Analysis of Generalized Debye-Hückel Equation from Poisson-Fermi Theory

Chin-Lung Li

Institute of Computational and Modeling Science,
National Tsing Hua University, Hsinchu 300,
Taiwan. E-mail: chinlungli@mail.nd.nthu.edu.tw

Jinn-Liang Liu

Corresponding author. Institute of Computational and Modeling Science,
National Tsing Hua University, Hsinchu 300,
Taiwan. E-mail: jliu@mx.nthu.edu.tw

(Dated: November 6, 2018)

Abstract. The Debye-Hückel equation is a fundamental physical model in chemical thermodynamics that describes the free energy (chemical potential, activity) of an ion in electrolyte solutions at variable salt concentration, temperature, and pressure. It is based on the linear Poisson-Boltzmann equation that ignores the steric (finite size), correlation, and polarization effects of ions and water (or solvent molecules). The Poisson-Fermi theory developed in recent years takes these effects into account. A new Debye-Hückel equation is derived from the Poisson-Fermi theory and is shown to consistently reduce to the classical equation when these effects vanish in limiting cases. As a result, a linear fourth-order Poisson-Fermi equation is presented for which unique solutions are shown to exist for spherically symmetric systems. Moreover, a generalized Debye length is proposed to include the size effects of ions and water. Numerical results produced by the generalized Debye-Hückel equation, which is also analytical (algebraic), are shown to agree with experimental data on the individual activity coefficients of eight 1:1 and six 2:1 electrolytes with only three adjustable parameters. By contrast, the existing extended (classical) Debye-Hückel equations such as the Pitzer equations can have several to tens of thousands of empirical parameters due to explosive combinations of wide ranges of composition, temperature, and pressure.
1. INTRODUCTION

Thermodynamic modeling of aqueous electrolyte solutions plays a fundamental role in chemical and biological sciences and engineering [1, 9, 10, 17, 19, 20, 22, 24, 35, 37, 39, 40, 45, 46]. Despite intense efforts in the past century, robust thermodynamic modeling of electrolyte solutions still remains a remote ambition [40] in the extended models from the classical Debye-Hückel (DH) theory due to the enormous number of parameters that need to be adjusted, carefully and often subjectively [12, 20, 40, 46]. For example, the Pitzer model requires 8 parameters for a ternary system and up to 8 temperature coefficients (parameters) for every Pitzer parameter in a temperature interval from 0 to about 200 °C [40, 46]. It is indeed a frustrating despair (frustration on p. 11 in [22] and despair on p. 301 in [39]) that approximately 22,000 parameters for combinatorial solutions of the most important 28 cations and 16 anions in salt chemistry have to be extracted from the available experimental data for one temperature [46]. The Pitzer model is still the most widely used DH model with unmatched precision for modeling aqueous electrolyte solutions over wide ranges of composition, temperature, and pressure [40].

The Debye-Hückel theory [8] is based on a linearization of the nonlinear Poisson-Boltzmann (PB) equation that was developed by Gouy [15] and Chapman [6] in early 1910s and ignores the steric (finite size), correlation, and polarization effects of ions and water. However, tremendous technological advances of experimental tools in modern sciences render physical details of biological and chemical systems at atomic scale [4, 16] for which these effects can no longer be ignored for modeling electrolyte solutions in numerous applications [1, 9, 10, 20]. The Poisson-Fermi (PF) theory developed in recent years takes these effects into account and has been shown to illustrate the importance of these effects in a range of areas from electric double layers [2, 26, 34] and ion activities [31, 32] to biological ion channels [26, 28, 30, 33, 34].

Based on the numerical PF model developed in [31, 32], we derive, analyze, and verify a generalized DH equation from the PF model to account for these three effects. The PF model is a fourth-order nonlinear partial differential equation (PDE), where the fourth-order term describes the correlation effect of ions and the polarization effect of water molecules both in a mean-field approximation. The finite-size (steric) effect of all particles (ions and water treated as non-uniform spheres) is described by a steric potential that is defined by a
void fraction function in the solvent domain, i.e., the voids between spheres are expressed as a function that varies in the domain with the variation of electric potential if the solvent domain is subject to external electric fields. The steric potential can be considered as a mean-field approximation of the Lennard-Jones (L-J) potential between any pair of ions and water molecules, which describes the net inter-molecular force and thus defines the distance (voidness) between the pair. L-J potentials are highly oscillatory and hence not suitable for mean-field calculations due to approximation and convergence issues [26, 30].

The main results of the present work are summarized as follows: (i) A fourth-order lineal PF equation is presented for which we show that unique solutions exist for spherical symmetric systems such as the ionic activity model considered here. (ii) A generalized Debye length — a measure of how far the electrostatic effect of an ion in solution persists [8] — is proposed to include the size effects of ions and water molecules, which have been ignored in the classical Debye length. (iii) A correlation length [25] — a measure of how strongly correlations between ions develop [2, 42] and how easily water molecules in electrolyte solutions are polarized in response to an electric field [26, 28, 30] — is shown to be a non-empirical parameter (in contrast to empirical ones in [2, 26, 28, 30, 42]) that depends not only on the salt concentration but also on the sizes of ions and water (in contrast to that of size independence in [25]). (iv) The generalized DH equation and Debye length are shown to reduce to their classical versions when the steric and correlation effects are ignored. (v) The generalized DH equation — an equation that describes how electrolyte solutions behave differently from ideality — is shown to fit experimental data [48] of single ion activities of eight 1:1 and six 2:1 electrolytes with only three adjustable parameters in contrast to that of the Pitzer model. The numerical results produced by the generalized DH equation is purely algebraic in contrast to those in [31, 32] by numerical PDEs. The analytical DH formula with the same parameters can also be easily used to calculate mean activity coefficients of electrolytes in mixture or at variable temperature [32].

The remaining of the paper is organized as follows. The Poisson-Fermi theory is briefly described in Section 2 from which we give a detailed derivation and analysis of the generalized Debye-Hückel equation in Section 3. The derivation is based on a linear Poisson-Fermi equation in Section 3.1, which is a fourth-order PDE and is transformed to two second-order PDEs in Section 3.2 for which general solutions are found for spherical symmetric systems. In Section 3.3, a unique solution is found for the second-order PDEs in a specific
domain that consists of effective Born, hydration shell, and solvent spherical subdomains for modeling the solvation energy of an ion in general binary electrolytes. We present a full set of interface and boundary conditions for these two PDEs on which the unique potential solution is derived. This electrostatic potential accounts for correlation, steric, polarization, and hydration effects that are absent in the classical DH theory. It also leads to a generalized DH equation in Section 3.4 for algebraically calculating individual or mean activity coefficients of binary electrolytes. In Section 3.4, we show that the generalized equation consistently reduces to the classical DH equation when these effects are ignored. Moreover, asymptotic analyses of the linear PF equation (Section 3.2) and the generalized DH equation (Section 3.4) are also given as the generalized Debye length tends to infinite (or equivalently the salt concentration tends to zero) for infinite dilute electrolytes, the correlation length tends to zero (without correlations), or the volumes of ions and water tend to zero (without size effects). In Section 4, numerical results by the generalized DH model and an extended DH model by Hückel [18] are given to compare with the experimental data in [48] and to show different properties between these two models. Some concluding remarks of this work are made in Section 5.

