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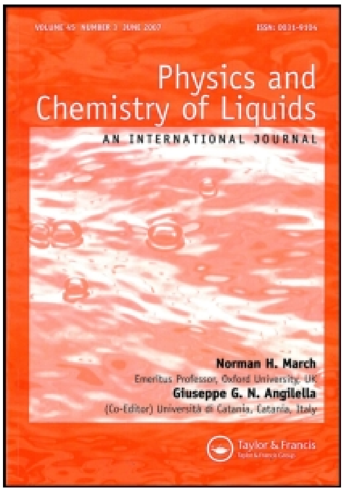

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Dielectric screening properties in molten salts

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The theory of dielectric screening in molten salts is re-examined, using the charge–charge correlation functions $S_{zz}(q)$. The inverse dielectric function $1/\varepsilon(q)$ is newly obtained in terms of $S_{zz}(q)$. This $1/\varepsilon(q)$ is multiplied onto the attractive part of the inter-ionic potential between cation and anion, in order to obtain the screened attractive potential $\phi^{+-}_{\text{screened attractive}}(r)$. A simplified but effectively screened repulsive potential is added to $\phi^{+-}_{\text{screened attractive}}(r)$ to get the total screened potential $\phi^{+-}_{\text{screened}}(r)$. By using the computer simulation for molten NaCl, $S_{zz}(q)$, and $1/\varepsilon(q)$ are obtained. The total screened potential $\phi^{+-}_{\text{screened}}(r)$ so as to carry on the above procedure agreed fairly to the potential of mean force defined by the partial pair distribution function between cation and anion, $g_{+-}(r)$. A similar calculation was also carried out for molten RbBr, starting from the observed $S_{zz}(q)$. And results for this system were fairly acceptable. From these, it is considered that the screened inter-ionic potential at a long distance between cation and anion in a molten salt is equivalent to the potential of mean force in it. These facts make it possible to use the potential of mean force obtained experimentally for the calculation of the deviation from the Nernst–Einstein relation in molten salts.

Keywords: Dielectric screening; Molten salt; Charge–charge correlation functions; Theory

1. Introduction

Some time ago, the dielectric screening property in molten salts was investigated [1]. Its property is closely related to the charge fluctuation of the constituents. The charge fluctuation in a molten salt is represented by the charge–charge correlation function $S_{zz}(q)$ which is easily obtainable from the partial structure factors in its molten salt.

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As a matter of fact, the dielectric screening function $\varepsilon(q)$ of a monovalent molten salt is described, in the momentum representation, as follows [1],

$$\frac{1}{\varepsilon(q)} = 1 - \left\{4\pi e^2 \beta n_0 \frac{S_{zz}(q)}{q^2}\right\} \tag{1}$$

where $\beta = 1/k_\mathrm{B}\mathrm{T}$, and n_0 is the number density of constituent ions. On the other hand, partial structure factors in various molten salts have been obtained by a combination of different methods of diffraction experiments for the same molten salts [2–7].

Several attempts to obtain the dielectric screening functions by using these experimental structure factors and equation (1) have been carried out [8,9]. The obtained results indicated, however, a negative sign in the small q region, suggesting a difficulty in an appropriate explanation. Since then there has been hardly any further study of experimentally obtainable dielectric function in molten salts.

In this article, we wish to re-examine this theory and seek whether other plausible and useful dielectric functions in molten salts are obtainable or not.

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2. Brief survey for charge–charge structure factors in a molten salt

Let us consider a typical molten salt system $\mathrm{A}_\nu\mathrm{B}_\mu$ of $x_\nu = x\mu = 0.5$, $z^+ = -z^- = z = 1$ and $n^+ = n^- = n_0$. The charge–charge structure factors defined by Hansen–McDonald [1] are useful quantitative representations, and are written as follows,

$$S_{zz}(q) \equiv \frac{\langle \rho_{q^z} \rho_{-q^z} \rangle}{N} = \sum_\nu \sum_\mu z_\nu z_\mu S_{\nu\mu}(q) \tag{2}$$

$$S_{\nu\mu}(q) = x_\nu \delta_{\nu\mu} + 2n_0 x_\nu x_\mu \int_0^\infty \frac{\sin(qr)}{qr} \{g_{\nu\mu}(r) - 1\} 4\pi r^2 \mathrm{d}r \tag{3}$$

Using the partial pair distribution functions $g_{\nu\mu}(r)(\nu,\ \mu = +, -)$, $S_{zz}(q)$ is given by,

$$S_{zz}(q) = 1 + \frac{n_0}{2} \int_0^\infty \frac{\sin(qr)}{qr} [\{g_{++}(r) - 1\} + \{g_{--}(r) - 1\} - 2(g_{+-}(r) - 1\}] 4\pi r^2 \mathrm{d}r \tag{4}$$

On the other hand, the concentration–concentration fluctuation in r-space $g_{cc}(r)$ defined by Bhatia–Thornton representation [10] is written as follows,

$$\begin{aligned} g_{cc}(r) &= x_\nu^2 x_\mu^2 [\{g_{++}(r) - 1\} + \{g_{--}(r) - 1\} - 2\{g_{+-}(r) - 1\}] \\ &= \frac{1}{16} [\{g_{++}(r) - 1\} + \{g_{--}(r) - 1\} - 2\{g_{+-}(r) - 1\}] \end{aligned} \tag{5}$$

Corresponding to $g_{cc}(r)$, the concentration–concentration structure factor $S_{cc}(q)$ is defined as follows,

$$\begin{aligned} S_{cc}(q) &= x_\nu x_\mu + 2n_0 \int_0^\infty \frac{\sin(qr)}{qr} g_{cc}(r) 4\pi r^2 \mathrm{d}r \\ &= \frac{1}{4} + 2n_0 \int_0^\infty \frac{\sin(qr)}{qr} g_{cc}(r) 4\pi r^2 \mathrm{d}r \end{aligned} \tag{6}$$

Inserting (5) into (6) and using (4), we have,

$$S_{zz}(q) = 4S_{cc}(q) \tag{7}$$

Using the formulae obtained in this section, the dielectric screening functions in terms of $S_{zz}(q)$ will be shown in the next section.

