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Dielectric screening properties in molten noble-metal halides

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Abstract

The inverse dielectric function $1/\varepsilon(q)$ is newly obtained in terms of the charge–charge correlation functions $S_{ZZ}(q)$ by the re-examined theory of dielectric screening in molten salts. The new theory is applied to the molten noble-metal halides, *i.e.* AgBr and CuBr, in order to obtain $S_{ZZ}(q)$, and in due course, $1/\varepsilon(q)$. The inter-ionic screened potential $\phi_{sc}^{+-}(r)$ is estimated using $1/\varepsilon(q)$. The obtained screened potential $\phi_{sc}^{+-}(r)$ is treated as the potential of mean force to obtain the partial pair distribution function between cation and anion $g_{+-}(r)$. The results are compared to those obtained by diffraction experiments and molecular dynamics simulation. The deviation from Nernst–Einstein relation in the transport properties is also discussed.

Keywords: Dielectric screening; Charge–charge structure factor; Noble-metal halides; Molecular dynamics simulation

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1. Introduction

The dielectric screening properties in molten salts have been a matter of particular interest. There is a close relationship between the dielectric screening and the charge fluctuation of the constituents of the substances. The charge–charge structure factor, or $S_{ZZ}(q)$, defined by Hansen and McDonald [1] indicates the charge fluctuation in a molten salt. $S_{ZZ}(q)$ can be obtained from their partial structure factors by means of diffraction experiments or simulation [2]. The dielectric screening function $\varepsilon(q)$ of a mono-valent molten salt has been represented by $S_{ZZ}(q)$ as follows:

$$\frac{1}{\varepsilon(q)} = 1 - \left\{ \frac{4\pi e^2 \beta n S_{ZZ}(q)}{q^2} \right\} \tag{1}$$

where $\beta = 1/k_B T$ and n is the number density of constituent ions [1].

Several attempts have been made at deriving the dielectric screening functions from these experimental structure factors. However, the obtained results indicate a *negative* sign in the small q region, which shows the difficulty in the appropriate explanation of the results [3,4], because $\varepsilon(q)$ must be *positive* in the meaning of the potential screening. In this situation, we have proposed the *new* equation of $\varepsilon(q)$ and $S_{ZZ}(q)$ in molten salts which is different from Eq. (1) and applied it to molten alkali-halides [5].

In order to test the new theory, we focus on molten noble-metal halides, *e.g.* AgBr and CuBr. It is well known that the noble-metal halides are the typical example of the superionic conductors, which is a group of substances that exhibit high values of ionic conductivity while in the solid state. The mechanism of high ionic conductivity in the superionic conductors has been widely investigated because of their novel physical behavior and technological importance [6]. CuBr shows superionic conduction in its alpha phase, where copper ions statistically distribute around the bromine bcc cubic, and copper ions can move one site to another. However, AgBr has a rock salt structure in its solid state and does not exhibit superionic conduction, though it is also one of the noble-metal halides. We have investigated the structural and transport properties of noble-metal halides by molecular dynamics simulations [7,8]. In this study, as a serial work, we apply the new theory to molten AgBr and CuBr to examine the dielectric screening effect in molten phase, because the screened

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potentials are the fundamental subject of the transport properties.

2. Brief summary of charge–charge structure factors in a molten salt

The theory of the dielectric screening in molten salt has been re-examined using $S_{ZZ}(q)$ in the previous work [5]. We briefly summarize its procedure as follows. We consider a typical binary molten salt system $A_\nu B_\mu$. N_ν and N_μ stand for the number of ion species + and −. With the total number of particles N, the concentration of species ν is expressed as $x_\nu = N_\nu/N = 0.5$. The densities of particles are $n^+ = n^- = n/2$ and $n = N/V$, where V is the volume of the system. The effective charges of ions are $z^+ = -z^- = z$. Then, $S_{ZZ}(q)$ is written as follows [1]:

$$S_{ZZ}(q) = \frac{\langle \rho_q^Z \rho_{-q}^Z \rangle}{N} = \Sigma_\nu \Sigma_\mu z_\nu z_\mu S_{\nu\mu}(q) \tag{2}$$

where $S_{\nu\mu}(q)$ is a partial structure factor, *i.e.* the Fourier transformation of the pair distribution function of ion ν around ion μ in r-space, $g_{\nu\mu}(r)$. $S_{\nu\mu}(q)$ is defined as

$$S_{\nu\mu}(q) = x_\nu \delta_{\nu\mu} + n x_\nu x_\mu \int_0^\infty \left(\frac{\sin qr}{qr}\right) \{g_{\nu\mu}(r) - 1\} 4\pi r^2 \, \mathrm{d}r \tag{3}$$