2. POISSON-FERMI THEORY

For an aqueous electrolyte system with $K$ species of ions, the entropy model proposed in [28, 34] treats all ions and water of any diameter as nonuniform hard spheres, and regards the water as the $(K+1)^{th}$ species and the voids between these hard spheres as the $(K+2)^{th}$ species. The total volume $V$ of the system can be calculated exactly by the identity

$$ V = \sum_{i=1}^{K+1} v_i N_i + V_{K+2}, $$

where $v_i = 4\pi a_i^3/3$ with radius $a_i$, $N_i$ is the total number of the $i^{th}$ species particles, and $V_{K+2}$ denotes the total volume of all the voids. In the bulk solution, we have the bulk concentrations $C_i^B = \frac{N_i}{V}$ and the bulk volume fraction of voids $\Gamma^B = \frac{V_{K+2}}{V}$. Dividing the volume identity by $V$, $\Gamma^B = 1 - \sum_{i=1}^{K+1} v_i C_i^B$ is expressed in terms of nonuniform $v_i$ and $C_i^B$ for all particle species. If the system is spatially inhomogeneous with variable electric or steric fields, as in realistic biological and chemical systems, the bulk concentrations then change to concentration functions $C_i(r)$ that vary with positions, and differ from their constant values
$C_i^B$ at location $r$ in the solvent domain $\Omega_s$. Consequently, the void volume fraction becomes a function $\Gamma(r) = 1 - \sum_{i=1}^{K+1} v_i C_i(r)$ as well.

It is shown in [28, 34] that the distribution (concentration) of particles in $\Omega_s$ is of Fermi-like type

$$C_i(r) = C_i^B \exp \left( -\beta_i \phi(r) + \frac{v_i}{v_0} S^{\text{trc}}(r) \right), \quad S^{\text{trc}}(r) = \ln \left( \frac{\Gamma(r)}{\Gamma_B} \right),$$

since it saturates, i.e., $C_i(r) < \frac{1}{v_i}$ for any arbitrary (or even infinite) electric potential $\phi(r)$ at any location $r \in \Omega_s$ for all $i = 1, \cdots, K + 1$ (ions and water), where $\beta_i = q_i/k_BT$ with $q_i$ being the charge on species $i$ particles and $q_{K+1} = 0$, $k_B$ is the Boltzmann constant, $T$ is an absolute temperature, and $v_0 = \left( \sum_{i=1}^{K+1} v_i \right)/(K + 1)$ an average volume. The steric potential $S^{\text{trc}}(r)$ first proposed in [26] is an entropic measure of crowding or emptiness of particles at $r$. If $\phi(r) = 0$ for all $r$, then $\Gamma(r) = \Gamma_B$ and hence $S^{\text{trc}}(r) = 0$. The factor $v_i/v_0$ in (2) shows that the steric energy $\frac{v_i}{v_0} S^{\text{trc}}(r) k_B T$ of a type $i$ particle at $r$ depends not only on the steric potential $S^{\text{trc}}(r)$ but also on its volume $v_i$ similar to the electric energy $\beta_i \phi(r) k_B T$ that depends on both the electric potential $\phi(r)$ and its charge $q_i$. The steric potential is a mean-field approximation of Lennard-Jones (L-J) potentials that describe local variations of L-J distances (and thus empty voids) between every pair of particles. L-J potentials are highly oscillatory and extremely expensive and unstable to compute numerically.

A nonlocal electrostatic formulation of ions and water is proposed in [34] to describe the correlation effect of ions and the polarization effect of polar water. The formulation yields the following fourth-order Poisson-Fermi equation [42]

$$\epsilon_s \left( l_c^2 \nabla^2 - 1 \right) \nabla^2 \phi(r) = \rho(r), \quad r \in \Omega_s,$$

where $\epsilon_s = \epsilon_w \epsilon_0$, $\epsilon_w$ is the dielectric constant of bulk water, $\epsilon_0$ is the vacuum permittivity, $l_c = \sqrt{l_B l_D/48}$ is a density-density correlation length independent of specific ionic radius [25], $l_B$ and $l_D$ are the Bjerrum and Debye lengths, respectively, $\nabla$ is the gradient operator in $\mathbb{R}^3$, $\nabla^2 = \nabla \cdot \nabla$, and $\rho(r) = \sum_{i=1}^K q_i C_i(r)$ is ionic charge density. It is shown in [34] that the fourth-order PF equation (3) reduces to the classical second-order PB equation when $l_c = v_i = 0$ for all $i$, i.e., the correlation, steric, and polarization effects are ignored. Eq. (3) was first proposed in [42] (with $v_i = 0$ for all $i$) and subsequently derived in [2, 34] (with $v_i \neq 0$) from different perspectives of electrostatics.
3. DERIVATION AND ANALYSIS OF GENERALIZED DEBYE-HÜCKEL EQUATION

3.1. Linear Poisson-Fermi Equation

For simplicity, we consider a general binary \((K = 2)\) electrolyte \(C_{z_1}A_{z_2}\) with the valences of the cation \(C^{z_1+}\) and anion \(A^{z_2-}\) being \(z_1\) and \(z_2\), respectively. In the bulk situation \((\phi(r) = S^{trc}(r) = 0)\), the charge neutrality condition \(q_1N_1 + q_2N_2 = 0\) of the system implies that

\[
\beta_2 = \frac{q_2}{k_B T} = \frac{-N_1 q_1}{N_2 k_B T} = \frac{-N_1}{N_2} \beta_1 = \frac{-C_1^B}{C_2^B} \beta_1,
\]

\[
C_2^B = \frac{N_2}{V} = \frac{-q_1 N_1}{q_2 V} = \frac{-q_1 C_1^B}{q_2},
\]

and hence

\[
\epsilon_s \left( l^2 \nabla^2 - 1 \right) \nabla^2 \phi(r) = q_1 C_1(r) + q_2 C_2(r) = q_1 \left[ C_1(r) - \frac{C_1^B}{C_2^B} C_2(r) \right]. \quad (4)
\]

