A theory of electrical conductivity of non-equivalent molten salts

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A theory of electrical conductivity of non-equivalent molten salts

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The electrical conductivity of non-equivalent molten salts has been theoretically investigated based on the linear response theory, which is an extension from the expression for equivalent molten salts as we have developed in the previous papers. The velocity correlation functions are expressed in terms of pair potentials and pair distribution functions. Using these functions and Langevin equations for ions, the relations among the conductivity coefficients are obtained. It is shown that the ratio of partial conductivities σ^+/σ^- is equal to $|z^+|m^-/|z^-|m^+$, which is an extensive expression from the inverse mass ratio in the case of equivalent molten salts. Numerical results for molten $CaCl_2$ and AlF_3 are presented, which agree well with the results of experiments and molecular dynamics simulations.

1. Introduction

This is a serial work on the theoretical derivation of the partial conductivities in various type molten salts. In previous papers, we have carried out the theoretical treatment for the electrical conductivities of equivalent molten salts, and their mixtures. Equivalent molten salts are those whose valences are all of the same magnitude. The theory has been starting from the generalized Langevin equation for cation and anion in these systems and using the Kubo-Green formula with the help of various velocity correlation functions between a chosen pair of ions in them [1–3]. From these, one of the obtained important results is that the ratio of partial conductivities of cation and anion in a pure equivalent molten salt σ^+/σ^- is always equal to their inverse mass ratio m^-/m^+. And in the case of pseudo binary molten $[AX]_{1-c}[AYl]_c$, this golden rule is converted to $(m_A \sigma_A^+) = (m_X \sigma_X^-) + (m_Y \sigma_Y^-)$ [4]. Another interesting result is that the coefficient of $(t^2/2)$ in the Taylor expansion form of velocity correlation function is just proportional to the inverse effective friction constant of the constituent ions [1–3].

It is interesting to know how the golden rule $\sigma^+/\sigma^- = m^-/m^+$ is modulated in non-equivalent molten salts and also whether the effective friction constant acting on the cation is the same or not on anion. Non-equivalent molten salts are those with asymmetric charges. $A_2^{1+}Y^{2-}$-type or $M^{2+}X_2^{1-}$-type molten salt and $M^{3+}X_3^{1-}$-type molten salt are concerned as the example of non-equivalent ones. Practical molten salts corresponding to these types are, e.g. A_2CO_3 (A = Li, Na and K) systems, which are nowadays applied for the oxygen–hydrogen fuel cell [5], and MCl_2 (M = Mg, Ca), which is useful for an industrial chemistry extracting metallic Mg and Ca. Taking account of another industrial applications, molten AlF_3 also seems to be useful for extracting metallic aluminum.

In the following sections, however, we will start from the momentum conservation law in obtaining the velocity correlation functions of arbitrary ion pairs at $t = 0$ to obtain the ratio of partial conductivities. The theory of partial conductivity coefficients will be clarified from the statistical mechanical approach to make sure its validity by Langevin equation in the later section.

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2. Velocity correlation functions

We begin the theoretical approach from the momentum conservation law, which is expressed in the center of mass system as,

$$\sum_{i=1}^{n+} \mathbf{p}_i^+(0) = -\sum_{k=1}^{n-} \mathbf{p}_k^-(0) \qquad (1)$$

where n^+ and n^- are numbers of cation and anion, respectively. Taking ensemble average of (1), it is straightforward to obtain the following relation,

$$n^+ \left\langle \mathbf{p}_j^+(0)\cdot\mathbf{p}_i^+(0) \right\rangle = -n^- \left\langle \mathbf{p}_j^+(0)\cdot\mathbf{p}_k^-(0) \right\rangle \qquad (2)$$

then we have,

$$\left\langle \mathbf{v}_j^+(0)\cdot\mathbf{v}_i^+(0) \right\rangle = -(n^- m^-/n^+ m^+)\left\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0) \right\rangle \quad (3)$$

In a similar way,

$$\left\langle \mathbf{v}_k^-(0)\cdot\mathbf{v}_l^-(0) \right\rangle = -(n^+ m^+/n^- m^-)\left\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0) \right\rangle \quad (4)$$

In equations (3) and (4), $\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle$ is expressed as,

$$\left\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0) \right\rangle = -3k_{\mathrm{B}}T/\langle m \rangle \qquad (5)$$

In (5), $\langle m \rangle$ is the average mass of anion and cation which is defined as $\langle m \rangle = (c^+ m^+ + c^- m^-)$. where $c^+ = n^+/n$ and $c^- = n^-/n$. Equation (5) is derived by the statistical mechanical treatment, which we will show as follows. Hereafter, we omit the time identification (0) in the case $t = 0$. According to the equi-partition rule, we knew the following relation for a classical system,

$$\left\langle \mathbf{p}_i^+\cdot\partial H/\partial \mathbf{p}_i^+ \right\rangle = 3k_{\mathrm{B}}T \qquad (6)$$

We assume that the Hamiltonian H is represented by the following terms of kinetic energies of cations and anions, and all of pair-wise potentials between two ions,

$$H = \sum_i \left(\mathbf{p}_i^{+2}/2m^+\right) + \sum_k \left(\mathbf{p}_k^{-2}/2m^-\right)$$

$$+ \sum_{i,j} \phi^{++}\left(\left|\mathbf{r}_i^+ - \mathbf{r}_j^+\right|\right)$$

$$+ \sum_{i,k} \phi^{+-}\left(\left|\mathbf{r}_i^+ - \mathbf{r}_k^-\right|\right) + \sum_{k,l} \phi^{--}\left(\left|\mathbf{r}_k^- - \mathbf{r}_l^-\right|\right) \quad (7)$$

