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Author(s)	MATSUNAGA, Shigeki; KOISHI, Takahiro; TAMAKI, Shigeru
Citation	物性研究 (2006), 87(1): 70-71
Issue Date	2006-10-20
URL	http://hdl.handle.net/2433/110647
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Ionic conductivities of non-equivalent molten salts by molecular dynamics simulations

Shigeki MATSUNAGA[1], **Takahiro KOISHI**[2], and **Shigeru TAMAKI**[3]

[1]Nagaoka National College of Technology, Nagaoka 940-8532, Japan, Phone/Fax +81-258-34-9252, e-mail :matsu@nagaoka-ct.ac.jp

[2]Ebisuzaki Computational Astrophysics Laboratory, The Institute of Physical and chemical Research (RIKEN), Wako 351-0198, Japan
[3]Department of Physics, Faculty of Science, Niigata University, Niigata 950-2181, Japan

これまで我々は等価溶融塩のイオン伝導度について検討してきたが、本研究は理論面での非等価溶融塩への拡張である。イオン伝導度は速度相関関数および二体ポテンシャルで表され、また Langevin方程式を用いてイオン伝導度の比 σ^+/σ^- が $|z^+|m^-/|z^-|m^+$ に等しいことが示された。これは等価溶融塩の場合の逆質量比の関係の非等価溶融塩への拡張となっている。また、溶融$CaCl_2$及びAlF_3についての理論の計算結果とシミュレーションの良い一致を得た。

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, starting from generalized Langevin equation for cation and anion in these systems and using Kubo-Green formula with the help of various velocity correlation functions between a chosen pair of ions in them [1,2,3]. 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^+. It is interesting to know how the golden rule $\sigma^+/\sigma^- = m^-/m^+$ is modulated in such non-equivalent molten salts. $M^{2+}Y^{1-}{}_2$-type molten salt and $M^{3+}Y^{1-}{}_3$ -type molten salt are concerned as the non-equivalent ones. Practical molten salts corresponding to these types are, e.g., $CaCl_2$, which is useful for an industrial chemistry extracting metallic Ca. Taking account of another industrial applications, molten AlF_3 seems also to be useful for extracting metallic aluminum. At first, we derive the partial conductivities of $M^{2+}Y^{1-}{}_2$-type molten salt from microscopic point of view based on the Kubo-Green linear response theory using a simplified Langevin equation. The starting Langevin equation for either cation M or anion Y is written as follows [4],

$$m^{\pm}(dv_i^{\pm}(t)/dt) = -m^{\pm}\gamma^{\pm}v_i^{\pm}(t) + z^{\pm}e\varepsilon_i(t) + z^{\pm}eE \qquad (1)$$

where $m^{\pm}$ is the ion's mass, $v_i^{\pm}(t)$ is the ion's velocity at the time t, $\gamma^{\pm}$ is the effective friction constant acting on either cation or anion, $z^{\pm}$ is the ion's charge, $\varepsilon_i(t)$ is the random fluctuating force acting on ion *i*, and E is the applying external field. If we assume that this force at time *t*, is not influenced by its former or later time t' ($\neq t$), then we have

$$<\varepsilon_i(t)\varepsilon_i(t')> = \alpha\delta(t-t') \qquad (2)$$

where α means the strength of random fluctuating field. Using (1) and (2), then we have the following ensemble averages,

$$<v_i^{\pm 2}(t)> = (\alpha z^{\pm 2}e^2/2m^{\pm 2}\gamma^{\pm}) \qquad (3)$$

According to the equi-partition rule, we have

$$(1/2)n^+m^+ < v_i^{+2}(t)> + (1/2)n^-m^- < v_k^{-2}(t)> = (3/2)nk_BT \qquad (4)$$

where n is defined as $n = n^+ + n^-$.

Combine (1) and (4), then α is expressed as,

$$\alpha = \{(3/2)nk_BT\}/[(n^+z^{+2}e^2/4m^+\gamma^+) + (n^-z^{-2}e^2/4m^-\gamma^-)] \qquad (5)$$

Equation (1) can be extended to the current density $j^{\pm}(t)$ with the mean random fluctuating field $\varepsilon(t)$, instead of $v_i^{\pm}(t)$ and $\varepsilon_i(t)$, as,

$$j^{\pm}(t) = \sum_{i=1}^{n\pm} z^{\pm}ev_i^{\pm}(t) \qquad (6)$$

and

$$\varepsilon(t) = (1/n)\sum_{i=1}^{\nu}\varepsilon_i(t) \qquad (7)$$

then we have,

$$<\varepsilon(t)\varepsilon(t')> = (1/n^2)\Sigma_i^n<\varepsilon_i(t)\varepsilon_i(t')> = (\alpha/n)\delta(t-t')$$
$$= 6k_BT\delta(t-t')/[\{(n^+z^{+2}e^2/m^+\gamma^+)\} + \{(n^-z^{-2}e^2/m^-\gamma^-)\}] \qquad (8)$$