Since

\[
C_i(r) = C_i^B \exp \left( -\beta_i \phi(r) \right) \left( \frac{\Gamma(r)}{\Gamma^B} \right)^{\frac{\nu_i}{\nu_0}}, \quad i = 1, 2,
\]

\[
C_3(r) = C_3^B \left( \frac{\Gamma(r)}{\Gamma^B} \right)^{\frac{\nu_3}{\nu_0}},
\]

we obtain

\[
\frac{\Gamma(r)}{\Gamma^B} = \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\nu_3}{\nu_0}} \left( \frac{C_3^B}{C_3^B} \right)^{\frac{\nu_0}{\nu_3}}, \quad (5)
\]

\[
C_i(r) = C_i^B \exp \left( -\beta_i \phi(r) \right) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\nu_i}{\nu_3}}. \quad (6)
\]

Substituting Eq. (6) into (5) yields

\[
\left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\nu_3}{\nu_0}} = \frac{1 - \nu_1 C_1^B \exp \left( -\beta_1 \phi(r) \right) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\nu_1}{\nu_3}}}{\Gamma^B} - \frac{\nu_2 C_2^B \exp \left( -\beta_2 \phi(r) \right) \left( \frac{C_3^B}{C_3^B} \right)^{\frac{\nu_2}{\nu_3}} + \nu_3 C_3(r)}{\Gamma^B}. \quad (7)
\]

Assuming that the functional \(C_3(\phi(r)) = C_3(r)\) can be expressed by Taylor’s formula

\[
C_3(r) = b_0 + b_1 \phi(r) + O(\phi^2(r)), \quad (8)
\]
we then have

\[
\left( \frac{C_3(r)}{C_3^B} \right)^\alpha = \left( \frac{b_0}{C_3^B} \right)^\alpha + \alpha \left( \frac{b_1}{C_3^B} \right) \left( \frac{b_0}{C_3^B} \right)^{\alpha-1} \phi(r) + O(\phi^2(r))
\]

\[
= \left( \frac{b_0}{C_3^B} \right)^\alpha + \alpha \left( \frac{b_1}{b_0} \right) \left( \frac{b_0}{C_3^B} \right)^\alpha \phi(r) + O(\phi^2(r)) \quad \text{for } \alpha \geq 0.
\]

Consequently, the left hand side of Eq. (7) can be written as

\[
\left( \frac{C_3(r)}{C_3^B} \right)^{\frac{a_0}{\nu_3}} = \left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} + \frac{v_0 b_1}{v_3 b_0} \left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} \phi(r) + O(\phi^2(r))
\]

(10)

and the right hand side gives

\[
1 - v_1 C_1^B \exp(-\beta_1 \phi(r)) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{a_1}{\nu_3}} - v_2 C_2^B \exp(-\beta_2 \phi(r)) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{a_2}{\nu_3}} - v_3 C_3(r)
\]

\[
= 1 - v_1 C_1^B \left( 1 - \beta_1 \phi(r) + O(\phi^2(r)) \right) \left[ \left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} + \frac{v_0 b_1}{v_3 b_0} \left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} \phi(r) + O(\phi^2(r)) \right]
\]

\[
- \frac{v_3 \left( b_0 + b_1 \phi(r) + O(\phi^2(r)) \right)}{\Gamma_B}
\]

\[
1 - v_1 C_1^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_1}{\nu_3}} - v_2 C_2^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_2}{\nu_3}} - v_3 b_0
\]

\[
= \frac{v_1 C_1^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_1}{\nu_3}} \left[ \beta_1 - \left( \frac{v_0}{v_3} \right) \left( \frac{b_0}{b_0} \right) \right]}{\Gamma_B} \phi(r)
\]

\[
+ \frac{v_2 C_2^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_2}{\nu_3}} \left[ \beta_2 - \left( \frac{v_0}{v_3} \right) \left( \frac{b_0}{b_0} \right) \right] - v_3 b_1}{\Gamma_B} \phi(r) + O(\phi^2(r)).
\]

(11)

Therefore, the constant terms in Eqs. (10) and (11) give

\[
\left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} = 1 - v_1 C_1^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_1}{\nu_3}} - v_2 C_2^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_2}{\nu_3}} - v_3 b_0
\]

(12)

whereas the first-order terms yield

\[
\frac{v_0 b_1}{v_3 b_0} \left( \frac{b_0}{C_3^B} \right)^{\frac{a_0}{\nu_3}} = \frac{v_1 C_1^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_1}{\nu_3}} \left( \beta_1 - \frac{v_0 b_1}{v_3 b_0} \right)}{\Gamma_B}
\]

\[
+ \frac{v_2 C_2^B \left( \frac{b_0}{C_3^B} \right)^{\frac{a_2}{\nu_3}} \left( \beta_2 - \frac{v_0 b_1}{v_3 b_0} \right) - v_3 b_1}{\Gamma_B}.
\]

(13)
Note that \( b_0 = C_3^B \) is a solution of Eq. (12). To determine if this solution is unique, we define the function

\[
f(x) = \Gamma^B x^{\frac{\alpha_0}{3}} + v_1 C_1^B x^{\frac{\alpha_1}{3}} + v_2 C_2^B x^{\frac{\alpha_2}{3}} + v_3 C_3^B x - 1
\]

that gives

\[
\lim_{x \to 0^+} f(x) = -1, \quad \lim_{x \to \infty} f(x) = \infty > 0,
\]

\[
f'(x) = \frac{v_0}{v_3} \Gamma^B x^{\frac{\alpha_0}{3} - 1} + \frac{v_1}{v_3} v_1 C_1^B x^{\frac{\alpha_1}{3} - 1} + \frac{v_2}{v_3} v_2 C_2^B x^{\frac{\alpha_2}{3} - 1} + v_3 C_3^B > 0.
\]

