction of the field leading to conductivity. For the potential barrier seen by an interstitial ion jumping from one interstitial position to another, due to electric field \( E \), an additional term \( -qE x \) is added, where \( q \) is the charge on the mobile ion. The subsequent saddle-point energy keeps on decreasing by an amount \( \frac{1}{2} qaE x \) [\( x = \frac{a}{2} \) where 'a' is interionic distance].

A jump in the direction of the field, therefore, takes place with increased probability [Fig. 3.b].

\[
\omega = [\nu_0] \exp \left[ -\left( \frac{\Delta G + \frac{1}{2} qaE}{kT} \right) \right]
\]

(4)

and a jump against the field takes place with reduced probability

\[
\omega'' = [\nu_0] \exp \left[ -\left( \frac{\Delta G + \frac{1}{2} qaE}{kT} \right) \right]
\]

(5)
Fig. 3.1 a) Dependence of jump frequency \( \omega \) on the potential barrier seen by the ions.

Fig. 3.1 b) Variation of saddle point energy with potential barrier.
The net number of ions moving per unit volume in the direction of field

\[ n^1 = n [\omega' - \omega'' ] = n \omega q a E / kT \]  \hspace{1cm} (6)

assuming \( q a E \ll kT \). Here 'n' is the number of interstitial ions per unit volume. Therefore, current density \( J \) is given by

\[ J = na^2 q^2 \omega E / kT \]  \hspace{1cm} (7)

Hence ionic conductivity is given by

\[ \sigma = J/E = na^2 q^2 \omega /kT \]  \hspace{1cm} (8)

or

\[ \sigma = n q \mu \]

where \( \mu \), is the mobility, is given by

\[ \mu = a^2 q \omega / kT \]  \hspace{1cm} (9)

If the charge carriers can jump to more than one forward position, then equation (8) has to be multiplied by additional factor.

A similar expression holds good for the vacancy or interstitialcy mechanism. If \( x \) is the mole fraction of defect concentration then \( n = N x \), where \( N \) is the total number of ions per unit volume and can be written as

\[ \sigma = (Na^2 q^2 /kT) x. \omega = (Na^2 q^2 /kT) x \nu_o \exp (-\Delta G /kT) \]  \hspace{1cm} (10)

or \[ \sigma = \sigma_0 /T \exp (-\Delta G /kT) \]  \hspace{1cm} (11)

where \( \sigma_0 = Na^2 q^2 x \nu_o /K \)  \hspace{1cm} (12)
If more than one type of charge carriers are present this has to be summed for all different carriers.

A net ion transport can also be obtained if instead of an electric field gradient, a concentration gradient is maintained, which results in diffusion of ions.

### 3.2 Temperature dependence of the conductivity

The conductivity of a solid ionic conductor can be written as

\[ \sigma = \sum n_j q_j \mu_j \]  \hspace{1cm} (13)

Where \( n_j \), \( q_j \), and \( \mu_j \) are the concentrations, electrical charge and mobility, respectively, of \( j^{th} \) mobile charge carrier and the summation is over the different types of charge carriers. The temperature dependence of \( \sigma \) arises from the temperature dependence of \( n \) or \( \mu \) or both. In general the temperature dependence of \( n \) can be quite complicated since it can be influenced by the relative amounts of intrinsic defects and impurities as well as the possible association and/or precipitation [13] of these impurities and defects. Not only is the concentration of intrinsic defects and activated process, but so is the motion of the defects as well, since work is required to move the defect from its equilibrium position of minimum energy to the saddle point which separates it from another position of minimum energy. The rate at which a defect traverses a barrier is

\[ v = v_0 \exp \left( -\frac{\Delta G}{kT} \right) \]  \hspace{1cm} (14)
is called the jump frequency. $\Delta G$ is Gibbs free energy required to move the defect across the energy barrier, and $v_o$ is the vibrational (or attempt) frequency of the defect in the direction which carries it over the barrier. $v_o$ is typically comparable to a phonon frequency and is often taken to be the frequency of oscillation of the ion within the cell associated with its lattice site. In superionic conductors, where one species is more mobile than the others, the less mobile ions are said to constitute the "cage" while the attempt frequency measures the vibration of the mobile ion within the case. The diffusion coefficient (isotropic case) is given by

$$D = A r^2 v_o$$  \hspace{1cm} (15)

where $A$ is a dimensionless geometrical factor of order unity $r$ is jump distance. Substituting the value of jump frequency (equation 14) in equation (15).

