



An analytical longitudinal dielectric function of primitive electrolyte solutions and its application in predicting thermodynamic properties



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ABSTRACT

In this paper, the longitudinal dielectric function $\epsilon_l(k)$ of primitive electrolyte solutions is discussed. Starting from a modified mean spherical approximation, an analytical dielectric function in terms of two parameters is established. These two parameters can be related to the first two decay parameters $k_{1,2}$ of the dielectric response modes of the bulk system, and can be determined using constraints of $k_{1,2}$ from statistical theories. Furthermore, a combination of this dielectric function and the molecular Debye-Hückel theory [J. Chem. Phys. 135(2011)104104] leads to a self-consistent mean field description of electrolyte solutions. Our theory reveals a relationship between the microscopic structure parameters of electrolyte solutions and the macroscopic thermodynamic properties, which is applied to concentrated electrolyte solutions.

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1. Introduction

The longitudinal dielectric function $\epsilon_l(k)$ of an isotropic solution is the wave-number-dependent longitudinal component of the wave-vector-dependent static dielectric tensor $\epsilon_{\alpha\beta}(\mathbf{k})$, which describes the charge response of a bulk system to an external electric potential [1,2]. This dielectric function has important applications in solvation processes [3–5], in electron transfer processes [6–9], in physics of electrostatic absorption [10–13], and in ionic criticality [14,15]. $\epsilon_l(k)$ can be evaluated experimentally or theoretically, however, and in most cases only numerical values of $\epsilon_l(k)$ are available. So a suitable model of the dielectric function would not only provide a reasonable fitting function of $\epsilon_l(k)$, but would also be a good starting point to study Coulomb-interaction-related phenomena.

For polar fluids, the simplest model of $\epsilon_l(k)$ is to take $\epsilon_l(k) = \epsilon_s$ with ϵ_s the bulk dielectric constant, where the k -dependence is neglected as in the Born model of solvation [16–18]. Later studies reveals the existence of dramatic k -dependence of $\epsilon_l(k)$, that is, the dielectric function becomes negative in certain region of k [19,20], so more sophisticated models are proposed to capture such features. For example, a phenomenological Landau Hamiltonian which contains two independent polarization modes, is used

to derive an analytical expression of $\epsilon_l(k)$ for polar fluids [21,22]. This theory can well explain the main feature of dielectric function from experiments or from molecular dynamics simulations, and has been successfully applied to polar fluids such as water, acetonitrile and dimethyl [23]. It is also possible to build $\epsilon_l(k)$ with other number of polarization modes, and the interested readers can refer to Ref [24] for a comprehensive review.

For electrolyte solutions, an expression of the dielectric function $\epsilon_s/\epsilon_l(k) = \frac{k_D^2}{k_D^2 + k^2}$ can be found from the Debye-Hückel (DH) theory [25], which describes the dielectric response by a linearized Poisson-Boltzmann equation as $\nabla^2\phi(r) = k_D^2\phi(r)$, with $\phi(r) = \frac{q}{\epsilon_s} \frac{e^{-k_D r}}{r}$ a Yukawa electric potential and k_D the inverse Debye length that related to the ionic strength [26]. However, such a dielectric function is only valid for dilute solution, and is not suitable for concentrated electrolytes. Another systematic way to derive analytical expressions for $\epsilon_l(k)$ is to use analytical radial distribution function $g_{ij}(r)$ from the integral equation theory, such as the mean spherical approximation (MSA) and its extensions [2,27,28]. In our previous studies on electron transfer processes in electrolyte solutions, a half empirical analytical functional has been used to fit the numerical $\epsilon_l(k)$ calculated from Hypernetted chain (HNC) theory or molecular dynamics simulations [8,9].