3. Dielectric screening function expressed in terms of $S_{zz}(q)$

In order to derive the dielectric screening function, we will consider the same molten salt system considered in the preceding section. If a charge $e\rho_{\text{ext}}(r)$ were introduced from outside into this system at the position r, then there occurs an induced charge $e\rho_{\text{ind}}(\boldsymbol{r})$. Therefore, we have the following Poisson equations in electrostatic unit,

$$\text{div} D(\boldsymbol{r}) = 4\pi e\rho_{\text{ext}}(\boldsymbol{r}) \tag{8}$$

$$\text{div} E(\boldsymbol{r}) = 4\pi e\{\rho_{\text{ext}}(\boldsymbol{r}) + \rho_{\text{ind}}(\boldsymbol{r})\} \tag{9}$$

where $D(\boldsymbol{r})$ and $E(\boldsymbol{r})$ are the electric displacement and the electric field, respectively.

The electric potential $\phi(r)$ due to this external charge density is given by

$$E(\boldsymbol{r}) = -\text{grad}\phi(r) \tag{10}$$

Using (9) we have

$$\nabla^2\phi(\boldsymbol{r}) = -\frac{4\pi e\rho_{\text{ext}}(r)}{\varepsilon} \tag{11}$$

$$= -4\pi e\{\rho_{\text{ext}}(\boldsymbol{r}) + \rho_{\text{ind}}(\boldsymbol{r})\} = -4\pi e\rho_{\text{ext}}(\boldsymbol{r})\left\{1 + \frac{\rho_{\text{ind}}(\boldsymbol{r})}{\rho_{\text{ext}}(\boldsymbol{r})}\right\} \tag{12}$$

where ε is the dielectric constant, but it may be extended to an $\boldsymbol{r}$-dependent term written as $\varepsilon(\boldsymbol{r})$. In their text book, Hansen and McDonald [1] took partly $\varepsilon(\boldsymbol{r}) = 1$ for the dielectric function in molten salts and obtained the formula expressed as shown in equation (1). Now we can express each quantity $\varepsilon(\boldsymbol{r})$, $\phi(\boldsymbol{r})$, and $\rho_{\text{ext}}(\boldsymbol{r})$ in this equation as the following Fourier representations,

$$\varepsilon(\boldsymbol{r}) = \sum_q \underline{\varepsilon}(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{r}},\ \phi(\boldsymbol{r}) = \sum_q \underline{\phi}(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{r}},\ \rho_{\text{ext}}(\boldsymbol{r}) = \sum_q \underline{\rho}_{\text{ext}}(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$

$$\text{and} \quad \rho_{\text{ind}}(\boldsymbol{r}) = \sum_q \underline{\rho}_{\text{ind}}(\boldsymbol{q})e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{13}$$

Under the assumption that the dielectric function $\underline{\varepsilon}(\boldsymbol{q})$ is isotropic, which means $\varepsilon(q)$, and putting some of these into equation (11), we have

$$q^2\varepsilon(q)\underline{\phi}(\boldsymbol{q}) = 4\pi e\underline{\rho}_{\text{ext}}(\boldsymbol{q}) \tag{14}$$

where here and elsewhere in this paper we use the convention $\underline{A}(\boldsymbol{q}) = \{A_x(\boldsymbol{q}), A_y(\boldsymbol{q}), A_z(\boldsymbol{q})\}$. Since $e\rho_{\text{ind}}(r)$ is a charge fluctuation caused by the insertion of

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the external charge $e\rho_{\rm ext}(r)$, it might be expressed in the following form, by using the linear charge response function $\chi_{zz}(q)$,

$$e\underline{\rho}_{\rm ind}(\boldsymbol{q}) = \chi_{zz}(q)e\underline{\phi}(\boldsymbol{q}) \tag{15}$$

Based on the fluctuation dissipation theorem, $\chi_{zz}(q)$ is expressed in terms of $S_{zz}(q)$ as follows,

$$\chi_{zz}(q) = -\beta n_0 S_{zz}(q) \tag{16}$$

A detailed discussion on this equation is described in the Appendix A. Compare equations (11) and (12), the inverse dielectric function $1/\varepsilon(q)$ is expressed as follows,

$$\frac{1}{\varepsilon(q)} = \frac{\mathrm{FT}\{\mathrm{div}\boldsymbol{E}(r)\}}{\mathrm{FT}\{\mathrm{div}\boldsymbol{D}(r)\}} = \frac{\boldsymbol{q}\cdot\boldsymbol{E}(q)}{\boldsymbol{q}\cdot\boldsymbol{D}(q)} = 1 + \frac{\underline{\rho}_{\rm ind}(\boldsymbol{q})}{\underline{\rho}_{\rm ext}(\boldsymbol{q})} \tag{17}$$

where FT means the Fourier component. Putting (14) and (15) into (17), and using (16), we have

$$\frac{1}{\varepsilon(q)} = 1 + \frac{4\pi e^2\chi_{zz}(q)}{\varepsilon(q)q^2} = 1 - \frac{4\pi e^2\beta n_0 S_{zz}(q)}{\varepsilon(q)q^2} \tag{18}$$

or

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + (\kappa_s^2/q^2)S_{zz}(q)} \tag{19a}$$

where

$$\kappa_s^2 = 4\pi e^2\beta n_0 \tag{19b}$$

Equation (19a) results from an isotropic configuration of surrounded ions, which condition can be satisfied by a symmetric configuration in the short-range region in the molten salt of almost perfectly ionized ions such as in molten NaCl and CsCl. If the ions' configuration deviates extremely from an isotropic one, which can be, for instance, seen in molten CuI in which the oscillation of $g^{\text{Cu–I}}(r)$ for the distance r coincides basically with that of $g^{\text{Cu–Cu}}(r)$ [6], then the dielectric screening may include some anisotropic effect and the application of equation (19a) becomes insufficient. A rather simplified revision for such a case is the insertion of a parameter δ into equation (19a) defined as,