$S_{\nu\mu}(q)$ and $g_{\nu\mu}(r)$ directly reflect the ionic configuration and are easily obtainable from neutron diffraction experiment or molecular dynamics simulation.

In the case that an external charge $e\rho_{\mathrm{ext}}(\mathbf{r})$ is introduced from outside into this system at the position $\mathbf{r}$, then a charge $e\rho_{\mathrm{ind}}(\mathbf{r})$ is induced. By the Gauss's law, the divergence of the electric displacement $\boldsymbol{D}(\mathbf{r})$ and the electric field $\boldsymbol{E}(\mathbf{r})$ are related to $e\rho_{\mathrm{ext}}(\mathbf{r})$ and $e\rho_{\mathrm{ind}}(\mathbf{r})$, respectively. The screened charge is expressed as $\rho_{\mathrm{ext}}(\mathbf{r})/\varepsilon$. In general, the dielectric constant ε may be extended to an isotropic r-dependent term written as $\varepsilon(r)$. Besides, $\rho_{\mathrm{ext}}(\mathbf{r})/\varepsilon(r)$ can be replaced by $\rho_{\mathrm{ext}}(\mathbf{r}) + \rho_{\mathrm{ind}}(\mathbf{r})$. Taking the ratio of the Fourier transformation of the Gauss's law for $e\rho_{\mathrm{ind}}(\mathbf{r})$ to $e\rho_{\mathrm{ext}}(\mathbf{r})$, the inverse dielectric function $1/\varepsilon(q)$ is expressed as follows:

$$\frac{1}{\varepsilon(q)} = 1 + \left\{\frac{\rho_{\mathrm{ind}}(q)}{\rho_{\mathrm{ext}}(q)}\right\} \tag{4}$$

where we assume $\varepsilon(q)$ is isotropic, for simplicity.

Meanwhile, the electric potential $\phi(\mathbf{r})$ due to this external charge density is defined as

$$E(\boldsymbol{r}) = -\mathrm{grad}\,\phi(\boldsymbol{r}) \tag{5}$$

Using the Gauss's law, we have the Poisson equation, as

$$\nabla^2\phi(\boldsymbol{r}) = -\left\{\frac{4\pi e\rho_{\mathrm{ext}}(\boldsymbol{r})}{\varepsilon(\boldsymbol{r})}\right\} \tag{6}$$

Putting the Fourier representations of $\varepsilon(r)$, $\phi(\mathbf{r})$, $\rho_{\mathrm{ext}}(\mathbf{r})$ and $\rho_{\mathrm{ind}}(\mathbf{r})$, into Eq. (6) and taking $\mathbf{r} = 0$, then we have

$$q^2\varepsilon(q)\phi(q) = 4\pi e\rho_{\mathrm{ext}}(q) \tag{7}$$

$e\rho_{\mathrm{ind}}(\mathbf{r})$ is the charge fluctuation yielded by the insertion of the external charge $e\rho_{\mathrm{ext}}(\mathbf{r})$, where the under bar stands for vector. Therefore, $e\rho_{\mathrm{ind}}(\mathbf{r})$ might be expressed in the following form:

$$e\rho_{\mathrm{ind}}(q) = \chi_{ZZ}(q) e\phi_{\mathrm{ext}}(q) \tag{8}$$

where $\chi_{ZZ}(q)$ is the charge response function. On the basis of the fluctuation dissipation theorem, $\chi_{ZZ}(q)$ is expressed in terms of $S_{ZZ}(q)$ as [1]:

$$\chi_{ZZ}(q) = -\beta n S_{ZZ}(q) \tag{9}$$

Putting (7) and (8) into (4), and using (9), we have the relation between $1/\varepsilon(q)$ and $S_{ZZ}(q)$, as

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + (\kappa_\mathrm{s}^2/q^2) S_{ZZ}(q)} \tag{10}$$

where $\kappa_\mathrm{s}^2 = 4\pi e^2 \beta n$. It should be emphasized that Eq. (10) is the *new* relation between $1/\varepsilon(q)$ and $S_{ZZ}(q)$, and it is obviously different from Eq. (1).