$$D = A^2 r^2 v_o \exp (-\Delta G/kT)$$  \hspace{1cm} (16)

The conductivity $\sigma$ can be calculated from the diffusion constant $D$, by using the Einstein relation.

$$\sigma = ne^2 D/kT$$  \hspace{1cm} (17)

Substituting the value of the diffusion constant $D$ in above equation, we get

$$\sigma = (ne^2/kT) A r^2 v_o \exp (-\Delta G/kT)$$  \hspace{1cm} (18)

where

$n$ is the density of charge carriers (defects).
\( e \) is the charge of the defects,
\( k \) is the Boltzmann constant,
\( A \) is geometrical factor of order unity,
\( \nu_0 \) is the attempt frequency of the ion to hop over the barrier,
\( \Delta G \) is the Gibb's free energy required, to move the defect across the barrier, and
\( r \) is the jump distance.

It is known that at a given temperatures the concentrations of Schottky and Frenkel defects is given by equation (1) and (2). If for a given system the dominance of Frenkel defects is presumed of higher temperatures, then substitution of equation (2) in equation, (18) and using the relation \( \Delta G = \Delta H - T \Delta S \) yields
\[
\sigma = \sigma_0 / T \exp \left[ \frac{(-1/2) \Delta H_f + \Delta H_m}{kT} \right]
\]
where
\[
\sigma_0 = (\text{NN})^{1/2} \, e^2 \lambda A \nu_0 \, r^2 / k \exp \left( \frac{1}{2} \Delta S_f^i + \Delta S_m^i \right) / k
\]
Equation (19) describes the conductivity in the intrinsic region where defects are both formed and moved and there is a single mobile charged defect species. If, Schottky defect is assumed to be dominant equation (10) would be substituted in equation (18). In the case when more than one species is mobile, the right hand side of equation (19) should be replaced by a sum of such terms with the relevant exponents and pre factors.

In dealing with experimental data, equation (3) is more commonly written as
\[
\sigma T = \sigma_0 \exp \left( -E / kT \right)
\]
and the measured activation energy $E$ is

$$E = \frac{1}{2} \Delta H_f + \Delta H_m$$  \hspace{1cm} (22)$$

In the intrinsic regime, where the change in carrier concentration with $T$ is negligible, the measured activation energy is simply associated with the motion of the mobile species (assuming that the mobility of the species dominates), and

$$E = H_m$$  \hspace{1cm} (23)$$

Reference to equation (11) indicates that a plot of $\log \sigma T$ versus $T^{-1}$ should yield a linear response over the appropriate temperature range. By making measurements on samples over a sufficiently broad temperature range, it is possible to evaluate the various activation energies (or enthalpies). An idealized response for an ionic crystal showing various conduction regimes of interest in the present work is depicted in Fig (3.2). In the extrinsic regime (I), the response is determined by the concentration of thermally produced defects and by the mobility of the more mobile species of these defects. Deviations from I and II can be observed at both high and low temperatures. Regime III occurs at high temperature and indicates a change in the conduction process. Here, the conduction is usually also intrinsic as in regime II, and the transition from regime II to regime III could signify a change, say, from conduction by vacancy motion to conduction by interstitial motion. At sufficiently low temperatures, so-called 'association' regime is some times observed. In this regime, concentration of defects decreases with decreasing temperature than in
Fig. 3.2 An idealized representation of log $\sigma T$ versus $T^{-1}$ showing the various conduction regimes observed in normal solid ionic conductors.
the regime I because the impurity and associated defect become bound (i.e., associate), forming a neutral pair which does not contribute to the conductivity. In this regime activation energy is

\[ E = \Delta H_m + \Delta H_a / 2 \]

where \( \Delta H_a \) is the binding or association enthalpy of the aliovalent impurity and associated defect.

It has been the practice to plot \( \log \sigma T \) against \( T^{-1} \) and to fit various portions of this plot with straight lines whose slopes were then interpreted in the manner described above. In the intrinsic region the slope of the plot is equated with \( \left[ \left( \frac{1}{2} \right) \Delta H_f + \Delta H_m \right] \). Evaluation of \( \Delta H_m \) from the upper portion of the extrinsic position of the plot then allowed \( \Delta H_f \) to be derived.