Therefore, the coefficient \( b_0 = C_3^B \) is unique. Similarly, by Eq. (13), we have

\[
\frac{v_3 b_1}{v_3 C_3^B} = \frac{v_1 C_1^B \left( \beta_1 - \frac{v_1 b_1}{v_3 C_3^B} \right) + v_2 C_2^B \left( \beta_2 - \frac{v_2 b_1}{v_3 C_3^B} \right) - v_3 b_1}{\Gamma^B}
\]

\[
= \frac{\beta_1 C_1^B (v_1 - v_2) - (v_1^2 C_1^B + v_3^2 C_3^B) b_1}{\Gamma^B},
\]

\[
\Gamma^B v_0 b_1 = \beta_1 C_1^B C_3^B v_3 (v_1 - v_2) - \left( v_1^2 C_1^B + v_3^2 C_2^B + v_3^2 C_3^B \right) b_1,
\]

and hence the coefficient \( b_1 = \frac{\beta_1 C_1^B C_3^B v_3 (v_1 - v_2)}{\Gamma^B v_0 + (v_1^2 C_1^B + v_3^2 C_2^B + v_3^2 C_3^B)} \) is unique by Eqs. (12) and (13). From Eqs. (4), (6), and (9), we have

\[
q_1 \left[ C_1(r) - \frac{C_1}{C_2} C_2(r) \right]
\]

\[
= q_1 C_1^B \left[ \exp(-\beta_1 \phi(r)) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\alpha_0}{3}} - \exp(-\beta_2 \phi(r)) \left( \frac{C_3(r)}{C_3^B} \right)^{\frac{\alpha_0}{3}} \right]
\]

\[
= q_1 C_1^B \left\{ (1 - \beta_1 \phi(r) + O(\phi^2(r))) \left[ \left( \frac{b_0}{C_3^B} \right)^{\frac{\alpha_0}{3}} + \frac{v_1 b_1}{v_3 b_0} \left( \frac{b_0}{C_3^B} \right)^{\frac{\alpha_0}{3}} \phi(r) + O(\phi^2(r)) \right] - (1 - \beta_2 \phi(r) + O(\phi^2(r))) \left[ \left( \frac{b_0}{C_3^B} \right)^{\frac{\alpha_0}{3}} + \frac{v_2 b_1}{v_3 b_0} \left( \frac{b_0}{C_3^B} \right)^{\frac{\alpha_0}{3}} \phi(r) + O(\phi^2(r)) \right] \right\}
\]

\[
= q_1 C_1^B \left\{ (1 - \beta_1 \phi(r) + O(\phi^2(r))) \left[ 1 + \frac{v_1 b_1}{v_3 C_3^B} \phi(r) + O(\phi^2(r)) \right] - (1 - \beta_2 \phi(r) + O(\phi^2(r))) \left[ 1 + \frac{v_2 b_1}{v_3 C_3^B} \phi(r) + O(\phi^2(r)) \right] \right\}
\]

\[
= q_1 C_1^B \left[ (\beta_2 - \beta_1) + \frac{(v_1 - v_2) b_1}{v_3 C_3^B} \right] \phi(r) + O(\phi^2(r)),
\]

which implies the following result.

**Theorem 3.1.** If Taylor’s formula (5) holds for the functional \( C_3(\phi(r)) = C_3(r) \), we then have the linear Poisson-Fermi equation

\[
e_s \left( \frac{\partial^2}{\partial x^2} - 1 \right) \nabla^2 \phi(r) = \frac{-C_1^B q_1}{k_B T} \left[ (q_1 - q_2) - \Lambda q_1 \right] \phi(r)
\]

(14)
for any binary ($K = 2$) electrolyte solutions, where

$$\Lambda = \frac{C_B^1 (v_1 - v_2)^2}{\Gamma^B v_0 + (v_1^2 C_B^1 + v_2^2 C_B^2 + v_3^2 C_B^3)}.$$  \hspace{1cm} (15)

Consequently, we obtain a generalized Debye length

$$l_{DPF} = \left( \frac{\epsilon_s k_B T}{C_B^1 ((1 - \Lambda)q_1^2 - q_1 q_2)} \right)^{1/2}.$$  \hspace{1cm} (16)

**Remark 3.1.** The generalized Debye length $l_{DPF}$ appears to be first proposed in the literature to our knowledge, where $\Lambda$ is a dimensionless quantity corresponding to the size effects. It depends not only on the charges but also on the sizes of all particles (ions and water). By contrast, the classical Debye length $l_D$ \cite{23} depends only on charges but not sizes, since all particles were treated as volumeless points in the classical Debye-Hückel formulation of the linear Poisson-Boltzmann equation \cite{23}. Note that the generalized length reduces to the classical length if $v_1 = v_2 \neq 0$ (two ionic species having equal radius and thus $\Lambda = 0$) or $v_1 = v_2 = v_3 = 0$ (all particles are points). The linear PF equation (14) is simplified to

$$(1 - l_c^2 \nabla^2) \nabla^2 \phi(r) = \kappa^2 \phi(r),$$  \hspace{1cm} (17)

where $\kappa^2 = \frac{C_B^1}{\epsilon_s k_B T} [(q_1 - q_2) - \Lambda q_1]$ and $\kappa^{-1} = l_{DPF}$. It reduces to the linear PB equation if both correlation ($l_c = 0$) and steric ($\Lambda = 0$) effects are ignored. Note that $l_{DPF}$ (or $l_D$) is proportional to $\frac{1}{\sqrt{C_B^1}}$.

**Remark 3.2.** Since $l_{DPF}$ includes the size effect, the correlation length $l_c$ should be generalized to $l_c = \sqrt{l_B l_{DPF}/48}$ for taking this effect into account as well. Consequently, the generalized correlation length is not universal \cite{23} but size dependent in contrast to that in \cite{25} derived from $l_D$. Correlation lengths used in previous works \cite{2, 26, 31, 34, 42} are all empirical constants that depend specifically on the size and/or valence of a particular ion of interest. The correlation length used here is not an empirical parameter.

### 3.2. General Solutions of Linear PF Equation in Spherical Symmetric System

Analytical solutions of the linear PB equation are in general not available for arbitrary domains except for special cases such as spherical domains \cite{21}. The classical DH equation was derived from the linear PB equation in a spherically symmetric system \cite{23}. We now find a general solution of the linear PF equation (14) in such a system using mathematical
techniques in standard texts [21]. We first transform Eq. (14) into the following two second-order elliptic PDEs

\[ \nabla^2 \phi(r) = \frac{1}{\epsilon_s} \psi(r), \quad (18) \]

\[ \nabla^2 \psi(r) = -\frac{\epsilon_s \kappa^2}{l_c^2} \phi(r) + \frac{1}{l_c} \psi(r), \quad (19) \]

by introducing the extra unknown function \( \psi(r) \) [26], which is a density-like function as can be seen from Eq. (3) by setting \( l_c = 0 \). These two equations can be written in matrix form as

\[
\begin{bmatrix}
\nabla^2 \phi(r) \\
\nabla^2 \psi(r)
\end{bmatrix} =
\begin{bmatrix}
0 & \frac{1}{\epsilon_s} \\
-\frac{\epsilon_s \kappa^2}{l_c^2} & \frac{1}{l_c}
\end{bmatrix}
\begin{bmatrix}
\phi(r) \\
\psi(r)
\end{bmatrix} =
M
\begin{bmatrix}
\phi(r) \\
\psi(r)
\end{bmatrix}.
\] (20)