Eq. (10) results from an isotropic configuration of surrounded ions. This condition can be satisfied by a symmetric configuration in the short-range region in the molten salt that is almost perfectly ionized ions such as molten alkali-halides. If the ions' configuration is extremely different from an isotropic one, then the dielectric screening may include some anisotropic effect and the application of Eq. (10) becomes insufficient. For instance, this effect can be seen in molten copper halides such as CuBr, in which the oscillation of $g_{\mathrm{Cu-Br}}(r)$ for the distance r coincides basically with that of $g_{\mathrm{Cu-Cu}}(r)$ [9]. A rather simplified revision in such case is the insertion of a parameter δ into Eq. (10), as

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + \delta(\kappa_\mathrm{s}^2/q^2) S_{ZZ}(q)} \tag{11}$$

The role of parameter δ is the reduction of the screening effect by the structural anisotropy. Therefore, the value of δ may be in the range of $0 < \delta \leq 1$ and the condition $\delta = 1$ may occur in a well-symmetric configuration. In the region of higher values of $q > 10\ \mathrm{A}^{-1}$, we usually take $S_{ZZ}(q) \cong 1$, hence Eq. (11) becomes:

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + \delta(\kappa_\mathrm{s}^2/q^2)} \tag{12}$$

Meanwhile, the inverse dielectric function in the long wavelength limit is already well known by the theory of classical one component plasma [1,10]. Starting from the continuity equation relating to the charge and taking Fourier transforms under the condition of long wavelength limit, and using the well-known Thomas–Fermi type screening potential, the inverse dielectric function near the long wavelength limit is written as follows:

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + (\lambda_\mathrm{s}^2/q^2)} \tag{13}$$

As shown in Eq. (13), $1/\varepsilon(q)$ in its higher q-region and very lower q-region is expressed by a similar form as Eq. (12), although their screening constants are quite different. In the intermediate region, $1/\varepsilon(q)$ exhibits an oscillating behavior due to the effect of $S_{ZZ}(q)$. It is apparent that Eq. (12) is equal to zero at $q = 0$. And therefore, $1/\varepsilon(q)$ is in the region $0 \leq 1/\varepsilon(q) \leq 1$ for

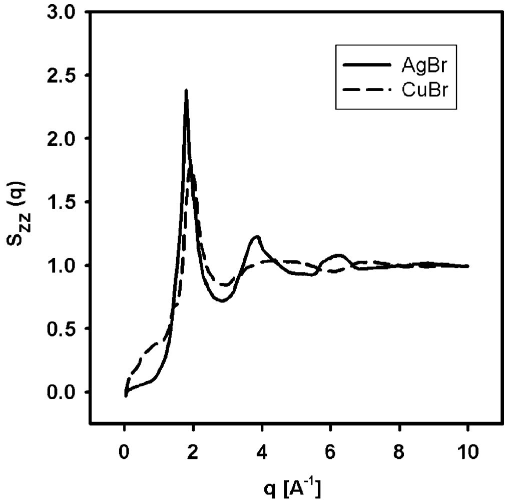

Fig. 1. $S_{ZZ}(q)$ of molten AgBr (solid line) and CuBr (dashed line).

any positive values of $S_{ZZ}(q)$. At this point, it should be stressed that the validity of Eqs. (10) and (12) is also confirmed by this fact in the meaning of screening; $1/\varepsilon(q)$ remains positive for all positive q value.