3.3 Theories: For single/poly crystalline Fast Ion conducting solids:

Theories have been proposed to describe high ionic motion in fast ion conducting solids with cationic disordered phases, phase transitions in supersonic solids, \( \beta \)-aluminas, oxygen ion conductors etc. The salient features of various theories have been presented briefly.

3.3.1 Defects Transport Theory of Fast ion conductors:

The defect transport theory developed for normal ion conductors also be extended to superionic solids like fluoride ion conductors (\( \beta - \text{PbF}_2 \)) and some oxygen ion conductors. Bonne and Schoonman in 1971 [15] successfully explained ion transport ion PbF\(_2\)
using defect theory and similarly Etsell and Flenges applied it to
Zro - Y₂O₃ [16].

3.3.2. Fast ion conductors with phase Transition:

Most of the cationic and some fluoride ion conductors have
phase transition characterized by an abrupt increase in conductivity.
Hubermann [17] has showed that Frenkel pair attractive interaction is
responsible for such superionic phase transition. Where as, Rice
et. al., [18] proposed that the supersonic phase transition is due to the
interstitial defects interacting with the strain field they induce. Welch
and Dienes [19, 20] gave a generalized model combining both the
above models. They suggested that thermally generated defect
concentration modified the free energy of ionic crystal resulting in
phase transition.

3.3.3 Fast ion conductors with second order phase Transition

Supersonic solids with second order phase transition like,
CaF₂, LaF₂, SrF₂, etc. are typical examples of this type. The
conductivity changes in this type solid electrolytes is dealt by "Lattice
Gas theories". In lattice gas models ions are considered as "Lattice
Gas" hopping from one lattice point to another. These theories
interpret phase transition behavior in terms of the change in enthalpy
of motion due to various ion interactions. The first extensive treatment
was given by Sato and Kikuchi, in 1971 [21, 22], using path probability
method to explain the ionic transport in β" alumina and β - alumina
Later, ionic polaron theory was developed analogous to the anti ferromagnetic Ising model \cite{4} Leaderman et. al in 1976 have developed a model to couple order parameter with static strain and explained the phase transition in Rb Ag$_4$ I$_5$ \cite{23}.

3.4 Microscopic models:

Various microscopic theories have also been developed. Rice and Roth \cite{24} developed "Free ion model" in 1972 and they assured that a mobile ion can be excited from localized states to free ion like states, in which ion propagates through out the solid.

"The Domain model" described by van Gool and Bottleberghs \cite{25}, explains low value of activation energy as due to the movement of walls between the domains of ordered configuration. Later "jump diffusion models' of ions in a periodic lattice, including the effect of polarazability and correlated jumps, have been developed \cite{26}. These microscopic models are the foundations of current theoretical developments.

3.5 Recent developments in the theory of ordered fast ion conductor:

Much progress has been made in the recent past in the understanding of various properties of superionic conductors. These developments include; advancements in lattice gas theories, liquid like models, dynamical properties, universal ac-response of conductivity and computer simulation method to study ion transport.
3.5.1 Lattice Gas Models and other Theories

The Lattice Gas models, developed by Sato and Kukuchi, takes into account only the nearest neighbour interactions \[25,26\] Bunde et al. \[27\] have developed the theory for the conductivity of a lattice gas taking into account of long range coulombic interactions. They have shown that the conductivity is thermally activated and the activation energy is proportional to strength of coulombic interactions. The many particle hopping in coulombic lattice gas was developed by Bunde et al. in 1985 \[28\]. Furthermore, Tanaka et al. \[29\] have developed the lattice gas theory to the honey comb lattice by taking into account of the second order perturbation of hopping ion. Recently, the phonon interaction was considered by Tomayase \[30\].

The Ag I type fast ion conductors show fluid like features and these systems can be considered as a liquid embedded in a periodic medium. The properties of these supersonic conductors were examined using Langavotion dynamics, Literature on such model studies are available \[10,31,32\].