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + \delta(\kappa_s^2/q^2)S_{zz}(q)} \tag{20}$$

The magnitude of δ may be in the range of $0 < \delta \le 1$ and the condition $\delta = 1$ may correspond to a symmetric configuration. In the region of higher values of $q > 10\,\text{Å}^{-1}$, we have usually $S_{zz}(q) \simeq 1$ which may also correspond to the condition $\delta = 1$, and then

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + (\kappa_s^2/q^2)} \tag{21}$$

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On the other hand, the inverse dielectric function in the long wavelength limit is already well known by the theory of the classical one component plasma [1,10]. Starting from the continuity equation relating the charge and taking Fourier transforms under the condition of long wavelengths, the relation between $\rho_{\mathrm{ind}}(q)$ and $\rho_{\mathrm{ext}}(q)$ is expressed as,

$$\rho_{\mathrm{ind}}(q) = \frac{-\rho_{\mathrm{ext}}(q)}{1 + (q^2/\lambda_s^2)} \tag{22}$$

where

$$\lambda_s^2 = 4\pi e^2 (2n_0)^2 \chi_T \tag{23}$$

Here χ_T being the isothermal compressibility and $2n_0 = n^+ + n^-$. If an external point charge ze is put at the position r, then we have the well-known Thomas–Fermi type screening potential by using equation (22), which indicates that the inverse dielectric function near the long wavelength limit is written as follow,

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + (\lambda_s^2/q^2)} \tag{24}$$

It is interesting that the inverse dielectric function $1/\varepsilon(q)$ in its higher-q region and very lower-q region is expressed by a similar form as shown in equations (21) and (24), although their screening constants are quite different. In the intermediate region, $1/\varepsilon(q)$ exhibits an oscillating behavior due to the effect of $S_{zz}(q)$, as a logical consequence. Using (6) and (7), $S_{zz}(q)$ is given by

$$S_{zz}(q) = \sum_{\nu}\sum_{\mu} z_\nu z_\mu S_{\nu\mu}(q) = 1 + 8n_0 \int_0^\infty \frac{\sin(qr)}{qr} g_{cc}(r) 4\pi r^2 \, \mathrm{d}r \tag{25}$$

where we take the ionic charges equal to the ionic valences as $z^+ = -z^- = z = 1$. Therefore, $1/\varepsilon(q)$ is converted to

$$\frac{1}{\varepsilon(q)} = \frac{1}{1 + \delta(\kappa_s^2/q^2)\left\{1 + 8n_0 \int_0^\infty (\sin(qr)/qr) g_{cc}(r) 4\pi r^2 \mathrm{d}r\right\}} \tag{26}$$

Under the assumption of $\delta = 1$, equation (19) is useful for deriving the inverse dielectric function, $1/\varepsilon(q)$, from experimental results for the partial structure factors and also equation (25) is applicable for deriving $1/\varepsilon(q)$ by a computer simulation. It is apparent that equation (24) is equal to zero at $q = 0$. And therefore, the inverse dielectric function $1/\varepsilon(q)$ has the following relation for any positive values of $S_{zz}(q)$,

$$0 \le \frac{1}{\varepsilon(q)} \le 1 \tag{27}$$

It is, therefore, possible to derive the inverse dielectric function $1/\varepsilon(q)$ if $S_{zz}(q)$ or $g_{cc}(r)$ are known by either the experimental method or computer simulation under the assumption of $\delta = 1$. In the following sections, we will show several results for $1/\varepsilon(q)$ by using experimental $S_{zz}(q)$ and simulated $g_{cc}(r)$.

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4. Screening for Coulomb potential in a molten salt

In a molten salt having charges of $z^+ = -z^- = 1$, the screened potential between a cation and an anion at a distance of r, $\phi^{+-}_{\text{screened}}(r)$, may be divided into two parts as follows,

$$\phi^{+-}_{\text{screened}}(r) = \phi^{+-}_{\text{screened repulsive}}(r) + \phi^{+-}_{\text{screened attractive}}(r) \tag{28}$$

Here $\phi^{+-}_{\text{screened repulsive}}(r)$ is the repulsive potential influenced by a small amount of screening effect in the short range distance between cation and anion, and $\phi^{+-}_{\text{screened attractive}}(r)$ is the screened attractive potential in the long range.

A utilization of equation (19a) for the repulsive potential seems not to be a good and enough approximation as the screening effect, because the application of linear response theory for a highly nonlinear functional form cannot give any good approximation, and therefore, equation (16) is a poor approximation for the repulsive potential because of its highly nonlinear functional form, and therefore, the screening effect for the direct repulsive potential should be treated in a different way. A simple consideration for the screening effect for the repulsive potential is the introduction of a parametric multiplier, hereafter taken as α, which can be multiplied to the well-known formula of the repulsive potential as multiplicand. Then the screened repulsive potential may be written as follows,

$$\phi^{+-}_{\text{screened repulsive}}(r) = \alpha\phi^{+-}_{\text{repulsive}}(r) \tag{29}$$

where $\phi^{+-}_{\text{repulsive}}(r)$ is the bare repulsive potential. On the other hand, the attractive screened potential $\phi^{+-}_{\text{screened repulsive}}(r)$ is effectively screened by the existence of other ions, although its bare-potential may be mainly ascribed to the form of Coulomb interacting potential. Let us put an ion of positive point charge at the origin. Then another ion of negative point charge in the region of attractive Coulomb potential at r feels the potential,

$$\phi^{+-}_{\text{attractive}}(r) = -\frac{e^2}{r} \tag{30}$$

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

$$\phi^{+-}_{\text{screened attractive}}(q) = -\frac{4\pi e^2}{\varepsilon(q)q^2} \tag{31}$$