In this study we demonstrate that the empirical function used in our previous studies can be derived from rigorous microscopic statistical theory of liquids. The correlation function $h_{ij}(r) = g_{ij}(r) - 1$ and the direct correlation function $c_{ij}(r)$ are two important concepts

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in the theory of simple liquids, and are related to each other via the Ornstein-Zernike(OZ) equation [2]. Furthermore, the OZ equation combined with a suitable closure of $c_{ij}(r)$ can be used to find the correlation function $h_{ij}(r)$. Our strategy is to use a modified mean spherical approximation as the closure of $c_{ij}(r)$, where the asymmetric part of $c_{ij}(r)$ inside the core domain is a linear function of r , from which $g_{ij}(r)$ and hence the longitudinal dielectric function $\epsilon_l(k)$ can be evaluated analytically. This $\epsilon_l(k)$ has two parameters which can be related to the first two decay parameters $k_{1,2}$ of the dielectric response modes of the bulk solutions. Using analytical constraints on $k_{1,2}$ from various statistical theories, actually we find a family of analytical dielectric function. Furthermore, this dielectric function is combined with our molecular Debye-Hückel(MDH) theory [25] to give a mean field description of the electrolyte solutions, where the dielectric response is characterized by a linear combination of DH-like response modes, and another analytical expression of dielectric function is derived. Our study establishes a relationship between the microscopic structure parameters such as the first two decay parameters $k_{1,2}$ and the thermodynamic properties of an electrolyte solution. Our strategy is applied to primitive model of electrolyte solutions, and the validity is tested for the thermodynamic properties.

This article is organized as following: in section 2 an analytical expression for $\epsilon_l(k)$ of an electrolyte solution is built from a modified mean spherical approximation, in section 3 the MDH theory of electrolyte solutions on the basis of $\epsilon_l(k)$ is introduced. Application to concentrated electrolyte solutions is shown in section 4. Finally a brief conclusion is drawn in section 5.

2. The static longitudinal dielectric function $\epsilon_l(k)$ from a modified mean spherical approximation

In this section, we will show how to derive an analytical $\epsilon_l(k)$ of electrolyte solutions based on a modified mean spherical approximation(MMSA).

Consider a restricted primitive model of electrolyte solutions. Ions are immersed in a continuum with bulk dielectric constant ϵ_s , the reduced temperature is $\beta = 1/k_B T$, e is the element charge and $Z_j = q_j/e$ is the charge number of the j -th ion. The particle number density of the i -th species is n_i , so $n = \sum_i n_i$ is the total number density, and $x_i = n_i/n$ is the molar fraction of i -th type particle. The interaction potential between two ions is $u_{ij}(r) = u_{ij}^s(r) + \frac{q_i q_j}{\epsilon_s r}$, with $u_{ij}^s(r)$ a hard sphere potential such that $u_{ij}^s(r) = \infty$, $r \leq \sigma_{ij}$ and $u_{ij}^s(r) = 0$, $r > \sigma_{ij}$. The cations and anions have the same diameter and opposite charges such that $\sigma_{++} = \sigma_{--} = \sigma_{+-} = \sigma_{-+} = \sigma$, $q_+ = -q_- = q = Ze$, where $+$ and $-$ denotes the cation and anion species, respectively.

According to statistical theory of simple liquids, the microscopic structure of a liquid can be described by the correlation function $h_{ij}(r) = g_{ij}(r) - 1$ or the direct correlation function $c_{ij}(r)$, and it is known that $h_{ij}(r)$ and $c_{ij}(r)$ are related to each other via the Ornstein-Zernike(OZ) equation [2]. We will use the MMSA closure combined with the OZ equation to find $h_{ij}(r)$ of an electrolyte solution, and the details are as following.

Due to the symmetry of the system, one can split the correlation function $h_{ij}(r)$ and the direct correlation function $c_{ij}(r)$ into a symmetric part and an asymmetric part [27], that is

$$h_{++}(r) = h_{--}(r) = h_s(r) + h_a(r), \quad (1)$$

$$h_{+-}(r) = h_{-+}(r) = h_s(r) - h_a(r), \quad (2)$$

$$c_{++}(r) = c_{--}(r) = c_s(r) + c_a(r), \quad (3)$$

$$c_{+-}(r) = c_{-+}(r) = c_s(r) - c_a(r), \quad (4)$$

Hereafter we denote $f_{ij}(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} f_{ij}(r) = \int_0^\infty f_{ij}(r) 4\pi \frac{\sin(kr)}{kr} r^2 dr$ as the three dimensional Fourier transform of $f_{ij}(r)$ with $f_{ij}(r) = h_{ij}(r)$ and $c_{ij}(r)$. The symmetric part $c_s(r)$ can be evaluated from the Percus-Yevick theory of hard sphere fluids as [2]