The dynamic conductivity \(\sigma(w)\) of ordered and disordered supersonic solids generally exhibit a power law in frequency \[33\].

\[
\sigma(w) \sim \begin{cases} 
A (i\omega)^n, & \omega \tau \gg 1 \\
\sigma(0), & W << 1
\end{cases}
\]

Where \(\omega\) The frequently, \(\tau\) the relaxation time, \(n\) the power-law exponent, \(A\) material dependent constant and \(\sigma(0)\) the d.c. conductivity. Were, \(\sigma(0)\ T^{-1}\) is thermally activated. The exponent \(n\)
"tends to increase by lowering temperature. This phenomena is generally know as "Universal ac - response " [34] power law spectra are also supported from quasielastic neutron scattering and nulearspin spin relaxation studies [35.37].

3.5.2 Computer Simulation methods

Computer simulation techniques are now a standard tool in the study of solid state ionic materials [38]. Three class of simulation techniques, like, static lattice, simulations, Molecular Dynamics and Monte Carlo methods have been employed to study the superionic solids.

3.5.3 Static Lattice Simulations

In this method, the lowest energy configuration of the crystal structure with certain defect parameters are obtained and the physical properties are evaluated. Methods based on the Mott- Littleton approximation [39] have proved to be particularly effective and for several systems yielded quantitative agreement with experimentally determined defect parameters [38, 40, 41].

3.5.4 Molecular Dynamics method

Classical equations of motions of an ensemble of particles are solved by including kinetic energy in the simulation. The dynamic details of the systems are directly available from molecular dynamical simulations [42]. The first molecular dynamical treatments to $\alpha$-AgI was given by Vashishta and Rahman [43, 44]. They calculated the diffusion constant of Silver ion in AgI and studied the microscopic
details of ion motion. Kobayashi et. al [45,46] applied the molecular dynamics method to study the silver ion diffusion in Ag$_2$Te and calculated transport parameters of Ag$_2$Te, which are in quite good agreement with experimental results. They have also suggested the possibility of high ionic conduction in new materials like, Ag I - Ag$_2$S system [47]. Most recent work includes structural and dynamical properties of ZrO$_2$ - Y$_2$O$_3$ investigated by Shimojo et. al [48], and sodium β Alumina by Zendejas et. al [49,50]

3.5.5 Monte Carlo Method.

This is essentially a technique of statistical mechanics [59, 52]. In this method, the ensemble configuration is generated by a succession of random moves. The same procedure is applied to study ionic transport in solids [52]. Ion hopping models are conceptually simple and are directly accessible by monte carlo simulations [51]. Tachibana and Dkazaki [53, 54] have used ion hopping models for caterpillar migration of mobile ions and simulated the Havens ratio of α-Agl type solids electrolytes. Mont carlo simulations in coulombic lattice gas have been studied by Dieterich et. al. [55].

3.6 Theories for composite solid electrolytes

Several phenomenologies have been invoked to explains enhancement in the conductivity of composite solid electrolytes. According to Wagner et. al [56], introduction of dispersed phase in the host lattice produces a space charge region at the host dispersoid interface facilitating ionic motion. The conductivity is expressed as the
sum of conductivity from host and that due to space charge region. Bunde et al [57, 58] have attempted to explain conductivity behavior in composites using percolation approach, by considering them as a mixture of normally conducting, insulating, and highly conducting bonds. Recently, the high ionic conductivities in Ag I - glass composites have been explained in the light of Macro Domain Model [59].

3.7 Models for transport in Polymer electrolytes

Many models have been proposed to explain the ion transport mechanism in the polymer electrolytes. Cohen and Turnbull [60] gave free-volume theory, free-volume picture, the ions are considered as hard spheres and are free to move in a volume fraction (voids), called free-volume. They have derived the probability distribution of void volumes in the total volume of the system. Later, following Cohen and Turnbull treatment, Ratner desired expression for diffusion constant based on free-volume theory [61]. The microscopic behaviors are dealt with Dynamic Bond Percolation Model [62, 63], in which the segmental mobility has also been included along with the ionic motion. The dynamic bond percolation model is able to describe very well the properties of dynamically disordered polymer electrolytes systems.

Different transport mechanisms for proton conduction have also been proposed. They include liquid like transport (in crystals like H-montmorillonite, H-Al montomorillonite), Grotthus mechanism and porton bond model [64, 65] applied to some organic systems like isopolyniobic alid and HUP.
REFERENCE

1) S. Chandra

2) A.L. Laskar and S. Chandra (Eds)

3) M.B. Salamon (Ed.)

