

EFFECTS OF POLARIZABILITY IN ION TRANSPORT: A STUDY BASED ON AN ANALYTICAL EXPRESSION OF THE VELOCITY AUTOCORRELATION FUNCTION

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ABSTRACT

An analytical expression for the polarizability dependent self-diffusion coefficient has been obtained by using a modified version of Zwanzig model for the velocity autocorrelation function. The model indicates that the ion transport coefficient increases with the polarizability.

Keywords : *Velocity autocorrelation function, Diffusion, Polarizability*

INTRODUCTION

Understanding the fundamental relationship between polarizability and ionic conduction is an important topic in the research field of molten and solid electrolytes. There are many studies concerning polarization effects in these materials, using for instance, impedance measurements, computer simulations, etc. However, there is little research that formulates analytically the problem and clarifies the role of the polarization in the ion transport. In the present paper, to describe the dynamics of mobile ions in an electric field, we employed the Zwanzig model [1] to calculate the velocity autocorrelation function (VACF) of mobile ions. Based on this model, an analytical expression for the polarizability dependent self-diffusion coefficient has been obtained. The obtained analytical expression enables us to understand the role of different physical quantities such as polarizability, valence, applied electric field, etc., in the ion transport coefficients.

THEORY AND RESULTS

The Zwanzig model is a simple jump diffusion model and has been used frequently to describe the velocity autocorrelation function of liquids. This model was based on and supported by computer simulation studies [2-4]. Although originally proposed for liquids, the concept of this model is applicable to non-crystalline solids. Based on the Zwanzig model, we adopt the following assumptions.

1. The particles that form the system execute harmonic vibrations around the positions where the potential is a minima.

2. When a particle diffuses, it jumps in a very short time to a new position which is almost equivalent to the old position. After the jump, the particle loses its memory.
3. The particle jump rate is defined as $1/\tau$, where, τ is the relaxation time. The harmonic oscillation in the potential well is described adequately by a fixed frequency ω as in the Einstein approximation.

By using these assumptions, it is possible to divide the motion of ions into the diffusion part and the vibration part. Since according to this model, the jumping time is very short, in the following, we will consider the effect of external electric field only on the vibration part.

If m is the particle mass, E_0 is the magnitude of the electric field, γ , ω_0 , Z , and ω are the attenuation factor, ion frequency, valence and external frequency, respectively, the equation of motion of an ion under the influence of electric field is

$$m\ddot{x} + 2\gamma m\dot{x} + m\omega_0^2 x = ZeE_0 \exp(-i\omega t) \quad (1)$$

and the solution is

$$x(t) = e^{-\gamma t} (C_1 \cos \omega_s t + C_2 \sin \omega_s t) + x_p e^{-i\omega t} \quad (2)$$

From it we obtain

$$\begin{aligned} \dot{x}(t) = & -\gamma e^{-\gamma t} (C_1 \cos \omega_s t + C_2 \sin \omega_s t) \\ & + e^{-\gamma t} (-C_1 \omega_s \sin \omega_s t + C_2 \omega_s \cos \omega_s t) - i\omega x_p e^{-i\omega t}. \end{aligned} \quad (3)$$

Here, $\omega_s^2 = \omega_0^2 - \gamma^2$. C_1 and C_2 are constants, and

$$\begin{aligned} x_p &= \frac{ZeE_0}{m} \frac{(\omega_0^2 - \omega^2) + i2\omega\gamma}{(\omega_0^2 - \omega^2)^2 + 4\omega^2\gamma^2} \\ &\equiv F_0 \frac{(\omega_0^2 - \omega^2) + i2\omega\gamma}{(\omega_0^2 - \omega^2)^2 + 4\omega^2\gamma^2} \\ &\equiv \alpha_R(\omega) + i\alpha_I(\omega) \end{aligned} \quad (4)$$

In the above expression, α_R and α_I denote the real and imaginary parts of x_p , respectively. The induced electric dipole moment can be written as Zex_p . If we set the initial displacement as $x(0)=0$, and the initial velocity equal to the free particle velocity at temperature T , we obtain.