The numerical result for $\phi^{+-}_{\text{screened attractive}}(r)$ is given by the inverse Fourier transformation $\mathrm{FT}\{\phi^{+-}_{\text{screened attractive}}(q)\}$. The repulsive potential $\phi^{+-}_{\text{repulsive}}(r)$ which is often approximated by either the Born–Mayer type potential or the inverse function of $r^n (n \leq 12)$. That is,

$$\phi^{+-}_{\text{repulsive}}(r) = A\exp(-br) \quad \text{or} \quad \phi^{+-}_{\text{repulsive}}(r) = \frac{B}{r^n}(n \leq 12) \tag{32}$$

where A, b, B and n are constants. Equation (28) is therefore converted to

$$\phi^{+-}_{\text{screened}}(r) = \alpha A\exp(-br) + \mathrm{FT}\left\{\phi^{+-}_{\text{screened attractive}}(q)\right\} \tag{33a}$$

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or

$$\phi^{+-}_{\text{screened}}(r) = \alpha \frac{B}{r^n} + \text{FT}\{\phi^{+-}_{\text{screened attractive}}(q)\} \tag{33b}$$

In the region of $S_{zz}(q) \sim 1$, equation (23) is applicable, and therefore we have

$$\phi^{+-}_{\text{screened attractive}}(q) = -\frac{4\pi e^2}{q^2}\frac{q^2}{q^2+\kappa_s^2} = -\frac{4\pi e^2}{q^2+\kappa_s^2} \tag{34}$$

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

$$\phi^{+-}_{\text{screened attractive}}(r) = -\frac{e^2}{r}\exp(-\kappa_s r) \tag{35}$$

The screening parameter κ_s is exactly equal to the inverse of the Debye screening length. Using (32) and (35), the effective potential between cation and anion in the region of $S_{zz}(q) \sim 1$ is then expressed as,

$$\phi^{+-}_{\text{screened}}(r) = \alpha A \exp(-br) - \frac{e^2}{r}\exp(-\kappa_s r) \tag{36a}$$

or

$$\phi^{+-}_{\text{screened}}(r) = \alpha \frac{B}{r^n} - \frac{e^2}{r}\exp(-\kappa_s r) \tag{36b}$$

It is emphasized that the inverse dielectric function $1/\varepsilon(q)$ as a 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, in order to obtain the effective screened potential.

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5. Equivalency between the screened pair potential and the potential of mean force

We have obtained an asymptotic form for the screened attractive potential, as shown in equation (35). The factor $\exp(-\kappa_s r)$ is familiar from the elementary Debye–Hückel theory and the corresponding pair distribution function $g_{+-}(r)$ is given by,

$$g_{+-}(r) = \exp\left\{\frac{\beta e^2}{r}\exp(-\kappa_s r)\right\} \tag{37}$$

In this section, we will prove that this asymptotic form of the screened attractive potential $\phi^{+-}_{\text{screened attractive}}(r)$ and the potential of mean force $U^{+-}(r)$ defined by the formula of $g_{+-}(r) = \exp[-U^{+-}(r)/k_BT]$ are equal to each other at the long distance of r, by using the Ornstein–Zernike equation. Putting a cation 1 at the origin and an anion 2 at the position r, and furthermore the third ion 3 at the position of r', then we have an approximate Ornstein–Zernike equation as follows,

$$-\beta U^{+-}(r) = -\beta\phi^{+-}(r) + n_0 \int \mathrm{d}\boldsymbol{r} c_{+-}(|\boldsymbol{r} - r'|)h_{--}(\boldsymbol{r}') \tag{38}$$

where $c_{+-}(r)$ is the direct correlation function between cation and anion, and $h_{--}(r')$ is equal to $(g_{--}(r') - 1)$. Here we have inferred that the third ion represented by 3 is mainly another neighboring anion located around the cation at the origin, because the ion 3 is located at a closer position to the origin, which means that its sign is negative. By Fourier transform, equation (38) is converted to the following form,

$$U^{+-}(q) = \phi^{+-}(q)\left[1 - \frac{c_{+-}(q)h_{--}(q)}{\beta n_0 \phi^{+-}(q)}\right] \tag{39}$$

On the other hand, it is well known that the direct correlation function $c_{+-}(r)$ has an approximate form for large r, as follows,

$$c_{+-}(r) \simeq -\beta\phi^{+-}(r) \tag{40}$$

The Fourier transform of equation (40) is immediately written as,

$$c_{+-}(q) \simeq -n_0\beta\phi^{+-}(q) \tag{41}$$

Putting (41) into (39), we have

$$U^{+-}(q) \simeq \phi^{+-}(q)\{1 + h_{--}(q)\} = \phi^{+-}(q)S_{--}(q) \tag{42}$$

