

A Simple Model for the Non-Arrhenius Ionic Conductivity in Superionic Glasses

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Many superionic conducting glasses follow the Arrhenius type temperature dependence of ionic conductivity. However, in some superionic conductors it has been discovered that the conductivity deviate from the Arrhenius type behavior. In this paper, we present a simple model that describes the non-Arrhenius type ionic conductivity based on the Zwanzig model of diffusion. From the theory, the condition for the appearance of non-Arrhenius type ionic conductivity has been obtained.

KEYWORDS: ionic conductivity, diffusion, non-Arrhenius behavior, glasses

1. Introduction

Many fast ion conductors exhibit the Arrhenius type temperature dependence of ionic conductivity. Some years ago, Kincs et al. measured the ionic conductivity of several glassy fast ionic conductors that were optimized to obtain the highest conductivity.¹⁾ Their measurement revealed that some glasses do not follow the simple Arrhenius law below the glass transition temperature. At low temperature, these glasses exhibit the usual Arrhenius temperature dependence. By increasing temperature, the ionic conductivity starts to fall below the expected value estimated from the low temperature Arrhenius law.

Several models have been proposed to explain the observed non-Arrhenius behavior. For instance, Ngai et al. applied the coupling theory.²⁾ Mei et al. applied their ion trapping model to describe the non-Arrhenius type conductivity.³⁾ Maass et al. studied the behavior using the Monte Carlo method.⁴⁾ In this paper, a simple theory based on the Zwanzig model⁵⁾ of diffusion is proposed to describe the non-Arrhenius behavior. The condition for the appearance of the non-Arrhenius behavior has been extracted from the model.

2. Theory

2.1 Zwanzig model

The Zwanzig model is a simple jump diffusion model and has been used frequently to describe the velocity auto correlation function of liquids. This model was based on and supported by computer simulation studies.⁶⁻⁹⁾ Although originally proposed for liquids, the concept of this model is applicable to non-crystalline solids.

The Zwanzig model is based on the following assumptions.

- The particles in a system perform approximate harmonic oscillations with frequency ω around the local potential minima formed by other particles.
- The particle remains there for a certain time, until it finds a saddle point or bottleneck in the potential surface and jumps to another potential minima.
- The volume of the entire system consists of a number of equivalent subvolumes V^* . One effect of the atomic jump is to rearrange the equilibrium positions of the particles in a particular subvolume while the equilibrium positions of the remaining particles are

unchanged. Another effect is to interrupt the harmonic oscillations of the normal modes associated with the region V^* . The motions in V^* after the jump are uncorrelated with the motions in V^* before the jump.

- The waiting time distribution for the jump affecting the content of any V^* is written as $\exp(-t/\tau)$, where τ is the lifetime.
- Harmonic oscillations in the region V^* are adequately described by a Debye approximation, characterized by longitudinal and transverse sound velocities.

By using these assumptions, the self diffusion coefficient is written as

$$D = \frac{k_B T}{MN} \sum_{\omega} \frac{\tau}{1 + \omega^2 \tau^2}, \quad (1)$$

where M and N are the particle mass and number of the modes respectively. Tankeshwar and Tosi approximated the frequency spectrum by an Einstein frequency.¹⁰⁾ By using this approximation, we have,

$$D = \frac{k_B T}{M} \frac{\tau}{1 + \omega^2 \tau^2}. \quad (2)$$

2.2 Temperature dependence of the ionic conductivity

The ionic conductivity in the material is described by the Nernst-Einstein relationship,

$$\sigma = nZe\mu, \quad (3)$$

where, n is the number of carriers, μ is the mobility, Z is the valence and e is the elementary charge. The number of carriers that contribute to the conduction process is given by

$$n(T) = n_0 \exp\left(-\frac{E_n}{k_B T}\right). \quad (4)$$

Here, n_0 is a constant that represents the number of carriers at the high temperature limit. E_n is the energy necessary for carrier creation. The mobility is given by