$$C_1 = -x_p \quad (5)$$

$$C_2 = \frac{1}{\omega_s} \left[\sqrt{\frac{kT}{m}} - \gamma x_p + i\omega x_p \right]. \quad (6)$$

Here, we have defined the polarizability,

$$P_R = \frac{Ze \alpha_R(\omega)}{4\pi\epsilon_0 E_0} = \frac{(Ze)^2}{4\pi\epsilon_0 m} \frac{1}{(\omega_0^2 - \omega^2)}. \quad (7)$$

From Eq. (2), the vibration part of the velocity autocorrelation function is written as

$$\frac{\langle \dot{x}(t)\dot{x}(0) \rangle}{\langle \dot{x}(0)\dot{x}(0) \rangle}_{vib} = \left(\frac{kT}{m} \right)^{\frac{1}{2}} \left\{ \begin{array}{l} -\gamma e^{-\gamma t} (C_1 \cos \omega_\delta t + C_2 \sin \omega_\delta t) \\ + e^{-\gamma t} (-C_1 \omega_\delta \sin \omega_\delta t + C_2 \omega_\delta \cos \omega_\delta t) \\ - i \alpha x_p e^{-i\omega t} \end{array} \right\}. \quad (8)$$

The diffusion part of the VACF can be accounted for as in the Zwanzig model, by multiplying the above expression by the factor $\exp(-t/\tau)$, the waiting time distribution for ion jumps that destroy the coherence of the oscillation at the potential minima [1-5]. The resulting expression for the real part of the VACF is

$$\text{Re}(C(t)) = \left(\frac{kT}{m} \right)^{\frac{1}{2}} \left\{ \begin{array}{l} -\gamma e^{-\gamma t} (\text{Re}(C_1) \cos \omega_\delta t + \text{Re}(C_2) \sin \omega_\delta t) \\ + e^{-\gamma t} (-\text{Re}(C_1) \omega_\delta \sin \omega_\delta t + \text{Re}(C_2) \omega_\delta \cos \omega_\delta t) \\ + \alpha_I \omega \cos \omega t - \alpha_R \omega \sin \omega t \end{array} \right\} \exp\left(-\frac{t}{\tau}\right) \quad (9)$$

where

$$\text{Re}(C_1) = -F_0 \frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + 4\omega^2\gamma^2} = -\alpha_R(\omega),$$

$$\begin{aligned} \text{Re}(C_2) &= \frac{1}{\omega_\delta} \left[\sqrt{\frac{kT}{m}} - F_0 \frac{(\omega_0^2 - \omega^2)\gamma}{(\omega_0^2 - \omega^2)^2 + 4\omega^2\gamma^2} - F_0 \frac{2\gamma\omega^2}{(\omega_0^2 - \omega^2)^2 + 4\omega^2\gamma^2} \right] \\ &= \frac{1}{\omega_\delta} \left[\sqrt{\frac{kT}{m}} - \gamma\alpha_R(\omega) - \omega\alpha_I(\omega) \right]. \end{aligned}$$

To analyze the obtained expression, consider the case where the external field is given by $E_0 \cos(\omega t)$ and the damping factor satisfies $\omega_0 \gg \gamma$. If the external field is not applied, Eq. (9) reduces to the VACF given by Zwanzig [1]. The behavior of Eq. (9) is illustrated in Figure 1. It shows that the effect of the polarizability on the behavior of VACF. We recognize that the magnitude of the VACF increases with the increase of the polarizability.

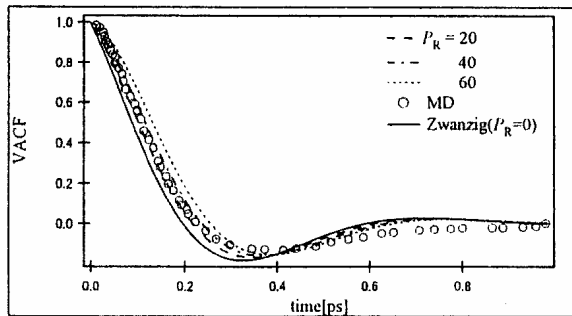


Figure 1. Behavior of VACF of Ag in molten AgI when the polarizability ($=P_R [\text{\AA}^3]$) is changed. The MD result was quoted from Reference [6].