The characteristic polynomial \( g(t) \) of the matrix \( M \) is given by

\[ g(t) = t^2 - \frac{1}{l_c^2} t + \frac{\kappa^2}{l_c^2} \]

and the distinct roots of \( g(t) \) are the eigenvalues

\[
\lambda_1 = \frac{1 - \sqrt{1 - 4l_c^2/\lambda_{DPF}^2}}{2l_c^2}, \quad \lambda_2 = \frac{1 + \sqrt{1 - 4l_c^2/\lambda_{DPF}^2}}{2l_c^2}
\] (21)

of \( M \) that can thus be decomposed as

\[
M = Q \begin{bmatrix}
\lambda_1 & 0 \\
0 & \lambda_2
\end{bmatrix} Q^{-1}, \quad Q = \begin{bmatrix}
\frac{l_c^2 \lambda_2}{\kappa^2} & \frac{l_c^2 \lambda_1}{\kappa^2} \\
1 & 1
\end{bmatrix}, \quad Q^{-1} = \frac{1}{\lambda_2 - \lambda_1} \begin{bmatrix}
\frac{\epsilon_s \kappa^2}{l_c^2} & -\lambda_1 \\
-\lambda_2 & \lambda_2
\end{bmatrix}.
\]

Denoting

\[
\begin{bmatrix}
\phi_*(r) \\
\psi_*(r)
\end{bmatrix} = Q^{-1} \begin{bmatrix}
\phi(r) \\
\psi(r)
\end{bmatrix},
\] (22)

Eq. (20) becomes

\[
\begin{bmatrix}
\nabla^2 \phi_*(r) \\
\nabla^2 \psi_*(r)
\end{bmatrix} =
\begin{bmatrix}
\lambda_1 & 0 \\
0 & \lambda_2
\end{bmatrix}
\begin{bmatrix}
\phi_*(r) \\
\psi_*(r)
\end{bmatrix}
\]

which, in spherically symmetric cases, is simplified to

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \phi_*(r)}{dr} \right) = \lambda_1 \phi_*(r),
\] (23)

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \psi_*(r)}{dr} \right) = \lambda_2 \psi_*(r),
\] (24)
where $r = |r|$ in $R^3$. The general solutions of these two equations are

$$
\phi_*(r) = \frac{Ae^{-\sqrt{\lambda_1}r}}{r} + \frac{Be^{\sqrt{\lambda_1}r}}{r}, \quad \psi_*(r) = \frac{Ce^{-\sqrt{\lambda_2}r}}{r} + \frac{De^{\sqrt{\lambda_2}r}}{r},
$$

where $A$, $B$, $C$, and $D$ are arbitrary constants. Consequently, the inverse mapping of Eq. (22) gives the general solutions of Eqs. (18) and (19) as

$$
\phi(r) = l_2^2 \epsilon_s \kappa^2 \left( \frac{Ae^{-\sqrt{\lambda_1}r}}{r} + \frac{Be^{\sqrt{\lambda_1}r}}{r} \right) + l_1^2 \epsilon_s \kappa^2 \left( \frac{Ce^{-\sqrt{\lambda_2}r}}{r} + \frac{De^{\sqrt{\lambda_2}r}}{r} \right),
$$

$$
\psi(r) = \frac{Ae^{-\sqrt{\lambda_1}r}}{r} + \frac{Be^{\sqrt{\lambda_1}r}}{r} + \frac{Ce^{-\sqrt{\lambda_2}r}}{r} + \frac{De^{\sqrt{\lambda_2}r}}{r}.
$$

### 3.3. Unique Solution of Linear PF Equation

The solvation energy – a fundamental quantity to measure the interaction of a solute with its solvent – of an ion in a bulk electrolyte solution can be calculated by Born models in a geometrically very simple setting [3]. Inspired by Born’s work [3], Debye and Hückel derived a unique analytical solution of the linear PB equation in spherically symmetric domains [8]. Motivated by Born and Debye-Hückel models, a ring-shaped domain as shown in Fig. 1 was proposed in [31] for solving numerically the nonlinear PF equation (3), where the system domain $\Omega = \Omega_i \cup \Omega_{sh} \cup \Omega_s$ is bounded with the volume $V$, $\Omega_i$ is the spherical domain occupied by the solvated ion $i$, $\Omega_{sh}$ is the hydration shell domain of the ion, $\Omega_s$ is the rest of solvent domain, and $O$ denotes the center (set to the origin $0$) of the ion. The radii of $\Omega_i$ and the outer boundary of $\Omega_{sh}$ are denoted by the effective Born (ionic cavity [38]) radius $R_i^{Born}$ and the hydration shell radius $R_i^{sh}$ (including first and second shells [41]), respectively.

Debye and Hückel [8] introduced the activity coefficient $\gamma_i$ of an ion of species $i$ in an electrolyte solution to describe the deviation of the chemical potential of the ion from ideality ($\gamma_i = 1$). The excess chemical potential $\mu_i^{ex} = k_B T \ln \gamma_i$ can be calculated by [3, 31]

$$
\mu_i^{ex} = \frac{1}{2} q_i \phi(0) - \frac{1}{2} q_i \phi^0(0),
$$

where $\phi(r)$ is a reaction potential [3] function and $\phi^0(r)$ is a potential function when the solvent domain $\Omega_s$ does not contain any ions at all with pure water only, i.e., when the solution is ideal. We seek an algebraic expression of the potential function $\phi(r)$ by solving
FIG. 1: The model domain Ω is partitioned into the ion domain Ω_{i} (with radius R_{i}^{Born}), the hydration shell domain Ω_{sh} (with radius R_{sh}^{i}), and the remaining solvent (bounded) domain Ω_{s}.