$$\mu(T) = \frac{Ze}{fk_B T} D, \quad (5)$$

where f is the Haven ratio. By substituting eq. (2) into eq. (5), we obtain

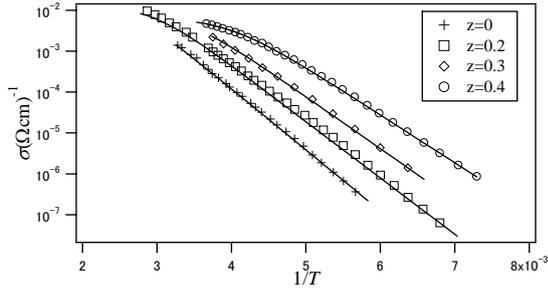


Fig. 1 Temperature dependence of the ionic conductivity in glassy $z\text{AgI}+(1-z)[0.525\text{Ag}_2\text{S}+0.475(\text{B}_2\text{S}_3:\text{SiS}_2)]$ for several compositions.¹⁾ Theoretical curves calculated by eq. (8) are denoted by full lines.

$$\mu(T) = \frac{Ze}{fM} \frac{\tau}{1 + \omega^2 \tau^2}. \quad (6)$$

In order to proceed, some discussion concerning the lifetime τ is necessary. The lifetime can be written as,

$$\frac{1}{\tau} = A \exp\left(-\frac{E_\tau}{k_B T}\right), \quad (7)$$

where A is a constant and E_τ is the average activation energy necessary for ion diffusion. From eqs. (3), (4), (6) and (7) we obtain the following expression for the ionic conductivity,

$$\sigma = \frac{(Ze)^2 n_0}{fMA} \exp\left(-\frac{E_n - E_\tau}{k_B T}\right) \times \left[1 + \omega^2 A^{-2} \exp\left(\frac{2E_\tau}{k_B T}\right)\right]^{-1}. \quad (8)$$

In the case where $\omega^2 A^{-2} \exp(2E_\tau/k_B T) \gg 1$, eq. (8) reduces to

$$\sigma_L = \frac{(Ze)^2 n_0 A}{fM \omega^2} \exp\left(-\frac{E_n + E_\tau}{k_B T}\right). \quad (9)$$

This Equation gives a simple Arrhenius type temperature dependence of the ionic conductivity. In other words, if the above condition is not satisfied, a non-Arrhenius temperature dependence of the ionic conductivity is observed. Eq. (9) indicates that when the ionic conductivity follows the Arrhenius law, the observed activation energy is given by $E_n + E_\tau$. In the next section, we will assume that $E_n \approx E_\tau$ to analyze the experimental data. It is interesting to note that according to eq. (9), the low frequency vibration mode is favorable for the ionic conduction.

3. Application of the model

Fig. 1 shows the temperature dependence of the ionic conductivity in glassy $z\text{AgI}+(1-z)[0.525\text{Ag}_2\text{S}+0.475(\text{B}_2\text{S}_3:\text{SiS}_2)]$. The symbols represent the measured data¹⁾ at different compositions and the full lines are the theoretical curves calculated by eq. (8). We can see that the theory can

Table I. Values of the best fitted parameters for glassy $z\text{AgI}+(1-z)[0.525\text{Ag}_2\text{S}+0.475(\text{B}_2\text{S}_3:\text{SiS}_2)]$.

	n_0 $\times 10^{28} [\text{m}^{-3}]$	$E_n - E_\tau$ [eV]	$E_{\text{exp}}/2$ [eV]	A $\times 10^{15} [\text{s}^{-1}]$	ωA^{-1} $\times 10^{-3}$
$z=0$	2.2	0.148	0.165	6.0	10
$z=0.2$	2.5	0.137	0.155	6.3	9.7
$z=0.3$	2.7	0.126	0.140	8.2	7.2
$z=0.4$	2.9	0.116	0.125	12	4.8

reproduce quite well the experimental data. For the Haven ratio, we have assumed a typical value of 0.5. The values of other parameters obtained by fitting are summarized in Table I. We can recognize that n_0 increases with the concentration of AgI. The increase in the carrier number density results in the decrease of the hopping distance and the increase of hopping rate factor A . The difference between the values of E_n or E_τ and $E_{\text{exp}}/2$ arises from the assumption used $E_n = E_\tau$. By relaxing this assumption we may improve the agreement between the theoretical ($E_n + E_\tau$) and the experimental E_{exp} values of the activation energies.

4. Conclusion

In this study, we have calculated the temperature dependence of the ionic conductivity by extending the Zwanzig model. The model can describe the non-Arrhenius type temperature dependence of the conductivity and reproduces quite well the experimental data. The condition for the appearance of the non-Arrhenius type ionic conductivity has been pointed out.

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