As seen in (1), the variable $\mathbf{p}_i^+$ is a function of $\mathbf{p}_j^+$ and $\mathbf{p}_k^-$, the derivative of Hamiltonian in respect to $\mathbf{p}_i^+$ is written as follows,

$$\frac{\partial H}{\partial \mathbf{p}_i^+} = \sum_j \left(\frac{\partial H}{\partial \mathbf{p}_j^+}\right)\cdot\left(\frac{\partial \mathbf{p}_j^+}{\partial \mathbf{p}_i^+}\right) + \sum_k \left(\frac{\partial H}{\partial \mathbf{p}_k^-}\right)\cdot\left(\frac{\partial \mathbf{p}_k^-}{\partial \mathbf{p}_i^+}\right) \quad (8)$$

$$= \sum_j \left(\frac{\mathbf{p}_j^+}{m^+}\right)\cdot\left(\frac{\partial \mathbf{p}_j^+}{\partial \mathbf{p}_i^+}\right) + \sum_k \left(\frac{\mathbf{p}_k^-}{m^-}\right)\cdot\left(\frac{\partial \mathbf{p}_k^-}{\partial \mathbf{p}_i^+}\right) \quad (9)$$

Multiplying $\mathbf{p}_i^+$ onto (9), we have

$$\mathbf{p}_i^+\cdot\frac{\partial H}{\partial \mathbf{p}_i^+} = \sum_j m^+ \mathbf{v}_i^+\cdot\mathbf{v}_j^+ \left(\frac{\partial \mathbf{p}_j^+}{\partial \mathbf{p}_i^+}\right)$$

$$+ \sum_k m^+ \mathbf{v}_i^+\cdot\mathbf{v}_k^- \left(\frac{\partial \mathbf{p}_k^-}{\partial \mathbf{p}_i^+}\right) \quad (10)$$

The ensemble average of (10) is given by the following relation,

$$n\left\langle \mathbf{p}_i^+\cdot\frac{\partial H}{\partial \mathbf{p}_i^+} \right\rangle = n^+ \left\langle m^+ \mathbf{v}_i^+\cdot\mathbf{v}_j^+ \left(\frac{\partial \mathbf{p}_j^+}{\partial \mathbf{p}_i^+}\right) \right\rangle$$

$$+ n^- \left\langle m^+ \mathbf{v}_i^+\cdot\mathbf{v}_k^- \left(\frac{\partial \mathbf{p}_k^-}{\partial \mathbf{p}_i^+}\right) \right\rangle \quad (11)$$

The distribution probabilities of ions' velocities, $\mathbf{v}_j^+$ and $\mathbf{v}_k^-$ around the ion i having the velocity $\mathbf{v}_i^+$ are equal to n^+/n and n^-/n, respectively. Therefore

$$\left\langle \mathbf{p}_i^+\cdot\frac{\partial H}{\partial \mathbf{p}_i^+} \right\rangle = (n^+/n)m^+ \left\langle \mathbf{v}_i^+\cdot\mathbf{v}_j^+ \right\rangle \left(\frac{\partial \left\langle \mathbf{p}_j^+ \right\rangle}{\partial \left\langle \mathbf{p}_i^+ \right\rangle}\right)$$

$$+ (n^-/n)m^+ \left\langle \mathbf{v}_i^+\cdot\mathbf{v}_k^- \right\rangle \left(\frac{\partial \left\langle \mathbf{p}_k^- \right\rangle}{\left\langle \partial \mathbf{p}_i^+ \right\rangle}\right) \quad (12)$$

Using (1), we have immediately $(\partial\langle\mathbf{p}_k^-\rangle/\partial\langle\mathbf{p}_i^+\rangle) = -n^+/n^-$ and therefore we obtain

$$\left\langle \mathbf{p}_i^+\cdot\frac{\partial H}{\partial \mathbf{p}_i^+} \right\rangle = (n^+/n)m^+ \left\langle \mathbf{v}_i^+\cdot\mathbf{v}_j^+ \right\rangle$$

$$- (n^+/n)m^+ \left\langle \mathbf{v}_i^+\cdot\mathbf{v}_k^- \right\rangle$$

$$= 3k_{\mathrm{B}}T \quad (13)$$

Insertion of (3) and (6) gives the following relation,

$$-(c^+ m^+ + c^- m^-)\left\langle \mathbf{v}_i^+\cdot\mathbf{v}_k^- \right\rangle = 3k_{\mathrm{B}}T \quad (14)$$

$$\therefore \left\langle \mathbf{v}_i^+\cdot\mathbf{v}_k^- \right\rangle = -3k_{\mathrm{B}}T/(c^+ m^+ + c^- m^-)$$

$$= -3k_{\mathrm{B}}T/\langle m \rangle \quad (15)$$

In a similar way,

$$\left\langle \mathbf{p}_k^- \cdot \frac{\partial H}{\partial \mathbf{p}_k^-} \right\rangle = (n^-/n)m^- \left\langle \mathbf{v}_k^- \cdot \mathbf{v}_l^- \right\rangle$$

$$+ (n^+/n)m^- \left\langle \mathbf{v}_i^+ \cdot \mathbf{v}_k^- \right\rangle \left(\frac{\partial \langle \mathbf{p}_i^+ \rangle}{\partial \langle \mathbf{p}_k^- \rangle} \right)$$

$$= -(c^+ m^+ + c^- m^-) \left\langle \mathbf{v}_i^+ \cdot \mathbf{v}_k^- \right\rangle$$

$$= 3k_B T \tag{16}$$

and again we have $\langle \mathbf{v}_i^+ \cdot \mathbf{v}_k^- \rangle = -3k_B T / \langle m \rangle$. If we consider a virtual particle with the mass of $\langle m \rangle = (c^+ m^+ + c^- m^-)$, its mean square velocity $\langle \mathbf{v}_i^+ \cdot \mathbf{v}_k^- \rangle = (\langle \mathbf{v}_i^{+2} \mathbf{v}_k^{-2} \rangle)^{(1/2)}$ is equal to the right hand side of (15). Therefore, (15) is equivalent to the averaged mean square velocities for cation and anion having the mass of $\langle m \rangle = (c^+ m^+ + c^- m^-)$.