Apart from a quantitative disagreement with either the experimental result or simulated one, $S_{--}(q)$ may be analogically expressed as follows, by using the random phase approximation [10],

$$S_{--}(q) = \frac{1}{1 + n_0\beta\phi^{--}(q)} \tag{43}$$

Here the pair potential between anions in its Fourier transform $\phi^{--}(q)$ is also approximately expressed as $4\pi e^2/q^2$, and then we have,

$$U^{+-}(q) = -\frac{4\pi e^2}{q^2 + \kappa_s^2} \tag{44}$$

and finally we have,

$$U^{+-}(r) = -\frac{e^2}{r}\exp(-\kappa_s r) \tag{45}$$

Therefore, $\phi^{+-}_{\text{screened attractive}}(r)$ described in equation (35) and the potential of mean force $U^{+-}(r)$ are equal to each other at the long distance of r. The expression of $\phi^{+-}_{\text{screened}}(r)$ is certainly not rigorous, and therefore there is inevitably a minor numerical discrepancy between this and $U^{+-}(r)$ in the numerical agreement. However, in an approximate sense, both functions are equivalent. In fact, the screened potential between the centered cation 1 and a neighboring anion 2 locating at an appropriate distance, is expressed in terms of the form of direct interacting potential multiplied by the inverse dielectric function $1/\varepsilon(q)$. The factor $1/\varepsilon(q)$ is evidently given by the force acting on the centered cation from all other neighboring ions represented by 3. Therefore, the screening potential is physically equivalent to the potential of mean force.

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6. Inverse dielectric function in molten NaCl obtained by computer simulation

It is not necessary to apply the dielectric function for the computer simulation, because the simulation procedure itself involves automatically the screening behaviors and only the utilization of appropriate bare inter-ionic potentials is required, although the ion's charges are not always equal to their valence ones. In fact, the effective charge z^* used in computer simulation is sometimes smaller than the ion's valence number because of a partly covalent character of the constituents. In the cases of MD or Monte-Carlo simulations, the effective charge in molten CuI is taken to be 0.6 [6]. In this section, we derive the charge–charge correlation function $S_{zz}(q)$ and the inverse dielectric function $1/\varepsilon(q)$ of molten NaCl by using MD simulation. The well-known Tosi–Fumi potentials are used as the bare inter-ionic potentials. The simulated $g_{++}(r)$, $g_{--}(r)$ and $g_{+-}(r)$ in the range of $r < 8\,\text{Å}$ agreed with the experimental results [2] and indicate a good isotropic configuration suggesting $\delta = 1$ and these quantities were inserted into equation (4). The obtained $S_{zz}(q)$ of molten NaCl is shown in figure 1, which agreed with that shown in the literature [1]. Putting this $S_{zz}(q)$ into (19a), we have the $1/\varepsilon(q)$ in molten NaCl as shown in figure 2. Using the obtained $1/\varepsilon(q)$ and taking $\alpha = 0.5$ as a trial screening factor for the repulsive potential and (33a), the estimated screened potential between cation and anion is shown in figure 3. So far the obtained screened potential is, more or less, close to the mean force $U^{+-}(r)$. A difference between $\phi^{+-}_{\text{screened}}(r)$ and $U^{+-}(r)$, which are shown in figure 3, may be caused by several reasons. One of them is that the inverse dielectric function is only applicable for a gradual slope of attractive potential and the screening for the repulsive part is restricted to a qualitative way as multiplying the parameter α. This treatment may diminish, more or less, the exactness of the result. The other reason is that we have used Tosi–Fumi potential for MD simulation in order to obtain $g_{+-}(r)$. Even though the obtained $g_{+-}(r)$ by this simulation is close to the experimental one in the range of $r < 8\,\text{Å}$, we are not sure of the

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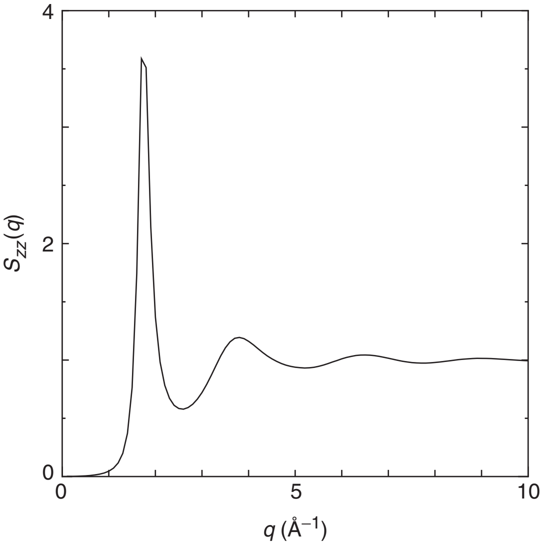

Figure 1. $S_{zz}(q)$ of molten NaCl obtained by MD simulation.

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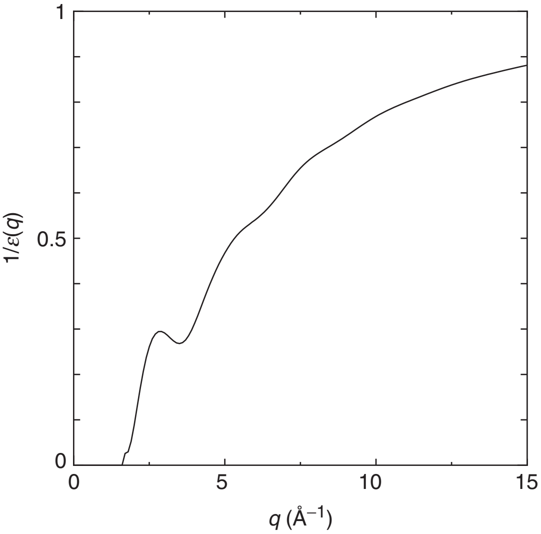

Figure 2. $1/\varepsilon(q)$ of molten NaCl.