In the evaluation of Eq. (9), materials parameters pertinent to molten AgI as given in Table 1 were used. Here, τ has been used as an adjustable parameter to reproduce the diffusion coefficient given in the Table. For the magnitude of the electric field we have chosen $2 \times 10^8 \text{ V/m}$ [7-9], which is a typical value of the local electric field in thin film systems. For comparison, if we use the value of $3 \times 10^4 \text{ V/cm}$, only indiscernible change in the VACF from the $P_R=0$ case is obtained.

Table 1: Parameters of Ag in molten AgI.

Parameters	Values
Ag ion mass	$1.79 \times 10^{-25} \text{ (kg)}$
Temperature	873(K)
Valence	1
Ag	$3.7 \times 10^{-9} \text{ m}^2/\text{s}$ (calculated, when $P_R=0$)
Self diffusion coefficient	$(3.8 \times 10^{-9} \text{ m}^2/\text{s})$ (MD[6])
Ion oscillation frequency	$8.1 \times 10^{12} \text{ (s}^{-1}\text{)}$
Relaxation time	$2.1 \times 10^{-13} \text{ (s)}$

By using the Green-Kubo formula and the VACF given in Eq. (8), we obtained the following expression for the self diffusion coefficient which includes the role of the polarizability explicitly,

$$D = \sqrt{\frac{kT}{m}} \left\{ -\gamma \left(C_1 \frac{B^{-1}}{1 + \omega_s^2 B^{-2}} + C_2 \frac{\omega_s B^{-2}}{1 + \omega_s^2 B^{-2}} \right) + \left(-C_1 \frac{\omega_s^2 B^{-2}}{1 + \omega_s^2 B^{-2}} + C_2 \frac{\omega_s B^{-1}}{1 + \omega_s^2 B^{-2}} \right) - i a x_p \frac{1}{i\omega + 1/\tau} \right\}, \quad (10)$$

$$\text{Re}(D) \approx \sqrt{\frac{kT}{m}} \left\{ \frac{4\pi\epsilon_0 E_0 P_R}{Ze} \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2} + \sqrt{\frac{kT}{m}} \frac{\tau}{1 + \omega_0^2 \tau^2} - \frac{4\pi\epsilon_0 E_0 P_R}{Ze} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right\}. \quad (10)'$$

Here, $B = \gamma + 1/\tau$. The behavior of the polarizability dependent self diffusion coefficient calculated from Eq. (10') is illustrated in Figure 2. It indicates that the self diffusion coefficient increases with the polarizability.

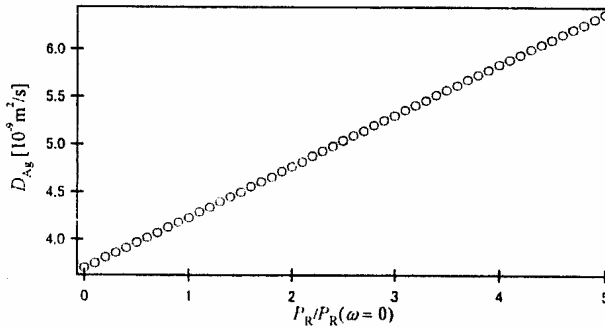


Figure 2: Self diffusion coefficient of Ag in molten AgI as a function of the polarizability.

CONCLUSION

An analytical expression for the polarization dependent VACF and self diffusion coefficient has been derived. The theory gives the rationale that diffusion increases with the polarizability. The obtained analytical expression enables us to understand the role of different physical quantities such as polarizability, valence, applied external field, etc., in the transport coefficients.

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