3. Current–current correlation functions

The Taylor expansion for the velocity correlation function $\langle \mathbf{v}_i^+(t) \cdot \mathbf{v}_j^+(0) \rangle$ is described as follows [7,8],

$$\left\langle \mathbf{v}_i^+(t) \cdot \mathbf{v}_j^+(0) \right\rangle = \left\langle \mathbf{v}_i^+(0) \cdot \mathbf{v}_j^+(0) \right\rangle$$

$$+ (t^2/2) \left\langle \mathbf{v}_i^+(0) \cdot \ddot{\mathbf{v}}_j^+(0) \right\rangle$$

$$+ (\text{higher order over } t^4) \tag{17}$$

In order to obtain the coefficient of $(t^2/2)$, we have to apply the Poisson equation as follows,

$$\mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_i^+ = -\sum_j^{n+} \left\{ \mathbf{p}_i^+ \cdot \mathbf{p}_j^+ / m^+ \right\}$$

$$\times \left(\partial^2 V / \partial \mathbf{r}_j^+ \partial \mathbf{r}_i^+ \right)$$

$$- \sum_k^{n-} \left\{ \mathbf{p}_i^+ \cdot \mathbf{p}_k^- / m^- \right\} \tag{18}$$

$$\times \left(\partial^2 V / \partial \mathbf{r}_k^- \partial \mathbf{r}_i^+ \right)$$

We take ensemble average of (18), then the first term remains, as,

$$\left\langle \mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_i^+ \right\rangle \equiv -3k_B T \times (1/3) \left[(n^{+2}) \int_0^\infty \{ (\partial^2 \phi^{++} / \partial r^2) \right.$$

$$+ (2/r)(\partial \phi^{++} / \partial r) \} g^{++}(r) 4\pi r^2 \mathrm{d}r \tag{19}$$

$$+ (n^{-2}) \int_0^\infty \{ (\partial^2 \phi^{+-} / \partial r^2)$$

$$+ (2/r)(\partial \phi^{+-} / \partial r) \} g^{+-}(r) 4\pi r^2 \mathrm{d}r$$

$$= -k_B T [n^{+2} \langle \phi^{++} \rangle + n^{-2} \langle \phi^{+-} \rangle] \tag{20}$$

In (20), the terms $\langle \phi^{++} \rangle$ and $\langle \phi^{+-} \rangle$ in the square brackets, [ ], are multiplied by the coefficients n^{+2} and n^{-2}, respectively, which represent the square of number densities of cations and anions around the cation concerned [9]. The meaning of the coefficient (1/3), see equation (14) in Ref 3. In (20), the terms $\langle \phi^{++} \rangle$ and $\langle \phi^{+-} \rangle$ stand for,

$$\langle \phi^{++} \rangle = \int_0^\infty \{ (\partial^2 \phi^{++} / \partial r^2) + (2/r)$$

$$\times (\partial \phi^{++} / \partial r) \} g^{++}(r) \cdot 4\pi r^2 \mathrm{d}r \tag{21}$$

$$\langle \phi^{+-} \rangle = \int_0^\infty \{ (\partial^2 \phi^{+-} / \partial r^2) + (2/r)$$

$$\times (\partial \phi^{+-} / \partial r) \} g^{+-}(r) \cdot 4\pi r^2 \mathrm{d}r \tag{22}$$

Similarly, $\langle \mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_{j\neq i}^+ \rangle$ is expressed as,

$$\left\langle \mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_{j\neq i}^+ \right\rangle = k_B T(n^{+2} \langle \phi^{++} \rangle) \tag{23}$$

Then, we have

$$\left\langle \mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_j^+ \right\rangle = -k_B T(n^{-2} \langle \phi^{+-} \rangle) \tag{24}$$

$$\therefore \left\langle \mathbf{v}_i^+ \cdot \ddot{\mathbf{v}}_j^+ \right\rangle = -(3k_B T)(n^{-2} \langle \phi^{+-} \rangle / 3m^{+2}) \tag{25}$$

Therefore, we have

$$\left\langle \mathbf{v}_i^+(t) \cdot \mathbf{v}_j^+(0) \right\rangle = \left\langle \mathbf{v}_i^+(0) \cdot \mathbf{v}_j^+(0) \right\rangle - (t^2/2)$$

$$\times \left\langle \mathbf{v}_i^+(0) \cdot \ddot{\mathbf{v}}_j^+(0) \right\rangle \tag{26}$$

$$+ (\text{higher order})$$

$$= \{ 3k_B T(n^- m^- / n^+ m^+) / \langle m \rangle \}$$

$$- (t^2/2)\{ 3k_B T(n^{-2} \langle \phi^{+-} \rangle / 3m^{+2})$$

$$+ (\text{higher order}) \tag{27}$$

Similarly, the cross term is expressed, as,

$$\left\langle \mathbf{p}_i^+ \cdot \ddot{\mathbf{p}}_k^- \right\rangle = k_B T(n^+ n^- \langle \phi^{+-} \rangle) \tag{28}$$

$$\therefore \left\langle \mathbf{v}_i^+ \cdot \ddot{\mathbf{v}}_k^- \right\rangle = (3k_B T)(n^+ n^- \langle \phi^{+-} \rangle / 3m^+ m^-) \tag{29}$$

then we have

$$\left\langle \mathbf{v}_i^+(t) \cdot \mathbf{v}_k^-(0) \right\rangle = \left\langle \mathbf{v}_i^+(0) \cdot \mathbf{v}_k^-(0) \right\rangle + (t^2/2)$$

$$\times \left\langle \mathbf{v}_i^+(0) \cdot \ddot{\mathbf{v}}_k^-(0) \right\rangle + (\text{higher order})$$