As mentioned before, Eq. (10) or Eq. (11) is useful to derive $1/\varepsilon(q)$ from the experimental partial structure factors. Eq. (3) is applicable to deriving $1/\varepsilon(q)$ from $g_{\nu\mu}(r)$ by computer simulation. As examples of $1/\varepsilon(q)$ for binary ionic melts, we will show the results of $1/\varepsilon(q)$ using experimental $S_{ZZ}(q)$ for AgBr and CuBr. As mentioned previously, $S_{ZZ}(q)$ is related to structure factors and pair distribution functions by Eq. (2). In this case, the summation in Eq. (2) is taken for ion species Ag or Cu and Br. The obtained $S_{ZZ}(q)$ for molten AgBr at 753 K and CuBr at 810 K are shown in Fig. 1. We can see the significant first peaks in $S_{ZZ}(q)$ at about 1.8 and 2.0 Å^{-1} for molten AgBr and CuBr, respectively. These peaks correspond to the oscillations of partial structure factors [2,9]. By substituting these $S_{ZZ}(q)$ into Eq. (11), We can obtain the inverse dielectric function $1/\varepsilon(q)$. The calculated results are shown in Fig. 2 with the calculated curve by Eq. (12) for comparison. It is clearly recognized that $1/\varepsilon(q)$ satisfies the condition $0 \leq 1/\varepsilon(q) \leq 1$. We can find the oscillatory features and the significant minimum at around 1.8 and 2.0 Å^{-1} for AgBr and CuBr, respectively. These features are yielded by the form of $S_{ZZ}(q)$ which have large maximum and oscillation. These results should be attributed to the effect that an ion in molten salts is susceptible to be surrounded by ions of opposite sign, which yields the large charge fluctuation and screening effect.

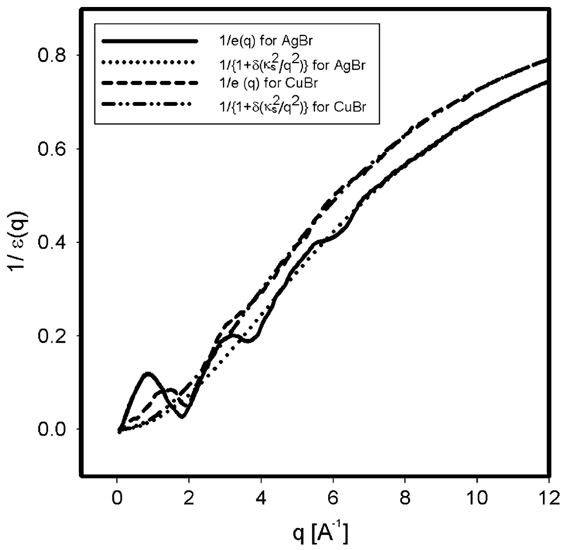

Fig. 2. $1/\varepsilon(q)$ of molten AgBr (solid line) and CuBr (dashed line) with $1/(1 + \delta(\kappa_s^2/q^2))$ for AgBr (dotted line) and CuBr (dashed and double dotted line) for comparison.

3. Screening effect for Coulomb potential in molten noble-metal halides

In a molten salt, the effective screened potential between a cation and an anion, $\phi_{\mathrm{sc}}^{+-}(r)$, may be divided into two parts, as

$$\phi_{\mathrm{sc}}^{+-}(r) = \phi_{\mathrm{rep\,sc}}^{+-}(r) + \phi_{\mathrm{at\,sc}}^{+-}(r) \tag{14}$$

Here $\phi_{\mathrm{rep\,sc}}^{+-}(r)$ is the direct repulsive potential between cation and anion in the short-range distance influenced by a small amount of screening effect, and $\phi_{\mathrm{at\,sc}}^{+-}(r)$ is the attractive screened potential in the long range. Eq. (9) is a poor approximation for the repulsive potential because of its highly non-linear functional form. Therefore, the screening effect for the direct repulsive potential part should be treated in a different way.

The attractive screened potential $\phi_{\mathrm{at\,sc}}^{+-}(r)$ is effectively screened by the existence of other ions. However, its bare-potential may be ascribed mainly to the form of Coulomb interacting potential. The attractive Coulomb potential between an ion z^+e at the origin, and another ion z^-e at the distance r is

$$\phi_{\mathrm{at}}^{+-}(r) = -\frac{z^2e^2}{r} \tag{15}$$

Then, the screened attractive potential in q-space is written as follows:

$$\phi_{\mathrm{at\,sc}}^{+-}(q) = -\frac{4\pi z^2e^2}{\varepsilon(q)q^2} \tag{16}$$

The numerical result for $\phi_{\mathrm{at\,sc}}^{+-}(r)$ is given by the inverse Fourier transformation. In the region of $S_{ZZ}(q) \sim 1$, Eq. (12) is applicable. Hence, for a symmetric configuration, we have

$$\phi_{\mathrm{at\,sc}}^{+-}(q) = -\frac{4\pi z^2e^2}{q^2 + \kappa_{\mathrm{s}}^2} \tag{17}$$

This equation is easily converted to the r-dependent expression as

$$\phi_{\mathrm{at\,sc}}^{+-}(r) = -\left(\frac{z^2e^2}{r}\right)\exp(-\kappa_{\mathrm{s}}r) \tag{18}$$

which has the form of the product of the Coulomb potential by the screened part.