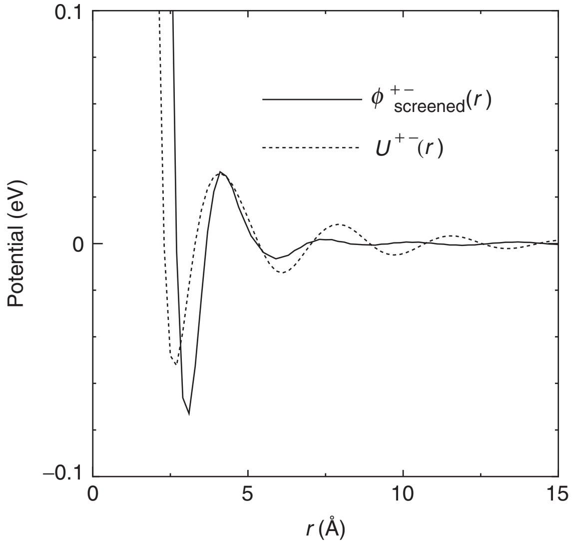

Figure 3. Screened inter-ionic potential between Na^{+} and Cl^{-} ions, $\phi^{+-}_{\text{screened}}(r)$ and $U^{+-}(r)\{= -k_B T \ln\ g_{+-}(r)\}$ of molten NaCl.

possibility of agreement in the range of distance beyond 8 Å, because the decaying tendency of $g_{+-}(r)$ obtained by simulation is slow, indicating a remarkable oscillation up to $r = 15$ Å. Usually it is hard to obtain any visible oscillation in the experimental $g_{+-}(r)$ beyond the distance of $r \sim 10$ Å. It is known that a Monte-Carlo simulation by using the deformation dipole model [11], which makes it possible to have a more rapid decaying for $g_{+-}(r)$, gives a better agreement for the experimental results of molten CsCl [12]. These facts suggest that the second and third peaks of $U^{+-}(r)$ obtained from

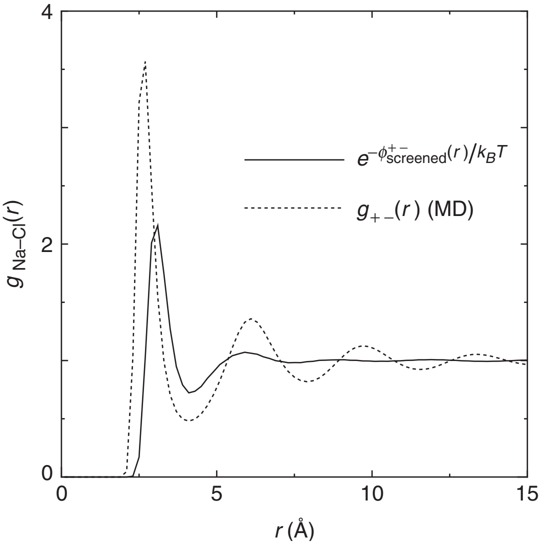

Figure 4. Pair distribution function $g_{+-}(r)$ and corresponding function of $\exp\{-\phi^{+-}_{\text{screened}}(r)/k_BT\}$ of molten NaCl.

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simulated $g_{+-}(r)$ should be diminished to some extent in the range of $r > 10$ Å. At the present stage, the obtained $\phi^{+-}_{\text{screened}}(r)$ is inevitably somewhat numerically different from $U^{+-}(r)$. By inserting the calculated $\phi^{+-}_{\text{screened}}(r)$ instead of $U^{+-}(r)$, however, the obtained $g_{+-}(r)$ is semi-quantitatively close to the simulated one, as shown in figure 4.

7. Inverse dielectric function obtained from experimental $S_{\nu\mu}(q)$

In this section, we will show $1/\varepsilon(q)$ of molten RbBr, using the experimental partial structure factors. The experimental data for $S_{\nu\mu}(q)$ are adopted from the article of Saito *et al.* [7] In figures 5 and 6, the experimentally obtained $S_{zz}(q)$ and the corresponding $1/\varepsilon(q)$ are shown. As seen in these figures, the larger $S_{zz}(q)$ rather than unity yields a relatively small quantity for $1/\varepsilon(q)$. This fact is physically plausible, because a large charge fluctuation at the position of r around a centered ion located at the origin indicates a larger distribution of ions of opposite sign at r, which naturally causes a large screening in comparison with that of an averaged distribution of ions.

Using the available repulsive potential for molten RbBr [7], we have calculated the screened potential for this molten salt, by putting the appropriate $1/\varepsilon(q)$ into equation (33b). The results are shown in figures 7 and 8 under the condition of $\alpha = 1$. As seen in figure 7, the screened inter-ionic potential between Rb^+ and Br^- ions, $\phi^{+-}_{\text{screened}}(r)$ has a deeper minimum in comparison with the potential of mean force, $U^{+-}(r)$, contrasting with the tendency of molten NaCl starting from the partial structure factors obtained by MD simulation. The most likely reason for this discrepancy seems to be an experimental uncertainty for the partial structure factors in their small-q regions. This uncertainty gives, in due course, a numerical error in the inverse dielectric function $1/\varepsilon(q)$ in the very small-q region, even though its magnitude is relatively small. On Fourier transformation, such a small uncertainty gives a remarkably large change in the screened

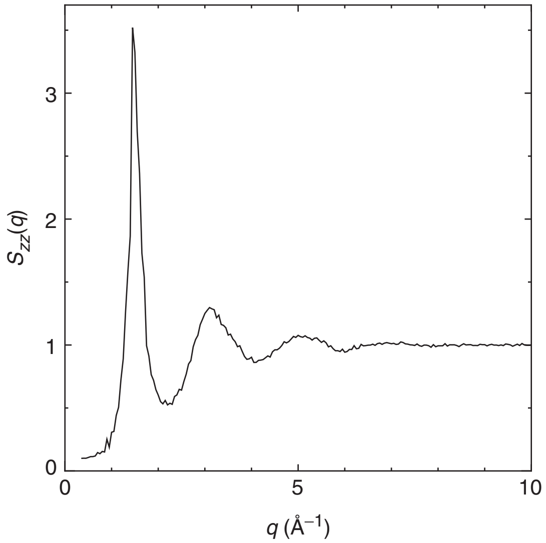

Figure 5. Experimental $S_{zz}(q)$ of molten RbBr.