$$= -3k_B T / m + (t^2/2) \tag{30}$$

$$\times \{ 3k_B T(n^+ n^- \langle \phi^{+-} \rangle / 3m^+ m^-) \}$$

$$+ (\text{higher order})$$

Similarly,

$$\left\langle \mathbf{p}_k^- \cdot \ddot{\mathbf{p}}_l^- \right\rangle = -k_B T(n^{+2} \langle \phi^{+-} \rangle)$$

$$\therefore \left\langle \mathbf{v}_k^- \cdot \ddot{\mathbf{v}}_l^- \right\rangle = -(3k_B T)(n^{+2} \langle \phi^{+-} \rangle / 3m^{-2}) \tag{31}$$

then we have,

$$\langle \mathbf{v}_k^-(t)\cdot\mathbf{v}_l^-(0)\rangle$$

$$= \langle \mathbf{v}_k^-(0)\cdot\mathbf{v}_l^-(0)\rangle + (t^2/2)\langle \mathbf{v}_k^-(0)\cdot\ddot{\mathbf{v}}_l^-(0)\rangle$$

$$+ (\text{higher order}) \tag{32}$$

$$= \{3k_BT(n^+m^+/n^-m^-)/\langle m\rangle\} - (t^2/2)$$

$$\times \{3k_BT(n^{+2}\langle\phi^{+-}\rangle/3m^{-2})\} + (\text{higher order})$$

On the other hand, the Kubo-Green type representations for the partial conductivities of cation and anion are given as follows [1–3],

$$\sigma^+ = (1/3k_BT)\int_0^\infty \langle \mathbf{j}^+(t)\cdot\mathbf{j}(0)\rangle \mathrm{d}t \tag{33}$$

and

$$\sigma^- = (1/3k_BT)\int_0^\infty \langle \mathbf{j}^-(t)\cdot\mathbf{j}(0)\rangle \mathrm{d}t \tag{34}$$

where $\mathbf{j}(t)$ is equal to $\mathbf{j}(t) = \mathbf{j}^+(t) + \mathbf{j}^-(t)$. Therefore, whenever we know the microscopic representations of $\langle\mathbf{j}^+(t)\cdot\mathbf{j}^+(t)\rangle$, $\langle\mathbf{j}^+(t)\cdot\mathbf{j}^-(0)\rangle$ and $\langle\mathbf{j}^-(t)\cdot\mathbf{j}^-(0)\rangle$, partial conductivities can be immediately obtained.

Using (26)–(32), and the charge neutrality condition $n^+z^+ + n^-z^- = 0$, current correlation functions $\langle\mathbf{j}^+(t)\cdot\mathbf{j}(t)\rangle$ and $\langle\mathbf{j}^-(t)\cdot\mathbf{j}(0)\rangle$ are expressed as follows,

$$\langle\mathbf{j}^+(t)\cdot\mathbf{j}(t)\rangle = \langle\mathbf{j}^+(t)\cdot\mathbf{j}^+(0)\rangle + \langle\mathbf{j}^+(t)\cdot\mathbf{j}^-(0)\rangle$$

$$= (n^{+2}z^{+2}e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0)\rangle$$

$$+ (n^+n^-z^+z^-e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$= (n^{+2}z^{+2}e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0)\rangle$$

$$- (n^{+2}z^{+2}e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$= (n^{+2}z^{+2}e^2/n)\langle (\mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0)\rangle$$

$$- \langle\mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle \equiv (n^{+2}z^{+2}e^2/n)Z_\sigma^+(t)$$

$$\tag{35}$$

$$\langle\mathbf{j}^-(t)\cdot\mathbf{j}(0)\rangle = \langle\mathbf{j}^-(t)\cdot\mathbf{j}^+(0)\rangle + \langle\mathbf{j}^-(t)\cdot\mathbf{j}^-(0)\rangle$$

$$= (n^+n^-z^+z^-e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$+ (n^{-2}z^{-2}e^2/n)\langle \mathbf{v}_k^-(t)\cdot\mathbf{v}_l^-(0)\rangle$$

$$= -(n^{-2}z^+z^-e^2/n)\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$+ (n^{-2}z^{-2}e^2/n)\langle \mathbf{v}_k^-(t)\cdot\mathbf{v}_l^-(0)\rangle \tag{36}$$

$$= (n^{-2}z^{-2}e^2/n)\left(\langle \mathbf{v}_i^-(t)\cdot\mathbf{v}_j^-(0)\rangle\right.$$

$$\left. - \langle\mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle\right)$$

$$\equiv (n^{-2}z^{-2}e^2/n)Z_\sigma^-(t)$$

Then, the partial conductivities are expressed as,

$$\sigma^+ = (n^{+2}z^{+2}e^2/3nk_BT)\int_0^\infty Z_\sigma^+(t)\mathrm{d}t \tag{37}$$

and

$$\sigma^- = (n^{-2}z^{-2}e^2/3nk_BT)\int_0^\infty Z_\sigma^-(t)\mathrm{d}t \tag{38}$$

Using (27), (30) and (32), we have,

$$Z_\sigma^+(t) = \langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0)\rangle - \langle\mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$= (3nk_BT/n^+m^+)\{1 - (t^2/2)n^+n^-\langle\phi^{+-}\rangle/3\mu$$

$$+ (\text{higher order})\} \tag{39}$$

$$Z_\sigma^-(t) = \langle \mathbf{v}_i^-(t)\cdot\mathbf{v}_j^-(0)\rangle - \langle\mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0)\rangle$$

$$= (3nk_BT/n^-m^-)\{1 - (t^2/2)n^+n^-\langle\phi^{+-}\rangle/3\mu$$

$$+ (\text{higher order})\} \tag{40}$$

where μ is the reduced mass defined as,

$$(1/\mu) = (c^-/m^+) + (c^+/m^-) = \langle m\rangle/m^+m^- \tag{41}$$

$$\therefore \sigma^+ = (n^+z^{+2}e^2/m^+)\int_0^\infty \{1 - (t^2/2)$$

$$\times (n^+n^-\langle\phi^{+-}\rangle/3\mu) + (\text{higher order})\}\mathrm{d}t \tag{42}$$