**analytically** the following system of second-order PDEs

\[
\begin{align*}
\epsilon_s \nabla^2 \phi(r) &= \psi(r) \text{ in } \Omega_s, \quad (29) \\
(1 - \hat{l}_\epsilon^2 \nabla^2) \psi(r) &= \epsilon_s k^2 \phi(r) \text{ in } \Omega_s, \quad (30) \\
\nabla^2 \phi(r) &= 0 \text{ in } \Omega_i \cup \Omega_{sh}, \quad (31)
\end{align*}
\]

for which the general solutions of (29) and (30) are given in (26) and (27), respectively. The boundary and interface conditions for \( \phi(r) \) and \( \psi(r) \) are

\[
\begin{align*}
\phi(r) &= \psi(r) = 0 \text{ at } |r| = \infty, \quad (32) \\
\psi(r) &= \epsilon_s k^2 \phi(r) \text{ on } \partial \Omega_{sh} \cap \partial \Omega_s, \quad (33) \\
[\phi(r)] &= 0 \text{ on } \partial \Omega_i \cup (\partial \Omega_{sh} \cap \partial \Omega_s), \quad (34) \\
[\nabla \phi(r) \cdot n] &= 0 \text{ on } \partial \Omega_{sh} \cap \partial \Omega_s, \quad (35) \\
[\epsilon(r) \nabla \phi(r) \cdot n] &= \epsilon_i \nabla \phi^*(r) \cdot n \text{ on } \partial \Omega_i, \quad (36)
\end{align*}
\]

where \( \partial \) denotes the boundary of a domain, the jump function \( [\phi(r)] = \lim_{r_{sh} \to r} \phi(r_{sh}) - \lim_{r_i \to r} \phi(r_i) \) at \( r \in \partial \Omega_i \) with \( r_{sh} \in \Omega_{sh} \) and \( r_i \in \Omega_i, \epsilon(r) = \epsilon_s \) in \( \Omega_{sh} \) and \( \epsilon(r) = \epsilon_i \) in \( \Omega_i \), \( \epsilon_i = \epsilon_{ion} \epsilon_0 \), \( \epsilon_{ion} \) is a dielectric constant in \( \Omega_i \), \( n \) is an outward normal unit vector at \( r \in \partial \Omega_i \), and \( \phi^*(r) = q_i/(4\pi \epsilon_i |r - 0|) \).

The additional Laplace equation (31) in \( \Omega_i \) avoids large errors in a direct approximation of the delta function \( \delta(r - 0) \) in the singular charge \( q_i \delta(r - 0) \) of the solvated ion located
at the origin $0$ by transforming the singular charge to the Green’s function $\phi^s(r)$ on $\partial\Omega_i$ in Eq. (36) as an approximate source of the electric field produced by the solvated ion [14]. From Eqs. (3) and (17), we observe that $\psi(r) = \epsilon_s \nabla^2 \phi(r) = -\rho(r) \approx \epsilon_s \kappa^2 \phi(r)$ when $l_c = 0$. Therefore, the interface condition (33) simply means that the function $\psi(r)$ satisfying Eq. (30) in $\Omega_s$ is prescribed as a negative charge density function $\epsilon_s \kappa^2 \phi(r)$ with $l_c = 0$ on the boundary $\partial\Omega_{sh} \cap \partial\Omega_s$. This interface condition can be derived from the charge neutrality condition of the entire system using Gauss’s divergence theorem, see Ref. [26] for the derivation, where all interface conditions are also presented and treated in great detail from numerical point of view. Note that, although the entire electrolyte solution in $\Omega$ is still in bulk condition, the excess chemical potential of the ion $i$ has been modeled by this PDE system in which the singular charge of the ion is treated as an external source that generates the electric potential function $\phi(r)$, i.e., the electrolyte solution in $\Omega \setminus \Omega_i$ is not treated in bulk condition.

The general solution of the Laplace equation (31) in a spherically symmetric domain is [21]

$$
\phi(r, \theta) = \sum_{n=1}^{\infty} \left( A_n r^n + B_n r^{-n-1} \right) P_n(\cos \theta),
$$

where $\theta$ is the polar angle of a vector $r$ and $P_n(\cos \theta)$ are Legendre polynomials. This implies that the solution is unique and

$$
\phi(r) = A_0 \text{ in } \Omega_i
$$

if $\phi(R_{i}^{Born}) = A_0$, since $r = 0 \in \Omega_i$ and thus $B_n = 0$ for all $n$, and $A_n = 0$ for all $n \neq 0$ as $r \to \infty$. Similarly, the solution is unique and

$$
\phi(r) = C_0 + \frac{D_0}{r} \text{ in } \Omega_{sh}
$$

if $\phi(R_{i}^{Born}) = C_0 + \frac{D_0}{R_{i}^{Born}}$ and $\phi(R_{i}^{sh}) = C_0 + \frac{D_0}{R_{i}^{sh}}$. We need 7 conditions to uniquely determine the 7 unknowns $A$, $B$, $C$, $D$, $A_0$, $C_0$, and $D_0$, and to prove that $\phi(R_{i}^{Born})$ and $\phi(R_{i}^{sh})$ are constants.

**Conds. 1 and 2.** By $\phi(r) = 0$ and $\psi(r) = 0$ in (32) as $r \to \infty$, (26), and (27), we obtain $B = D = 0$ and hence

$$
\phi(r) = \frac{A l_i^2 \lambda_1 r e^{-\sqrt{\lambda_1}r}}{\epsilon_s \kappa^2 r} + \frac{C l_i^2 \lambda_1 r e^{-\sqrt{\lambda_1}r}}{\epsilon_s \kappa^2 r} \text{ in } \Omega_s,
$$

$$
\psi(r) = \frac{A e^{-\sqrt{\lambda_1}r}}{r} + \frac{C e^{-\sqrt{\lambda_1}r}}{r} \text{ in } \Omega_s.
$$
Cond. 3. \[ \phi(r) = 0 \text{ on } \partial \Omega_{sh} \cap \partial \Omega_i \text{ in (34) and (38)}, \]

\[
\phi(R^{sh}_i) = \frac{A l^2 \lambda_2}{\epsilon_s \kappa^2} e^{-\sqrt{\lambda_1 R^{sh}_i}} + \frac{C l^2 \lambda_1}{\epsilon_s \kappa^2} e^{-\sqrt{\lambda_2 R^{sh}_i}} = C_0 + \frac{D_0}{r_i^{sh}},
\]

which implies that \( \phi(R^{sh}_i) \) is constant and

\[
A \lambda_2 e^{-\sqrt{\lambda_1 R^{sh}_i}} + C \lambda_1 e^{-\sqrt{\lambda_2 R^{sh}_i}} = \frac{\epsilon_s \kappa^2}{l^2_c} (C_0 R^{sh}_i + D_0).
\]