A simple treatment of the screening effect for the repulsive potential is the introduction of multiplicative parameter α to the repulsive part. Thus, the effective potential between cation and anion in the region of $S_{ZZ}(q) \sim 1$ is expressed as the sum of the screened repulsive potential and the screened attractive potential equation (18), which is expressed as

$$\phi_{\mathrm{sc}}^{+-}(r) = \alpha\left(\frac{B}{r^{n}}\right) - \left(\frac{z^{2}e^{2}}{r}\right)\exp(-\kappa_{\mathrm{s}}r) \tag{19}$$

Therefore, the inverse dielectric function $1/\varepsilon(q)$ as the screening effect can be multiplied onto the bare attractive inter-ionic potential between two ions in the q-space and the screening parameter α is also multiplied onto the repulsive potential in r-space to obtain the effective screened potential. It is not necessary, however, to apply the dielectric function in the procedure of the computer simulation, because the simulation itself involves automatically the screening behaviors and only the utilization of appropriate bare inter-ionic potentials is required.

From above discussions, it seems interesting to obtain the screened potential between anion and cation, Ag^{+} or Cu^{+} and Br^{-} in molten AgBr and CuBr. Besides, the experimental pair distribution function, *i.e.* $g_{\mathrm{BrAg}}(r)$ and $g_{\mathrm{BrCu}}(r)$ is obviously different [2,9]. We adopt the potential by Rahman, Vashishta and Parrinello (RVP) [11] as a bare inter ionic interaction, because it is often used for noble-metal halides. The RVP type potential sets for i and j ions are written as

$$V_{ij}(r) = \frac{H_{ij}}{r^{nij}} + \frac{z_{i}z_{j}e^{2}}{r} - \frac{P_{ij}}{r^{4}} \tag{20}$$

where the third term is charge–dipole interactions. The adopted parameters are taken from literature [12,13]. The screened potentials of molten AgBr and CuBr are obtained by the above procedure. The results are shown in Figs. 3 and 4, respectively. In the calculation, we adopt the value of δ as 0.50 and 0.40, and the value of α as 0.1 and 0.05 for AgBr and CuBr, respectively. The reduction of the depth of potential by screening effect is obviously recognized in Figs. 3 and 4. The characteristic oscillations are found in the screened potentials especially in molten CuBr, which may be caused by the charge fluctuation in the distribution of ions.

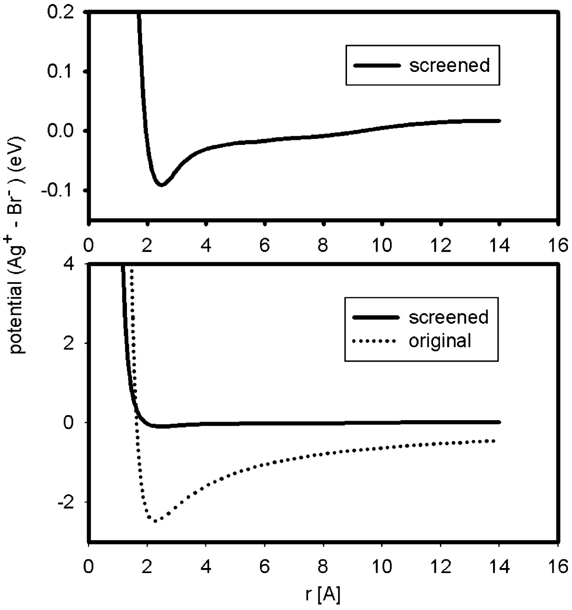

Fig. 3. The screened potential between Ag–Br (dotted line) with original one (solid line). (Bottom) The screened potential is also shown with different scale (top) to show its oscillatory feature.