According to the results obtained to this point, the following equation (43) is valid in the case that the correlation functions are given in the form $[1-(t^2/2)\gamma^{+2} + (\text{higher order})]$, as,

$$1/\gamma^+ = \int_0^\infty \{1 - (t^2/2)\gamma^{+2} + (\text{higher order})\}\mathrm{d}t \tag{43}$$

Using (43), (42) is expressed as,

$$\sigma^+ = (n^+z^{+2}e^2)(1/m^+\gamma^+) \tag{44}$$

where

$$\gamma^+ = (n^+n^-\langle\phi^{+-}\rangle/3\mu)^{1/2}. \tag{45}$$

Similarly

$$\sigma^- = (n^-z^{-2}e^2/m^-)\int_0^\infty \{1 - (t^2/2)$$

$$\times (n^+n^-\langle\phi^{+-}\rangle/3\mu)$$

$$+ (\text{higher order})\}\mathrm{d}t \tag{46}$$

$$= (n^-z^{-2}e^2)(1/m^+\gamma^-) \tag{47}$$

where

$$\gamma^- = (n^+n^-\langle\phi^{+-}\rangle/3\mu)^{1/2} \tag{48}$$

Comparing (45) and (48), we have,

$$\gamma^+ = \gamma^- = \gamma. \tag{49}$$

From (44), (47) and (49), we obtain the relation,

$$\sigma^+/\sigma^- = |z^+|m^-/|z^-|m^+ \tag{50}$$

which corresponds to the extension of the relation $\sigma^+/\sigma^- = m^-/m^+$ for equivalent binary salts to that of non-equivalent systems. For example, in the case $|z^+| = |+1|$ and $|z^-| = |-2|$ for molten $A_2^{1+}Y^{2-}$ salts, then (50) is $\sigma^+/\sigma^- = m^-/2m^+$.

4. Partial conductivities of molten salts

In this section, we will derive the partial conductivity coefficients of non-equivalent molten salt from microscopic point of view based on the generalized Langevin equation.

The starting Langevin equation for either cation A or anion Y is written as follows [6],

$$m^{\pm}\left(d\mathbf{v}_i^{\pm}(t)/dt\right) = -m^{\pm}\int_0^t \gamma^{\pm}(t-t')\mathbf{v}_i^{\pm}(t')dt'$$
$$+ \mathbf{R}_i^{\pm}(t) + z^{\pm}e\mathbf{E} \qquad (51)$$

where $\gamma^{\pm}(t)$ is the memory function in relation to the friction force acting on either cation or anion, $\mathbf{R}_i^{\pm}(t)$ is the stochastic or the random fluctuating force acting on ion i, and E is the applying external field. Taking the ensemble average, we have the following Laplace transformation [6],

$$\left\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_j^+(0) \right\rangle + i\omega\tilde{Z}^{++}(\omega) = \tilde{\gamma}^+(\omega)\tilde{Z}^{++}(\omega)$$
$$(52)$$
$$\text{(for } i=j \text{ and } i \neq j)$$

where

$$\tilde{Z}^{++}(\omega) = \int_0^\infty \exp(i\omega t)\left\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0) \right\rangle dt$$
$$= \int_0^\infty \exp(i\omega t)Z^{++}(t)dt \qquad (53)$$

and

$$\tilde{\gamma}^+(\omega) = \int_0^\infty \exp(i\omega t)\gamma^+(t)dt \qquad (54)$$

Meanwhile, the partial conductivity coefficients are given by the following formulas,

$$\sigma = \sigma^+ + \sigma^- = (\sigma^{++} + \sigma^{+-}) + (\sigma^{-+} + \sigma^{--}) \quad (55)$$

where conductivity coefficients σ^{++}, σ^{+-} and σ^{--} are expressed as follows,

$$\sigma^{++} = (1/3k_BT)\int_0^\infty \langle \mathbf{j}^+(t)\cdot\mathbf{j}^+(0)\rangle dt \qquad (56)$$

$$\sigma^{--} = (1/3k_BT)\int_0^\infty \langle \mathbf{j}^-(t)\cdot\mathbf{j}^-(0)\rangle dt \qquad (57)$$

and

$$\sigma^{+-} = \sigma^{-+} = (1/3k_BT)\int_0^\infty \langle \mathbf{j}^+(t)\cdot\mathbf{j}^-(0)\rangle dt \qquad (58)$$

Using (53) and (56), σ^{++} is written as,

$$\sigma^{++} = (n^{+2}z^{+2}e^2/3nk_BT)\int_0^\infty \left\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_j^+(0) \right\rangle dt$$
$$= (n^{+2}z^{+2}e^2/3nk_BT)\int_0^\infty Z^{++}(t)dt$$
$$= (n^{+2}z^{+2}e^2/3nk_BT)\tilde{Z}^{++}(0) \qquad (59)$$

In a similar way, we have

$$\sigma^{--} = (n^{-2}z^{-2}e^2/3nk_BT)\int_0^\infty \left\langle \mathbf{v}_k^-(t)\cdot\mathbf{v}_l^-(0) \right\rangle dt$$
$$= (n^{-2}z^{-2}e^2/3nk_BT)\int_0^\infty Z^{--}(t)dt$$
$$= (n^{-2}z^{-2}e^2/3nk_BT)\tilde{Z}^{--}(0) \qquad (60)$$

and

$$\sigma^{+-} = (n^+n^-z^+z^-e^2/3nk_BT)\int_0^\infty \left\langle \mathbf{v}_i^+(t)\cdot\mathbf{v}_k^-(0) \right\rangle dt \quad (61)$$