Taking similar treatments as [1], then we have,

$$j^{\pm}(t) = (n^{\pm}z^{\pm 2}e^2/m^{\pm}\gamma^{\pm})\varepsilon(t) \qquad (9)$$

On the other hand, the Kubo-Green type representations for partial conductivities are given as follows, [1,2,3]

$$\sigma^{\pm} = (1/3k_BT)\int_0^{\infty}< j^{\pm}(t)\,j(0)>dt = n^{\pm}z^{\pm 2}e^2/m^{\pm}\gamma^{\pm} \qquad (10)$$

where j(t) is equal to $j(t) = j^+(t) + j^-(t)$.

By Taylor expansion of second term of (10) and some algebraic manipulations, we have for $CaCl_2$,[5]

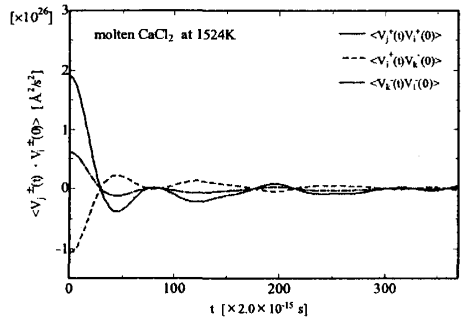

Fig.1 Velocity correlation functions of molten $CaCl_2$ at 1524K.

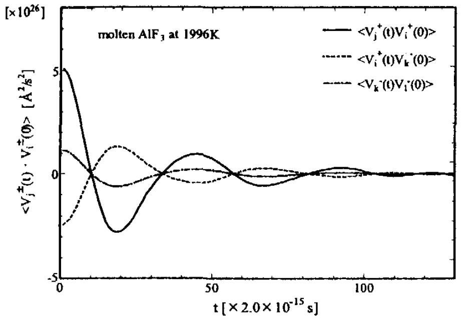

Fig.2 Velocity correlation functions of molten AlF_3 at 1996K.

$$\sigma^{\pm}=(n^{\pm}z^{\pm}e^2/m^{\pm})\int_0^{\infty}[1-\{(t^2/2)(2n_0\langle\phi^{+-}\rangle/9\mu)\}+(\text{higher order})]dt \qquad (11)$$

where

$$\langle\phi^{+-}\rangle=\int_0^{\infty}\{(\partial^2\phi^{+-}/\partial r^2)+(2/r)(\partial\phi^{+-}/\partial r)\}g^{+-}(r)\ 4\pi r^2 d r \qquad (12)$$

and μ is the reduced mass of $CaCl_2$,

$$1/\mu=(2/m^+)+(1/m^-) \qquad (13)$$

In (12), ϕ^{+-} is the inter ionic potential between anion and cation. Comparing the third term of (10) and (11), we have,

$$1/\gamma^{\pm}=\int_0^{\infty}\{1-(t^2/2)\gamma^{\pm 2}+(\text{higher order})\}dt \qquad (14)$$

We take $n^+=n_0$ and $n^-=2n_0$ for $CaCl_2$, then,

$$\gamma^{\pm}=(2n_0\langle\phi^{+-}\rangle/9\mu)^{1/2}. \qquad (15)$$

Then as the consequent, we have the relation, as,

$$\gamma^+=\gamma^-\equiv\gamma \qquad (16)$$

Therefore, we have the conductivity ratio, as,

$$\sigma^+/\sigma^-=|z^+|m^-/|z^-|m^+ \qquad (17)$$

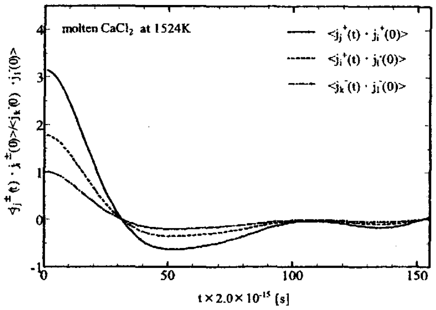

Fig.3 Current correlation functions of molten $CaCl_2$ at 1524K.

where $|z^+|=+2$ and $|z^-|=-1$ for molten $M^{2+}Y^{1-}{}_2$ salts. The equation (17) is the extension of the relation $\sigma^+/\sigma^-=m^-/m^+$ for equivalent binary salts to that of non-equivalent system. For molten AlF_3, we can ascertain the same relation as (17) is valid, where $|z^+|=+3$ and $|z^-|=-1$.