4) G.D. Mahan
Phys. Rev. B, 14 (2) 780, (1976),

5) C.A. Angell

6) J.N. Mundy

7) A. Bunde

8) W. Dieterich

9) G. Mahan
In "Superionic Solids"
G. Mahan and W Roth (Eds.)
Plenum Press, N Y (1976)
10) W. Dieterich, P. Flude and I. Paschel

11) W. Dieterish

12) T. Geisel
"Physics of Superionic solids",
Topics in current physics Vol. 15, Springer - Ver., p-201 (1979)

13) S. Flugge,
"Hand book de Physik"
(Springer - Verlag, Berlin (1957)

14) Lidiard, in
"Hand buch der Physik" S. Fluagge (Ed.)

15) R.W. Bonne and Schoonman.
J. Electrochem Sco, 124, 28, (1977)


17) B.A. Huberman

18) M.J. Rice, S. Stassler and G.A. Toombs.

19) D.O. Welch and G.T. Dienes
20) D. O. Welch and G. T. Dienes

21) H. Sato and R. Kikuchi

22) H. Sato and R. Kikuchi
In "Superionic Solids"
G. Mahan and W Roth (Eds.)
Plenum Press, N Y (1976)

23) F. L. Leaderman, M.B. Salamon and H. Peisl, Solid State
Commun., 19 147, (1976)

24) M. J. Rice and W.L. Roth

25) W. Van Gool and P.H. Bottleberghs

26) B.A. Huberman and P.N. Sen

27) A. Bunde, D.K. Chaturvedi and W. Dieterich

28) A. Bunde and W. Dieterich

29) J. Tanaka, Majed A Sewatarie, J. H. Barry, N.L. Sharma and
30) T. Tomoyase  

31) R.O. Rosenberg, Y. Boughaleb, A. Nitzan and M.A. Ratner  

32) Y. Boungheb, R.O. Rosenberg, M.A. Ratner and A. Nitzan  

33) A. J. Jonscher  

34) K. Funke,  


36) M. Techez, R. Mercier, J. P. Malugani and A.J. Dianox  

37) K. Funke, A Hoch and R.E. Lechver  

38) "Computer Simulation of Solids - Lecture Notes in Physics"  
    CRA Catlow and W.C. Mackrodt (Eds.)  

39) W.C. Mackvodt solid state ionics 12, 175, (1984)
40) J. H. Harding  

41) J. R. Ray, A. Rahman and P. Vashista  

42) P. Vashista and A. Rahaman  
In "Fast ion Transport in solids"  
Vashista, J.N. Mundy and G.K. Shenoy (Eds.)  

43) P. Vashita and A. Rahaman  

44) M. Kobayashi  

45) M. Kobayashi  

46) M. Kobayashi  

47) F. Shimoja, T. okabe, F. Tachihana , M. Kobayashi and H. okazaki  

48) M. A. Zendejas and J.O. Thomas  
49) J. O. Thomas and M.A. Zendejas, in
"Solid State Ionics - Materials and Applications"
B.V.R. Chowdari, Suresh Chandra. Shri Singh and P.C.
Srivastava (Eds.)

50) K. Binder and D. Strausser, in
"Application of Monte Carlo Methods in Statistical Physics"

51) G. E. Murch, A.D. Murvgy and G.R.A. Catlow

52) F. Tachibana and H. okazaki

53) F. Tachibana and H. okazaki

54) W. Dieterich, J. Petersen, A Bunde and H.E. Roman

55) T. Jow and J. B. Wagner (Jr.)

56) A. Bunde, W. Dieterich and E. Roman

57) A. Bunde, W. Dieterich and E. Roman
Solid State ionics, 18/19, 147, (1986).

58) S.W. Martin
59) M. H. Cohen and D. Turnbull

60) M. Ratner
   In "Polymer Electrolytes (Review - I)"
   J.R. Maccaluma and C.A. Vincent (Eds.)

61) S.D. Druger, A. Nitzan and M.A. Ratner

62) S.D. Druger, M.A. Ratner and A. Nitzan

63) B. K. Sen and S. Jen

64) B. K. Sen and S. Sen.
   Solid State Ionics, 18/19, 1025, (1986)