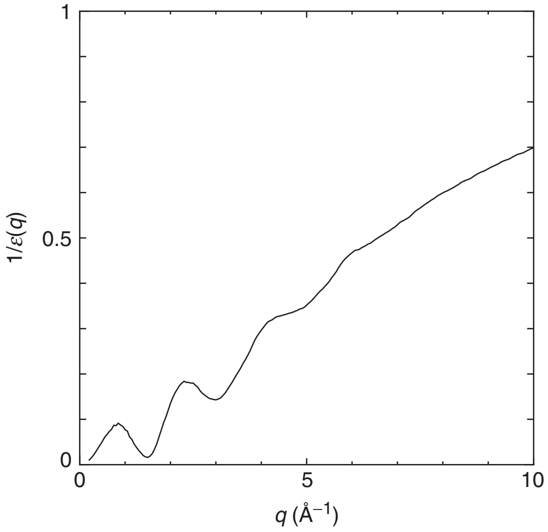

Figure 6. $1/\varepsilon(q)$ of molten RbBr.

inter-ionic potential. In fact, an artificial modification for the curve of $1/\varepsilon(q)$ in only the small-q region makes it possible to obtain a result similar to $U^{+-}(r)$.

8. Deviation from Nernst–Einstein relation

In this section, we wish to deal with a practical application of the potential of mean force $U^{+-}(r)$ in molten salts. The deviation, Δ, from the Nernst–Einstein relation in

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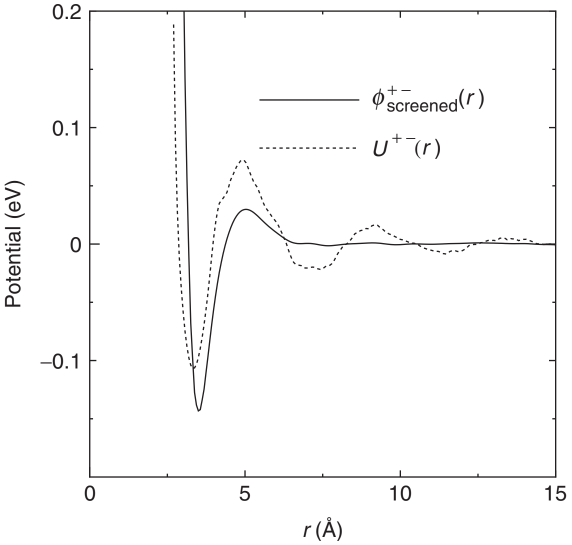

Figure 7. Screened inter-ionic potential between Rb^+ and Br^- ions, $\phi^{+-}_{\text{screened}}(r)$ and $U^{+-}(r)\{= -k_\text{B}T \ln\ g_{+-}(r)\}$ in molten RbBr, and corresponding partial pair distribution functions.

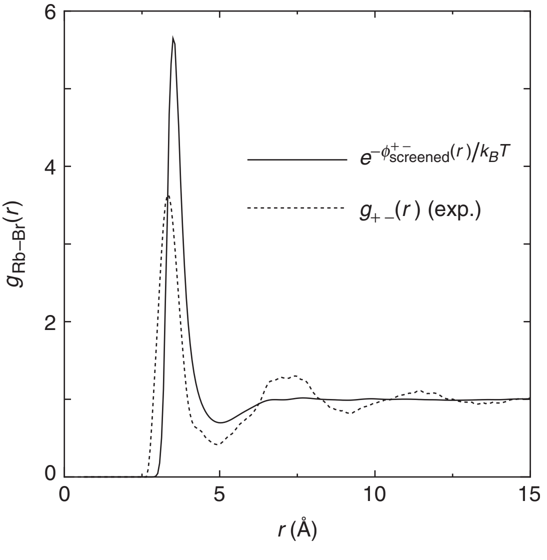

Figure 8. Pair distribution function $g_{+-}(r)$ and corresponding function of $\exp\{-\phi^{+-}_{\text{screened}}(r)/k_\text{B}T\}$ of molten RbBr.

monovalent molten salts, Δ is defined as follows,

$$\sigma = \sigma^+ + \sigma^- = \frac{n_0 e^2}{k_B T}(D^+ + D^-)(1 - \Delta) \tag{46}$$

The partial conductivities for cation and anion, σ^+ and σ^-, and the diffusion constants D^+ and D^- were already derived as before [13]. Taking these results, we have

$$\Delta = 1 - (1 - \Delta_{\mathrm{BR}})\frac{2/\alpha^0}{(1/\alpha^+) + (1/\alpha^-)} \tag{47}$$

where

$$\alpha^0 = n_0 \int_0^\infty \left(\frac{\partial^2 \phi^{+-}}{\partial r^2} + \frac{2}{r}\frac{\partial \phi^{+-}}{\partial r}\right) g_{+-}(r) 4\pi r^2 \mathrm{d}r \tag{48}$$

$$\alpha^+ = n_0/2 \int_0^\infty \left[\left\{\frac{\partial^2 \phi^{++}}{\partial r^2} + \frac{2}{r}\frac{\partial \phi^{++}}{\partial r}\right\} g_{++}(r) + 2\left\{\frac{\partial^2 \phi^{+-}}{\partial r^2} + \frac{2}{r}\frac{\partial \phi^{+-}}{\partial r}\right\} g_{+-}(r)\right] 4\pi r^2 \,\mathrm{d}r \tag{49}$$

$$\alpha^- = n_0/2 \int_0^\infty \left[\left\{\frac{\partial^2 \phi^{--}}{\partial r^2} + \frac{2}{r}\frac{\partial \phi^{--}}{\partial r}\right\} g_{--}(r) + 2\left\{\frac{\partial^2 \phi^{+-}}{\partial r^2} + \frac{2}{r}\frac{\partial \phi^{+-}}{\partial r}\right\} g_{+-}(r)\right] 4\pi r^2 \,\mathrm{d}r \tag{50}$$