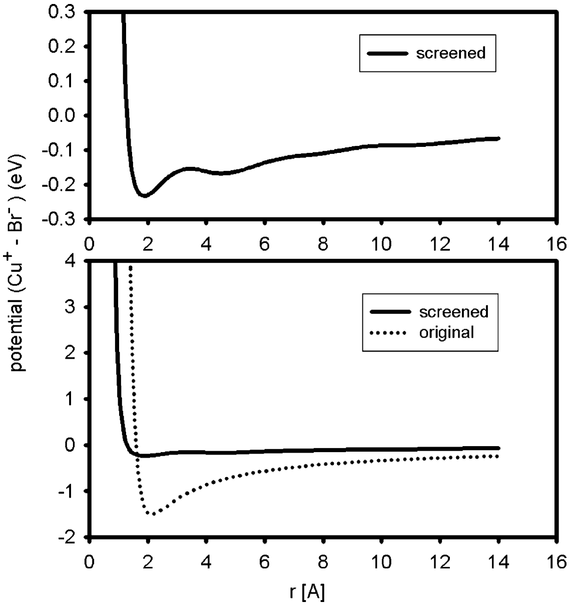

Fig. 4. The screened potential between Cu–Br (dotted line) with original one (solid line). (Bottom) The screened potential is also shown with different scale (top) to show its oscillatory feature.

4. Pair distribution functions

To confirm the results of screened potentials between cations and anions, we calculate the pair distribution functions by the potential of mean force $U^{+-}(r)$, which is defined by the following equation in relation to $g_{+-}(r)$ [1]:

$$g_{+-}(r) = \exp\left[\frac{-U^{+-}(r)}{k_{\mathrm{B}}T}\right] \tag{21}$$

Here we can take the screened potential $\phi_{\mathrm{sc}}^{+-}(r)$ as $U^{+-}(r)$, because Eq. (21) is originally suggested by weak interacting materials. In the previous work, we have proved that $\phi_{\mathrm{sc}}^{+-}(r)$ and $U^{+-}(r)$ are mathematically equivalent, basing our argument on the Ornstein–Zernike equation [5]. $g_{+-}(r)$ are obtained by inserting the calculated $\phi_{\mathrm{sc}}^{+-}(r)$ instead of $U^{+-}(r)$ into Eq. (21). They are shown in Figs. 5 and 6, together with those obtained by experiment and molecular dynamics (MD) simulation. The first peaks of $g_{+-}(r)$ almost agree well, though the oscillations in larger r region are not satisfactory reproduced. This fact may suggest that the screening effect is considerable especially in small r region, *i.e.* about the distance to the first nearest neighbors. In other words, the first nearest neighbor ions have the main contribution to the screening effects in molten salts.

The discrepancy in the larger r region between $g_{ij}(r)$'s are attributed to the difference between $\phi_{\mathrm{sc}}^{+-}(r)$ and $U^{+-}(r)$, which may be caused by several reasons, in addition to a margin of calculation error in Fourier transformation. One reason is that only the Coulomb attractive potential is used to derive $\phi_{\mathrm{sc\,at}}^{+-}(r)$, *i.e.* the attractive part of RVP type potential—P_{ij}/r^{4} is not used for

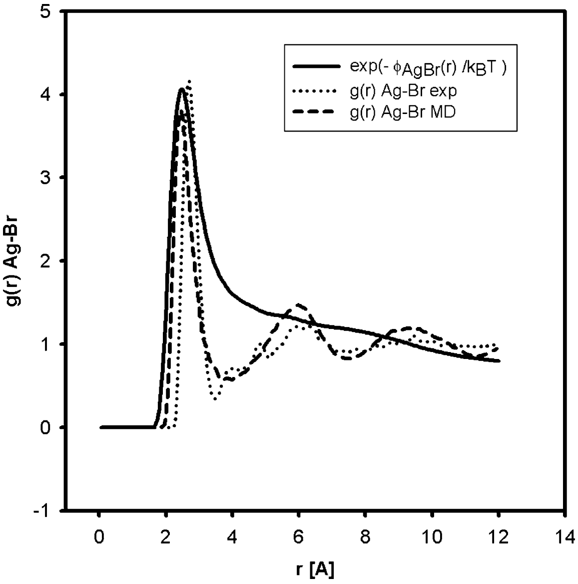

Fig. 5. $g_{ij}(r)$ for molten AgBr calculated using screened potential (solid line) with that obtained by experiment (dotted line) and by MD (dashed line).