Further consideration for conductivity coefficient, we have,

$$\sigma^{++}/\sigma^{+-}=\sigma^{+-}/\sigma^{--}=|z^+|m^-/|z^-|m^+ \qquad (18)$$

$$\sigma^{++}/\sigma^{--}=|z^+|^2(m^-)^2/|z^-|^2(m^+)^2 \qquad (19)$$

On the other hand, according to the momentum conservation law, it is straightforward to obtain the cross velocity correlation functions for molten $CaCl_2$, as,

$$\langle \mathbf{v}_j^+(0)\,\mathbf{v}_i^+(0)\rangle=-(2m^-/m^+)\langle \mathbf{v}_i^+(0)\,\mathbf{v}_k^-(0)\rangle \qquad (20)$$

$$\langle \mathbf{v}_k^-(0)\,\mathbf{v}_l^-(0)\rangle=-(m^+/2m^-)\langle \mathbf{v}_i^+(0)\,\mathbf{v}_k^-(0)\rangle \qquad (21)$$

$$\langle \mathbf{v}_i^+(0)\,\mathbf{v}_k^-(0)\rangle=-9k_BT/(m^++2m^-) \qquad (22)$$

For molten AlF3, we obtain the following relations, as,

$$\langle \mathbf{v}_i^+(0)\mathbf{v}_j^+(0)\rangle=-(3m^-/m^+)\langle \mathbf{v}_i^+(0)\mathbf{v}_k^-(0)\rangle \qquad (23)$$

$$\langle \mathbf{v}_k^-(0)\mathbf{v}_l^-(0)\rangle=-(m^+/3m^-)\langle \mathbf{v}_i^+(0)\mathbf{v}_k^-(0)\rangle \qquad (24)$$

$$\langle \mathbf{v}_i^+(0)\mathbf{v}_k^-(0)\rangle=-12\,k_BT/(m^++3m^-) \qquad (25)$$

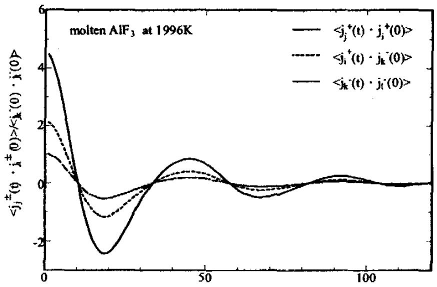

Fig.4 Current correlation functions of molten AlF_3 at 1996K.

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

$$V_{ij}(r)=Z_iZ_j\,e^2/r+B_{ij}\exp(-a_{ij}r)-C_{ij}/r^6 \qquad (26)$$

where the used potential parameters are taken from literature. The obtained pair distribution functions agree well with experiments or previous MD results. As is treated so far, the relations between velocity correlation functions are expected, i.e. (20), (21) and (22) for $CaCl_2$. For AlF_3, (23), (24) and (25) are applied. To confirm the validity of these relations, we calculate the velocity correlation functions as the functions of time. The results are shown in Fig.1 and Fig.2. Obviously seen in these figures, three velocity correlation functions oscillate with same phase, and the ratios of absolute value of them at arbitrary time t is in the same ratios as at t=0. The correlation functions at t=0 obtained by the theory and MD agree well within the error about 4%.

Fig.3 and Fig.4 show the current correlation functions of molten $CaCl_2$ and AlF_3 as functions of t, respectively. The graphs in Fig.3 and Fig.4 are normalized by $\langle j^-(0)\,j^-(0)\rangle$. From these results, the relation between the current correlation functions are numerically confirmed to be constant, as,

$$\langle j^+(t)\,j^+(0)\rangle/\langle j^+(t)\,j^-(0)\rangle=\langle j^+(t)\,j^-(0)\rangle/\langle j^-(t)\,j^-(0)\rangle=|Z^+|m^-/|Z^-|m^+ \qquad (27)$$

The ratios of the current correlation functions obtained by MD are 1.769 and 2.112, for $CaCl_2$ and AlF_3, respectively. The agreement with the theory is excellent. According to [2], the correlation functions have the same decaying form with time, which we write as f(t), then we have,

$$\sigma^{++}/\sigma^{+-}=\{\langle j^+(0)\,j^+(0)\rangle\int_0^{\infty}f(t)dt\}/\{\langle j^+(0)\,j^-(0)\rangle\int_0^{\infty}f(t)dt\}=\langle j^+(0)\,j^+(0)\rangle/\langle j^+(0)\,j^-(0)\rangle=|Z^+|m^-/|Z^-|m^+ \qquad (28)$$

$$\sigma^{+-}/\sigma^{--}=\{\langle j^+(0)\,j^-(0)\rangle\int_0^{\infty}f(t)dt\}/\{\langle j^-(0)\,j^-(0)\rangle\int_0^{\infty}f(t)dt\}=\langle j^+(0)\,j^-(0)\rangle/\langle j^-(0)\,j^-(0)\rangle=|Z^+|m^-/|Z^-|m^+ \qquad (29)$$

, which means we have numerically confirmed the relation corresponding to (18).

Acknowledgement:

This work was supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science and Culture.

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