and

$$\Delta_{\mathrm{BR}} = \frac{4\pi n_0}{3k_B T}\int_d^\infty \frac{\partial \phi^{+-}(r)}{\partial r} g_{+-}(r) r^3 \mathrm{d}r \tag{51}$$

where $\phi^{ij}(r)$ is an effective inter-ionic potential between ions i and j. $g_{ij}(r)$ is the partial pair distribution function between ions i and j as defined in the preceding section. In this equation, we can approximate that d is equal to the hard-core contact distance between cation and anion, if both ionic sizes are rigid. However, its assumption may not be always valid, on going to heavier atomic weight. Here, we will use the first maximum position of $g_{+-}(r)$ as the distance of ionic contact. The quantity Δ_{BR} is essentially caused by an asymmetric distribution of the surrounded ions around the centered ion under an applied external field; it was obtained by Berne and Rice [14], and recently certified by the present authors in a different way [13]. Since it was 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 Nernst–Einstein relation in a molten salt. The effective potential $\phi^{+-}(r)$ shown in (51) is equal to the potential of mean force acting on the ion at the origin from another ion of opposite sign located at the distance r, and therefore, it is possible to use the potential of mean force $U^{+-}(r)$ instead of $\phi^{+-}(r)$. Therefore, equation (51) is converted to,

$$\Delta_{\mathrm{BR}} = \frac{4\pi n_0}{3k_B T}\int_d^\infty \frac{\partial U^{+-}(r)}{\partial r} g_{+-}(r) r^3 \mathrm{d}r = -\frac{4\pi n_0}{3}\int_d^\infty \frac{\partial g_{+-}(r)}{\partial r} r^3 \mathrm{d}r \tag{52}$$

We can basically calculate the deviation Δ_{BR} from the Nernst–Einstein relation, by using (52), if the partial pair distribution function is experimentally obtained. However, because of the presence of the r^3 term in the integrand, convergence at large r is slow and full information on the approach of $g_{+-}(r)$ to unity is necessary. At the present stage, $g_{+-}(r)$'s in molten salts being satisfactory this requirement seem to be rare.

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9. Conclusion

In this article, we have newly revised a theory of dielectric function in molten salts. It is concluded that the screened inter-ionic potential between Na^+ and Cl^- ions in molten NaCl, carried out in the present procedure, seems to be equivalent to the so-called potential of mean force. Also the experimentally obtained screened potential in molten RbBr agrees semi-quantitatively with the potential of mean force obtained from $g_{+-}(r)$, within the order of magnitude.

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Appendix A: an inductive derivation of equation (16)

Consider a simple liquid of density ρ. The variation of single particle density $\Delta\rho^{(1)}(\boldsymbol{r}_1)$ at the position $\boldsymbol{r}_1$ caused by an external field $\Delta\phi(\boldsymbol{r}_1)$ and by surrounding particle 2 located at $\boldsymbol{r}_2$ is expressed in Yvon equation from [1],

$$\Delta\rho^{(1)}(\boldsymbol{r}_1) = -\beta\rho\Delta\phi(\boldsymbol{r}_1) - \beta\rho^2 \int h(\boldsymbol{r}_1, \boldsymbol{r}_2)\Delta\phi(\boldsymbol{r}_1)\,\mathrm{d}\boldsymbol{r}_2 \tag{A1}$$

where $h(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the pair correlation function defined by $h(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \{g(\boldsymbol{r}_1, \boldsymbol{r}_2) - 1\}$. Taking the Fourier transformation for (A1), we have

$$\begin{aligned}\Delta\underline{\rho}^{(1)}(\boldsymbol{q}) &= -\beta\rho\Delta\underline{\phi}(\boldsymbol{q}) - \beta\rho^2\underline{h}(\boldsymbol{q})\Delta\underline{\phi}(\boldsymbol{q}) \\ &= -[1 + \rho\underline{h}(q)]\beta\rho\Delta\underline{\phi}(\boldsymbol{q})\end{aligned} \tag{A2}$$

The corresponding Yvon equation for pair correlation function is expressed as,

$$\rho h(\boldsymbol{r}_0, \boldsymbol{r}_1) = -\beta\rho\phi(\boldsymbol{r}_0, \boldsymbol{r}_1) - \beta\rho^2 \int h(\boldsymbol{r}_1, \boldsymbol{r}_2)\phi(\boldsymbol{r}_0, \boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_2 \tag{A3}$$

where $\phi(\boldsymbol{r}_i, \boldsymbol{r}_j)$ means the interacting potential between the particles i and j. By Fourier transformation, equation (A3) is converted to the following form,

$$\Delta\rho^{(1)} = \rho h(q) = -[1 + \rho h(q)]\beta\rho\phi(q) \tag{A4}$$

It is emphasized that the function $[1 + \rho h(q)]$ oscillates around unity as a function of q. Let us now consider the molten salt discussed in the present article. If we put a cation at the position $\boldsymbol{r}_0$ and put anions at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, then the above function $[1 + \rho h(q)]$ is converted to $S_{zz}(q)$ which also oscillates around unity corresponding to the function $[1 + \rho h(q)]q$, and in addition, ρ is also converted to n_0 because the FT component of charge fluctuation is equal to $n_0 h_{+-}(q)$. Therefore, we have

$$n_0 h_{+-}(q) = -S_{zz}(q)\beta n_0 \phi^{+-}(q) = \chi_{zz}(q)\phi^{+-}(q) \tag{A5}$$

where

$$\chi_{zz}(q) = -\beta n_0 S_{zz}(q) \tag{A6}$$

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