The so-called fluctuation dissipation theorem in a molten salt is given by the following relations, [2,3]

$$m^{+2}\left\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_j^+(0) \right\rangle \tilde{\gamma}^+(\omega)$$
$$= \int_0^\infty \exp(i\omega t)\left\langle \mathbf{R}_i^+(t)\cdot\mathbf{R}_j^+(0) \right\rangle dt \qquad (62)$$
$$\text{(for } i=j \text{ and } i \neq j)$$

$$m^{-2}\left\langle \mathbf{v}_k^-(0)\cdot\mathbf{v}_l^-(0) \right\rangle \tilde{\gamma}^-(\omega)$$
$$= \int_0^\infty \exp(i\omega t)\left\langle \mathbf{R}_k^-(t)\cdot\mathbf{R}_l^-(0) \right\rangle dt \qquad (63)$$
$$\text{(for } k=l \text{ and } k \neq l)$$

Using (3) and (5) in (62) we have,

$$\tilde{\gamma}^+(\omega) = n^+/(3n^-\mu k_BT)\int_0^\infty \exp(i\omega t)$$
$$\times \left\langle \mathbf{R}_i^+(t)\cdot\mathbf{R}_j^+(0) \right\rangle dt \qquad (64)$$

Similarly,

$$\tilde{\gamma}^-(\omega) = n^-/(3n^+\mu k_BT)\int_0^\infty \exp(i\omega t)$$
$$\times \left\langle \mathbf{R}_k^-(t)\cdot\mathbf{R}_l^-(0) \right\rangle dt \qquad (65)$$

These are equivalent to the monatomic liquid of mass m as seen in Ref. [6]. If we assume that the correlation function obeys an exponentially decaying form of common friction

constant for cation and anion, $\tilde{\gamma}(0)$, then we have [2,3],

$$\left\langle \mathbf{R}_i^+(t){\cdot}\mathbf{R}_j^+(0)\right\rangle = \left\langle \mathbf{R}_i^+(0){\cdot}\mathbf{R}_j^+(0)\right\rangle \exp\left(-\tilde{\gamma}(0)t\right)$$

$$= (3n^-\mu k_B T/n^+)\tilde{\gamma}(0)^2\exp(-\tilde{\gamma}(0)t) \tag{66}$$

$$\left\langle \mathbf{R}_k^-(t){\cdot}\mathbf{R}_l^-(0)\right\rangle = \left\langle \mathbf{R}_k^-(0){\cdot}\mathbf{R}_l^-(0)\right\rangle \exp\left(-\tilde{\gamma}(0)t\right)$$

$$= (3n^+\mu k_B T/n^-)\tilde{\gamma}(0)^2\exp(-\tilde{\gamma}(0)t) \tag{67}$$

That is, the memory functions incorporating with the friction force in the Langevin equations for cation and anion are the same. In that case, comparing (54), (64) and (65), $\gamma^+(t)$ and $\gamma^-(t)$ are equal to each other and they are expressed as,

$$\gamma^+(t) = \gamma^-(t) \equiv \gamma(t) = \tilde{\gamma}(0)^2\exp(-\tilde{\gamma}(0)t) \tag{68}$$

Similarly, by using (16), the fluctuation dissipation theorem for $\left\langle \mathbf{v}_i^+(t){\cdot}\mathbf{v}_k^-(0)\right\rangle$ is written as,

$$m^+m^-\left\langle \mathbf{v}_i^+(0){\cdot}\mathbf{v}_k^-(0)\right\rangle\tilde{\gamma}(\omega)$$

$$= -\int_0^\infty \exp(i\omega t)\left\langle \mathbf{R}_i^+(t){\cdot}\mathbf{R}_k^-(0)\right\rangle\mathrm{d}t \tag{69}$$

The factor $\tilde{\gamma}(0)^2$ in (68) is obtained as follows,

$$\tilde{\gamma}(0)^2 = -\ddot{Z}_{ij}^{++}(0)/Z_{ij}^{++}(0) = -\ddot{Z}_{ij}^{--}(0)/Z_{ij}^{--}(0) \tag{70}$$

where

$$\ddot{Z}_{ij}^{++}(t) = \left\langle \dot{\mathbf{v}}_i^+(t){\cdot}\mathbf{v}_j^+(0)\right\rangle \quad \text{and} \quad \ddot{Z}_{ij}^{--}(t) = \left\langle \dot{\mathbf{v}}_k^-(t){\cdot}\mathbf{v}_l^-(0)\right\rangle.$$

Using (3)–(5), (25) and (31) in (70), we have,

$$\tilde{\gamma}(0) = \Omega = (\alpha_0/3\mu)^{1/2}, \tag{71}$$

where

$$\alpha_0 = n^+n^-\int_0^\infty \{(\partial^2\phi^{+-}/\partial\mathbf{r}^2) + (2/\mathbf{r})$$

$$\times (\partial\phi^{+-}/\partial\mathbf{r})\}g^{+-}(\mathbf{r}){\cdot}4\pi\mathbf{r}^2\mathrm{d}\mathbf{r}. \tag{72}$$

Thus, we have the same result for friction constant as (45) and (48). Using (52), (54) and (68) in (59), we have

$$\sigma^{++} = (n^{+2}z^{+2}e^2/3nk_BT)\left\langle \mathbf{v}_i^+(0){\cdot}\mathbf{v}_j^+(0)\right\rangle/\tilde{\gamma}(0) \tag{73}$$

Similarly,

$$\sigma^{--} = (n^{-2}z^{-2}e^2/3nk_BT)\left\langle \mathbf{v}_k^-(0){\cdot}\mathbf{v}_l^-(0)\right\rangle/\tilde{\gamma}(0) \tag{74}$$

and

$$\sigma^{+-} = (n^+n^-z^+z^-e^2/3nk_BT)\left\langle \mathbf{v}_i^+(0){\cdot}\mathbf{v}_k^-(0)\right\rangle/\tilde{\gamma}(0) \tag{75}$$