$$c_s(r) = -t_1 - 6\eta t_2 \left(\frac{r}{\sigma}\right) - \frac{\eta t_1}{2} \left(\frac{r}{\sigma}\right)^3, \quad r \leq \sigma \quad (5)$$

$$c_s(r) = 0, \quad r > \sigma \quad (6)$$

with $t_1 = \frac{(1-2\eta)^2}{(1-\eta)^4}$, $t_2 = -\frac{(2+\eta)^2}{4(1-\eta)^4}$, and $\eta = \frac{\pi}{6} n \sigma^3$ is the packing fraction of the electrolytes. This analytical $c_s(r)$ can be used to evaluate the symmetric part of the correlation function $h_s(r)$ based on the OZ equation $[1 + nh_s(k)][1 - nc_s(k)] = 1$. A modified mean spherical approximation is proposed to evaluate the asymmetric part $c_a(r)$, such that

$$c_a(r) = a + br, \quad r \leq \sigma \quad (7)$$

$$c_a(r) = -\frac{\beta Z^2 e^2}{\epsilon_s r}, \quad r > \sigma. \quad (8)$$

The Fourier transformation of $c_a(r)$ reads

$$\begin{aligned} c_a(k) &= \int_0^\infty dr 4\pi r^2 \frac{\sin(kr)}{kr} c_a(r) \\ &= \frac{\text{Cos}(k\sigma)(a_1 k^2 - a_2) + k \text{Sin}(k\sigma) a_3 + a_2}{k^4 n}, \end{aligned} \quad (9)$$

with $a_1 = 4\pi a \sigma n - 4\pi b n \sigma^2 - k_D^2$, $a_2 = -8\pi b n$ and $a_3 = 8\pi b \sigma n - 4\pi a n$.

From now on we show how to evaluate $\epsilon_l(k)$ with $c_a(k)$. The static charge structure factor $S_{zz}(k)$ of the bulk system can be evaluated as [2]

$$S_{zz}(k) = \sum_i Z_i^2 x_i + n \sum_{i,j} Z_i Z_j x_i x_j h_{ij}(k), \quad (10)$$

with $h_{ij}(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} h_{ij}(r)$ the Fourier transform of $h_{ij}(r)$. One can evaluate $h_a(k)$ using the OZ equation $[1 + nh_a(k)][1 - nc_a(k)] = 1$, and then $S_{zz}(k)$ reads

$$S_{zz}(k) = Z^2 (1 + nh_a(k)) = \frac{Z^2}{1 - nc_a(k)}. \quad (11)$$

According to the linear response theory in ionic fluids [2], the bulk dielectric function $\epsilon_l(k)$ is related to the static charge structure factor as

$$\frac{\epsilon_s}{\epsilon_l(k)} = 1 - \frac{4\pi \beta n e^2}{\epsilon_s k^2} S_{zz}(k), \quad (12)$$

and then a response function defined as $\chi(k) \equiv 1 - \frac{\epsilon_s}{\epsilon_l(k)}$ can be evaluated as

$$\chi(k) = \frac{4\pi \beta n e^2}{\epsilon_0 k^2} S_{zz}(k). \quad (13)$$

Combine Eq.(9), Eq.(10) and Eq.(13), the response function $\chi(k)$ is found to be

$$\chi(k) = \frac{k_D^2 k^2}{k^4 - (a_1 k^2 - a_2) \text{Cos}(k\sigma) - a_3 k \text{Sin}(k\sigma) - a_2}. \quad (14)$$

Eq.(14) represents a family of dielectric function with various control parameters, and is our key result. As one can see, this equation can be taken as a justification for the empirical fitting function used in our previous studies [8,9].

It is well known that the mean electrostatic potential $\phi(r)$ of an ion immersed in an electrolyte solution satisfies an asymptotic behavior as $\phi(r) \sim \sum_l \alpha_l \frac{e^{-k_l r}}{r}$, with k_l a decay parameter of the l -th Yukawa potential [29–32]. The decay parameters k_l can be

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