Cond. 4. By (33), we have

\[
\psi(R^{sh}_i) = \frac{A e^{-\sqrt{\lambda_1 R^{sh}_i}}}{R^{sh}_i} + \frac{C e^{-\sqrt{\lambda_2 R^{sh}_i}}}{R^{sh}_i} = \epsilon_s \kappa^2 \phi(R^{sh}_i)
\]

\[
= \frac{A l^2 \lambda_2 e^{-\sqrt{\lambda_1 R^{sh}_i}}}{R^{sh}_i} + \frac{C l^2 \lambda_1 e^{-\sqrt{\lambda_2 R^{sh}_i}}}{R^{sh}_i},
\]

\[
A e^{-\sqrt{\lambda_1 R^{sh}_i}} (i^2 \lambda_2 - 1) + C e^{-\sqrt{\lambda_2 R^{sh}_i}} (i^2 \lambda_1 - 1) = 0.
\]

Cond. 5. By (35), we have

\[
\left[ \frac{\partial \phi(r)}{\partial n} \right] = \lim_{r \to R^{sh}_i} \frac{d}{dr} \left( \frac{A l^2 \lambda_2}{\epsilon_s \kappa^2} e^{-\sqrt{\lambda_1 r}} + \frac{C l^2 \lambda_1}{\epsilon_s \kappa^2} e^{-\sqrt{\lambda_2 r}} \right) - \lim_{r \to R^{sh}_i} \frac{d}{dr} \left( C_0 + \frac{D_0}{r} \right)
\]

\[
= \lim_{r \to R^{sh}_i} \left[ -\frac{A l^2 \lambda_2 (\sqrt{\lambda_1 r} + 1) e^{-\sqrt{\lambda_1 r}}}{\epsilon_s \kappa^2} \right] - \lim_{r \to R^{sh}_i} \left[ \frac{C l^2 \lambda_1 (\sqrt{\lambda_2 r} + 1) e^{-\sqrt{\lambda_2 r}} + D_0}{\epsilon_s \kappa^2} \right]
\]

\[
= \frac{1}{(R^{sh}_i)^2} \left[ D_0 - \frac{A l^2 \lambda_2 (\sqrt{\lambda_1 R^{sh}_i} + 1) e^{-\sqrt{\lambda_1 R^{sh}_i}}}{\epsilon_s \kappa^2} \right]
\]

\[
- \frac{C l^2 \lambda_1 (\sqrt{\lambda_2 R^{sh}_i} + 1) e^{-\sqrt{\lambda_2 R^{sh}_i}}}{\epsilon_s \kappa^2}
\]

\[
A \lambda_2 (\sqrt{\lambda_1 R^{sh}_i} + 1) e^{-\sqrt{\lambda_1 R^{sh}_i}} + C \lambda_1 (\sqrt{\lambda_2 R^{sh}_i} + 1) e^{-\sqrt{\lambda_2 R^{sh}_i}} = \frac{D_0 \epsilon_s \kappa^2}{l^2_c}.
\]

Cond. 6. By \( \phi(r) = 0 \) on \( \partial \Omega_i \) in (34), we have

\[
\phi(R^{Born}_i) = C_0 + \frac{D_0}{R^{Born}_i} = A_0,
\]

which implies that \( \phi(R^{Born}_i) \) is constant.

Cond. 7. By (36), we have

\[
\left[ \epsilon(r) \frac{\partial \phi(r)}{\partial n} \right] = \epsilon_s \lim_{r \to R^{Born}_i} \frac{d}{dr} \left( C_0 + \frac{D_0}{r} \right) - \epsilon_i \lim_{r \to R^{Born}_i} \frac{dA_0}{dr} \frac{dA_0}{dr} = -\frac{\epsilon_s D_0}{(R^{Born}_i)^2}
\]

\[
= \epsilon_i \nabla \phi^* \cdot \mathbf{n} = \frac{q_i}{4\pi} \lim_{r \to R^{Born}_i} \frac{d}{dr} \frac{1}{r} = -\frac{q_i}{4\pi (R^{Born}_i)^2}.
\]
Therefore, we find

\[
A = \frac{q_i \kappa^2}{4 \pi l_c^2} \left[ e^{\frac{\sqrt{\lambda_1 R_i^{sh}}}{\lambda_2 (l_c^2 \lambda_1 - 1) (\sqrt{\lambda_1 R_i^{sh} + 1})}} - e^{\frac{\sqrt{\lambda_2 R_i^{sh}}}{\lambda_2 (l_c^2 \lambda_2 - 1) (\sqrt{\lambda_2 R_i^{sh} + 1})}} \right],
\]

\[
C = \frac{q_i \kappa^2}{4 \pi l_c^2} \left[ -\frac{\lambda_1 (l_c^2 \lambda_1 - 1)}{\lambda_2 (l_c^2 \lambda_2 - 1) (\sqrt{\lambda_1 R_i^{sh} + 1})} + \frac{\lambda_2 (l_c^2 \lambda_2 - 1)}{\lambda_1 (l_c^2 \lambda_1 - 1) (\sqrt{\lambda_2 R_i^{sh} + 1})} - 1 \right],
\]

\[
B = D = 0,
\]

\[
C_0 = \frac{q_i}{4 \pi \epsilon_s R_{i}^{sh}} \left[ \frac{\lambda_1 (l_c^2 \lambda_2 - 1)}{\lambda_2 (l_c^2 \lambda_1 - 1) (\sqrt{\lambda_1 R_i^{sh} + 1})} - \frac{\lambda_2 (l_c^2 \lambda_1 - 1)}{\lambda_1 (l_c^2 \lambda_2 - 1) (\sqrt{\lambda_2 R_i^{sh} + 1})} - 1 \right],
\]

\[
D_0 = \frac{q_i}{4 \pi \epsilon_s},
\]

\[
A_0 = C_0 + \frac{D_0}{R_i^{Born}}.
\]

Since

\[
\lambda_1 + \lambda_2 = \frac{1}{l_c^2},
\]

\[
\lambda_2 (l_c^2 \lambda_1 - 1) = \lambda_2 \left( \frac{\lambda_1}{\lambda_1 + \lambda_2} - 1 \right) = -\frac{\lambda_2}{\lambda_1 + \lambda_2} = -l_c^2 \lambda_2^2,
\]

\[
\lambda_1 (l_c^2 \lambda_2 - 1) = -l_c^2 \lambda_1^2,
\]

we introduce the symbol \( \Theta \) for \( C_0 \) such that

\[
\Theta = \lambda_2 (l_c^2 \lambda_1 - 1) - \lambda_1 (l_c^2 \lambda_2 - 1)
\]

\[
= \lambda_2 (l_c^2 \lambda_1 - 1) (\sqrt{\lambda_1 R_i^{sh} + 1}) - \lambda_1 (l_c^2 \lambda_2 - 1) (\sqrt{\lambda_2 R_i^{sh} + 1})
\]

\[
= -l_c^2 \lambda_2^2 + l_c^2 \lambda_1^2
\]

\[
= \frac{\lambda_1^2 - \lambda_2^2}{\lambda_1^2 (\sqrt{\lambda_2 R_i^{sh} + 1}) - \lambda_2^2 (\sqrt{\lambda_1 R_i^{sh} + 1})}
\]

\[
(39)
\]

We summarize our analysis as the following main result of the current study.