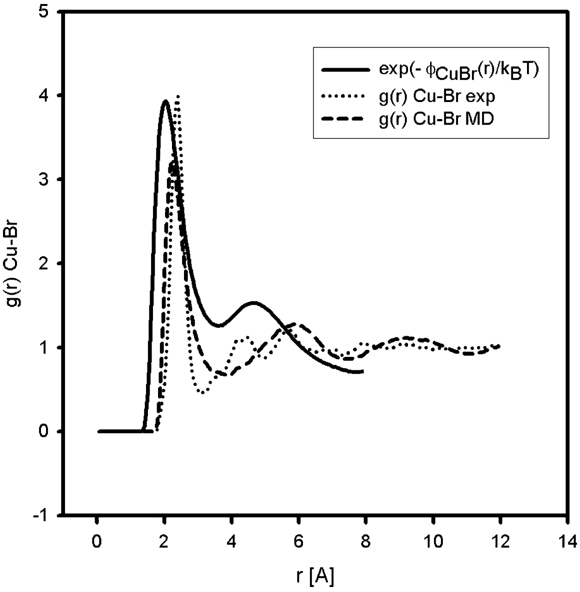

Fig. 6. $g_{ij}(r)$ for molten CuBr calculated using screened potential (solid line) with that obtained by experiment (dotted line) and by MD (dashed line).

simplicity. Another expected reason is that the non-symmetric structure in solid phase remains in molten phase, which may obstruct the screening effect in molten phase. In spite of above facts, however, it may be recognized that the calculated result for $\phi_{\mathrm{sc}}^{+-}(r)$ so as to carry on the above treatment is physically significant, and the obtained results are obviously affected by screening effect.

5. Deviation from Nernst–Einstein relation

In the previous sections, we have mainly discussed the screened pair potentials in connection with the structure and the dielectric function. In this section, we discuss the influence of the screening effect on the transport properties. It is known that there is a deviation from the Nernst–Einstein (NE) relation of the transport properties in the binary molten salts, which is defined as [10]:

$$\sigma = \sigma^{+} + \sigma^{-} = \left(\frac{nz^2e^2}{k_{\mathrm{B}}T}\right)(D^{+} + D^{-})(1 - \Delta) \tag{22}$$

where Δ is the deviation from NE relation. The equations of partial conductivities for cation and anion, σ^{+} and σ^{-}, and the diffusion constants, D^{+} and D^{-}, in binary molten salts were already derived in the pervious work on the basis of the linear response theory [14]. In accordance with these results, we have

$$\Delta = 1 - (1 - \Delta_{\mathrm{BR}})\left[\frac{2/\alpha^{0}}{(1/\alpha^{+}) + (1/\alpha^{-})}\right] \tag{23}$$

where

$$\alpha^{0} = n\int_{0}^{\infty}\left\{\frac{\partial^{2}\phi^{+-}}{\partial r^{2}} + \left(\frac{2}{r}\right)\left(\frac{\partial\phi^{+-}}{\partial r}\right)\right\} g_{+-}(r)4\pi r^{2}\,\mathrm{d}r \tag{24}$$

$$\alpha^{\pm} = \left(\frac{n}{2}\right)\int_{0}^{\infty}\left[\left\{\frac{\partial^{2}\phi^{\pm\pm}}{\partial r^{2}} + \left(\frac{2}{r}\right)\left(\frac{\partial\phi^{\pm\pm}}{\partial r}\right)\right\} g_{\pm\pm}(r) + 2\left\{\frac{\partial^{2}\phi^{+-}}{\partial r^{2}} + \left(\frac{2}{r}\right)\left(\frac{\partial\phi^{+-}}{\partial r}\right)\right\} g_{+-}(r)\right] 4\pi r^{2}\,\mathrm{d}r \tag{25}$$

and

$$\Delta_{\mathrm{BR}} = \left(\frac{4\pi n}{3k_{\mathrm{B}}T}\right)\int_{d}^{\infty}\left(\frac{\partial\phi^{+-}(r)}{\partial r}\right) g_{+-}(r)r^{3}\,\mathrm{d}r \tag{26}$$

where $\phi^{ij}(r)$ is an effective inter-ionic potential between ions i and j.