As the consequence, using (3)–(5) in above equations, we have the relations between the partial conductivity

coefficients, as,

$$\sigma^{++}/\sigma^{--} = |z^+|^2m^{-2}/|z^-|^2m^{+2} \tag{76}$$

and

$$\sigma^{++}/\sigma^{+-} = \sigma^{+-}/\sigma^{--} = |z^+|m^-/|z^-|m^+ \tag{77}$$

equations (76) and (77) correspond to the extensions of the relation $\sigma^{++}/\sigma^{--} = m^{-2}/m^{+2}$ and $\sigma^{++}/\sigma^{+-} = \sigma^{+-}/\sigma^{--} = m^-/m^+$ for equivalent binary salts, respectively [1–3].

The conductivities in non-equicharged molten salts have been treated by the microscopic theory to this time. In the following section, we will numerically confirm above results.

5. Numerical application

In order to confirm the results of the preceding sections, we perform the molecular dynamics (MD) simulations in non-equivalent molten binary salts, i.e. $CaCl_2$ and AlF_3. Tosi–Fumi type pair potentials are used in MD, which are expressed as,

$$V_{ij}(\mathbf{r}) = z_iz_je^2/\mathrm{r} + B_{ij}\exp(-a_{ij}\mathrm{r}) - C_{ij}/\mathrm{r}^6 \tag{78}$$

where parameters z_i and z_j stand for the charge of ions, and B_{ij}, a_{ij} and C_{ij} have their usual meaning [10]. The used potential parameters are those of Ping et al. [11] and Inoue et al. [12] for $CaCl_2$ and AlF_3, respectively. The simulations are carried out with 750 (250 Ca + 500 Cl) ions for $CaCl_2$ and 1000 (250 Al + 750 F) ions for AlF_3. The particles are prepared in a cubic cell and periodic boundary condition is used. The Coulomb interaction is calculated by Ewald method. Initial velocities are allocated with the Maxwellian distribution at a specific temperature, which is kept constant using the Nosé method [13] for 3000 time steps in order that the system will be equilibrated. Then, the calculation is carried out on NVE constant condition. One time step $\Delta t = 2.0 \times 10^{-15}$ s is used in Verlet's integration algorithm. The structural properties are obtained as the average of 2000 time steps. The correlation functions are obtained by 3000 samplings.

The pair distribution functions are defined as follows:

$$\langle n_{\alpha\beta}(\mathbf{r})\rangle\Delta\mathbf{r} = 4\pi\mathbf{r}^2\Delta\mathbf{r}\rho_\beta g_{\alpha\beta}(\mathbf{r}) \tag{79}$$

where $n_{\alpha\beta}(r)$ Δr denotes the number of β-type particles around an α-type particle between spherical shells of radii r and $r + \Delta r$. The bracket $\langle\rangle$ stands for the thermal average as well as the average over all α-type particles, and ρ_β is the mean number density of the β-type particles.

Figures 1 and 2 show the partial pair distribution functions of molten $CaCl_2$ at 1524 K and AlF_3 at 1996 K, respectively. As seen in figure 1, the obtained partial pair distribution functions $g_{CaCl}(\mathbf{r})$, $g_{ClCl}(\mathbf{r})$ and $g_{CaCa}(\mathbf{r})$ obtained by MD show the pronounced fist peaks at 2.6, 3.8 and 4.9 Å, respectively. Their features agree well with experiments [14], though the first peak of $g_{CaCa}(\mathbf{r})$ slightly
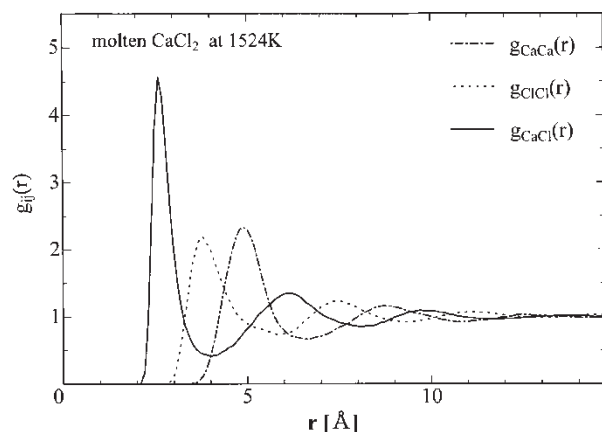
Figure 1. Partial pair distribution functions of molten $CaCl_2$ at 1524 K.

Figure 3. Velocity correlation functions of molten $CaCl_2$ at 1524 K.

appears at the larger side of **r** axis. Meanwhile, in figure 2, the partial pair distribution functions $g_{AlF}(r)$, $g_{FF}(r)$ and $g_{AlAl}(r)$ obtained by MD have their first peaks at 1.7, 2.5, 3.6 Å, respectively. The corresponding peaks can be seen in the MD results in Na_3AlF_6 melt in Ref. [15]. Therefore it can be concluded that the simulations give the adequate structural results. These facts prompt us to calculate correlation functions.