In Eq. (26), we can approximate that the parameter d is equal to the hard-core contact distance between cation and anion on the condition that both ionic sizes are rigid. This assumption, however, may not be always valid in the case of heavier weight atom. In this calculation, we will use the first maximum position of $g_{+-}(r)$ as the distance of ion's contact. The quantity Δ_{BR} was obtained by Berne and Rice [15], though recently certified by present authors in a different way [14]. Δ_{BR} is essentially caused by an asymmetric distribution of the surrounded ions around the centered ion under an applied external field. Since it has been found that values of α^{0}, α^{+} and α^{-} are numerically close to one another, we can take $\Delta \sim \Delta_{\mathrm{BR}}$ as the deviation from the NE relation in a molten salt.

In the region of $r>d$, the differentiation of potential $(\partial\varphi^{+-}(r)/\partial r)$ shown in above equations is equal to the mean force acting on the ion at the origin from other ion of opposite sign located at the distance r, and therefore, we have to use the effective screened potential as $\phi^{+-}(r)$ in above equations [14]. Hence we can use the potential of mean force $U^{+-}(r)$, instead of $\phi^{+-}(r)$ in Eq. (26). With Eq. (21), Eq. (26) is converted to the following form, as

$$\Delta_{\mathrm{BR}} = -\left(\frac{4\pi n}{3}\right)\int_{d}^{\infty}\left(\frac{\partial g_{+-}(r)}{\partial r}\right) r^{3}\,\mathrm{d}r \tag{27}$$

Table 1
Deviation from Nernst–Einstein relation in molten AgBr (753 K) and CuBr (810 K); Δ_{BR} (calc), Δ_{BR} (MD) by Eq. (27), Δ_{BR} (exp), and Δ (MD*) from Refs. [12,13]

	AgBr	CuBr
Δ_{BR} (calc)	−0.48	−0.44
Δ_{BR} (MD)	−0.45	−0.40
Δ_{BR} (exp)	−0.41	−0.49
Δ (MD*)	−0.42	−0.46

Δ(MD*) was calculated using correlation functions.

Using the simulated $g_{+-}(r)$ or $U^{+-}(r)$ in molten salts, we can calculate the deviation from NE relation, Δ_{BR}. In fact, we have calculated Δ_{BR} using Eq. (27) with obtained screened potentials and $g_{ij}(r)$ using Eq. (21), or $g_{ij}(r)$ obtained by experiment.

Using Eq. (27), the value of Δ_{BR} also can be estimated from $g_{ij}(r)$ obtained by MD. The procedure of MD simulation is essentially same as the previous works [7,8]. We briefly describe as follows. The MD calculations are carried out for AgBr and CuBr using 500 atoms (250 cations and 250 anions) placed in a cubic cell. The periodic boundary condition is used. The Coulomb interaction is calculated by the Ewald method [16] to avoid a margin of error yield by cutting of the long tail of Coulomb potential. The calculation of the structure is curried out on the condition that the number of the particles, the volume of the cell and the total energy of the system (NVE) are constant. The obtained $g^{+-}(r)$ to $r \sim 12$ Å are shown in Figs. 5 and 6, which agree well with those in literature [12,13]. Results of Δ_{BR} for molten AgBr and CuBr are shown in Table 1 with the values taken from literature [12,13]. The values agree within about 20% error, which suggests the consistency of the theory of screening effect on the structure and the transport properties in molten salts.

6. Conclusion

The theory of dielectric screening in molten salt has been reexamined with the new relation between $S_{\mathrm{ZZ}}(q)$ and $1/\varepsilon(q)$. The theory has been applied to molten AgBr and CuBr to examine the screening effect. Screened attractive potentials between cations and anions have been obtained by inverse Fourier transformation in q-space. The estimated screened potential has been used as a potential of mean force in order to obtain $g_{+-}(r)$. The results have agreed well with those obtained by experiment and MD simulation especially in small r region. The deviation from the Nernst–Einstein relation is also obtained. The discussions and the theoretical results from various points of view suggest the consistency of the theory.

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