As treated in previous sections, the relations between velocity correlation functions (3)–(5) have been proved. Following relations are expected for $CaCl_2$,

$$\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle = -9k_BT/(m^+ + 2m^-) \qquad (80)$$

$$\left\langle \mathbf{v}_j^+(0)\cdot\mathbf{v}_i^+(0)\right\rangle = -(2m^-/m^+)\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle \qquad (81)$$

$$\langle \mathbf{v}_k^-(0)\cdot\mathbf{v}_l^-(0)\rangle = -(m^+/2m^-)\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle \qquad (82)$$

For AlF_3,

$$\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle = -12k_BT/(m^+ + 3m^-) \qquad (83)$$

$$\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_j^+(0)\rangle = -(3m^-/m^+)\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle \qquad (84)$$

$$\langle \mathbf{v}_k^-(0)\cdot\mathbf{v}_l^-(0)\rangle = -(m^+/3m^-)\langle \mathbf{v}_i^+(0)\cdot\mathbf{v}_k^-(0)\rangle \qquad (85)$$

To confirm the validity of these relations, we calculate the velocity correlation functions as the functions of time. The results are shown in figures 3 and 4. Obviously seen in these figures, three velocity correlation functions oscillate with the same phase, and the ratios of absolute value of them at arbitrary time are in the same ratios at $t = 0$. In table 1, the comparison of numerical results of correlation functions at $t = 0$ obtained by the theory and MD are listed, which agree well within less the error about 4%.

Figure 5 and 6 show the current correlation functions of molten $CaCl_2$ and AlF_3 as functions of t, respectively. The graphs in figures 5 and 6 are normalized by $\langle \mathbf{j}^-(0)\cdot\mathbf{j}^-(0)\rangle$. From these results, the relation between the current correlation functions are numerically confirmed, as,

$$\frac{\langle \mathbf{j}^+(t)\cdot\mathbf{j}^+(0)\rangle}{\langle \mathbf{j}^+(t)\cdot\mathbf{j}^-(0)\rangle} = \frac{\langle \mathbf{j}^+(t)\cdot\mathbf{j}^-(0)\rangle}{\langle \mathbf{j}^-(t)\cdot\mathbf{j}^-(0)\rangle} = |z^+|m^-/|z^-|m^+ \quad (86)$$

The values of the left hand side of equation (86) obtained by MD are 1.769 and 2.112 for molten $CaCl_2$ and AlF_3, respectively. The results excellently agree with the right hand side of (86). According to the explanation in Ref. [2],

Figure 2. Partial pair distribution functions of molten AlF_3 at 1996 K.
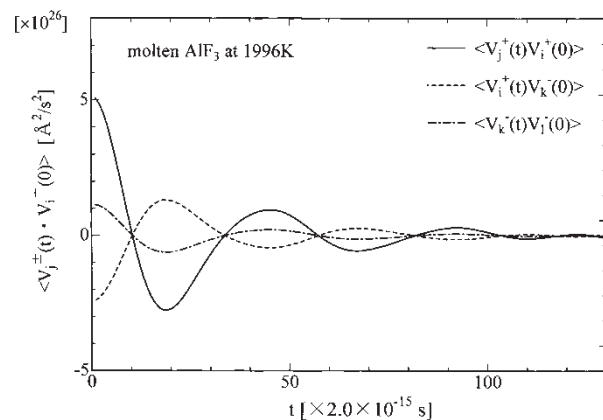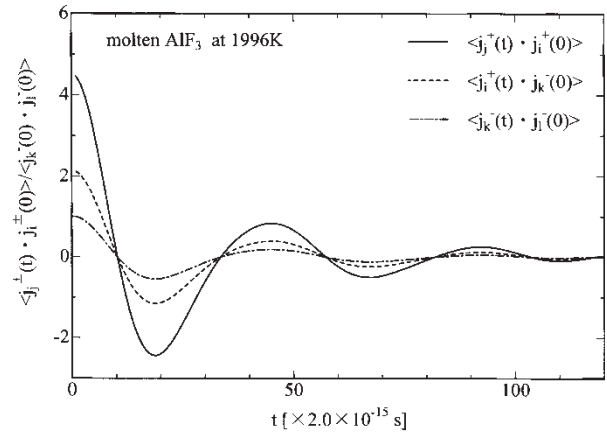

Figure 4. Velocity correlation functions of molten AlF_3 at 1996 K.

Table 2. Friction constants, total and partial conductivities and their ratios obtained by numerical calculation for molten $CaCl_2$ and AlF_3. The values of $m^-|z^+|/m^+|z^-|$ are also listed for comparison. The experimental value of σ_{tot} is estimated from Ref. 16.

	$CaCl_2$ at 1524 K	AlF_3 at 1996 K
γ	6.543×10^{13} (1/s)	2.814×10^{14} (1/s)
σ_{tot}	3.938 [1/Ω cm]	4.004 [1/Ω cm]
σ^+	2.516 [1/Ω cm]	2.717 [1/Ω cm]
σ^-	1.422 [1/Ω cm]	1.286 [1/Ω cm]
σ^+/σ^-	1.769	2.112
$|z^+|m^-/|z^-|m^+$	1.769	2.112
$\sigma_{tot}(exp)^{(15)}$	3.93 [1/Ω cm]	

of non-equivalent molten salts has been expressed by mass of ions and their charges as $|z^+|m^-/|z^-|m^+$. This is an extension formula from the inverse mass ratio in equivalent molten salts. The ratios of partial conductivity coefficients also have been proved to be $\sigma^{++}/\sigma^{+-} = \sigma^{+-}/\sigma^{--} = |z^+|m^-/|z^-|m^+$.

The numerical values of velocity correlation functions $\langle \mathbf{v}_i^+(0) \cdot \mathbf{v}_k^-(0) \rangle$ at $t = 0$ obtained by MD have been confirmed to be equal to $-9k_BT/(m^+ + 2m^-)$ and $-12k_BT/(m^+ + 3m^-)$ for molten $CaCl_2$ and AlF_3, respectively. Partial conductivities $\sigma^\pm$ have also been obtained through friction coefficient γ and $\langle \phi^{+-} \rangle$ for molten $CaCl_2$, AlF_3, which are directly calculated by the Tosi–Fumi type pair potentials and the pair distribution functions obtained by MD. The numerical results have confirmed that the ratio of partial conductivities σ^+/σ^- is equal to $|z^+|m^-/|z^-|m^+$. These numerical results precisely suggest the consistency of the theory.

Acknowledgements

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