**Theorem 3.2.** For a binary aqueous electrolytic solution in a spherically symmetric domain as shown in Fig. 1, the linear Poisson-Fermi model system (29) – (36) has the unique potential function

\[
\phi^{PF}(r) = \begin{cases} 
\frac{q_i}{4 \pi \epsilon_s R_i^{Born}} + \frac{q_i}{4 \pi \epsilon_s R_i^{sh}} (\Theta - 1) \text{ in } \Omega_i \\
\frac{q_i}{4 \pi \epsilon_s} + \frac{q_i}{4 \pi \epsilon_s R_i^{sh}} (\Theta - 1) \text{ in } \Omega_{sh} \\
\frac{q_i}{4 \pi \epsilon_s} \left[ \frac{\lambda_1^2 e^{-\sqrt{\lambda_2 (r-R_i^{sh})}} - \lambda_2^2 e^{-\sqrt{\lambda_1 (r-R_i^{sh})}}}{\lambda_1 (\sqrt{\lambda_2 R_i^{sh} + 1}) - \lambda_2 (\sqrt{\lambda_1 R_i^{sh} + 1})} \right] \text{ in } \Omega_s.
\end{cases}
\]
Remark 3.3. Note that \( \lim_{l_c \to 0} \lambda_1 = 1/l_{DPF}^2 \) (correlation effect is ignored), \( \lim_{l_c \to 0} \Theta = \lim_{C_i^B \to 0} \Theta = \lim_{l_{DPF} \to \infty} \Theta = 1 \) (correlation is ignored and electrolyte is infinite dilute). The linearized PF potential \( \phi^{PF}(r) \) reduces to the linearized PB potential \( \phi^{PB}(r) = q_i e^{-r/l_D}/(4\pi \epsilon_s r) \) as in standard texts (e.g. Eq. (7.46) in [23]) by taking \( \lim_{l_c \to 0} \phi^{PF}(r) \) with \( v_j = 0 \) for all \( j \) (steric effect is ignored), \( R_{i}^{sh} = 0 \), and \( r > 0 \).

3.4. Generalized Debye-Hückel Equation

As discussed in [44], the solvation free energy of an ion \( i \) should vary with salt concentrations, i.e., the Born energy

\[
-\frac{q_i^2}{8\pi \epsilon_0 R_{i}^0} \left(1 - \frac{1}{\epsilon_w}\right)
\]

in pure water (i.e. \( C_i^B = 0 \)) with a constant Born radius \( R_{i}^0 \) should be modified to depend on \( C_i^B \geq 0 \). Equivalently, the effective Born radius \( R_{i}^{Born} \) of the electrolyte solution in Fig. 1 varies with \( C_i^B \) and can be modified from \( R_{i}^0 \) by a simple formula [31]

\[
R_{i}^{Born}(C_i^B) = \theta(C_i^B) R_{i}^0, \quad \theta(C_i^B) = 1 + \alpha_1^i \left(\overline{C}_i^B\right)^{1/2} + \alpha_2^i C_i^B + \alpha_3^i \left(\overline{C}_i^B\right)^{3/2},
\]

where \( \overline{C}_i^B = C_i^B/M \) is a dimensionless bulk concentration, \( M \) is molarity (molar concentration), and \( \alpha_1^i, \alpha_2^i, \) and \( \alpha_3^i \) are adjustable parameters for modifying the experimental Born radius \( R_{i}^0 \) to fit experimental activity coefficients \( \gamma_i \) that change with the bulk concentration \( C_i^B \) of the ion. The Born radii \( R_{i}^0 \) given below are cited from [44], which are computed from the experimental hydration Helmholtz free energies of these ions given in [10]. The three parameters in [42] have physical or mathematical meanings unlike numerous parameters in the Pitzer model [12, 40, 46]. The first parameter \( \alpha_1^i \) is an adjustment of \( R_{i}^0 \) that accounts for the real thickness of the ionic atmosphere (Debye length), which is proportional to the square root of the ionic strength \( I = \frac{1}{2} \sum_i C_i^B z_i^2 \) in the DH theory [23]. The second \( \alpha_2^i \) and third \( \alpha_3^i \) parameters are adjustments in the next orders of approximation beyond the DH treatment of ionic atmosphere [31].

The potential value \( \phi^0(0) = \lim_{C_i^B \to 0} \phi^{PF}(0) = q_i/(4\pi \epsilon_s R_{i}^0) \) by \( \lim_{C_i^B \to 0} \Theta = 1 \) and \( \lim_{C_i^B \to 0} R_{i}^{Born}(C_i^B) = R_{i}^0 \). From (28) and (40), we thus obtain a generalized activity coefficient \( \gamma_i^{DHPF} \) as

\[
\ln \gamma_i^{DHPF} = -\frac{q_i^2}{8\pi \epsilon_s k_B T} \left( \frac{1}{R_{i}^{Born}(C_i^B)} - \frac{1}{R_{i}^0} + \frac{\Theta - 1}{R_{i}^{sh}} \right).
\]
Since the steric potential \( S^{\text{trc}}(r) \) in (2) takes particle volumes and voids into account, the shell volume \( V_{sh} \) of the shell domain \( \Omega_{sh} \) can be determined by the steric potential

\[
S^{\text{trc}}_{sh} = \frac{v_0}{v_w} \ln \frac{O_i^w}{V_{sh}C_{K+1}^B} = \ln \frac{V_{sh} - v_wO_i^w}{V_{sh}\Gamma^B}
\]  

(44)

[31], where the occupant (coordination) number \( O_i^w \) of water molecules is given by experimental data [41]. The shell radius \( R_{sh}^i \) is thus determined and depends not only on \( O_i^w \) but also on the bulk void fraction \( \Gamma^B \), namely, on all salt and water bulk concentrations \( (C_k^B) \).

**Remark 3.4.** The generalized activity coefficient \( \gamma_i^{DHPF} \) reduces to the classical \( \gamma_i^{DH} \) proposed by Debye and Hückel in 1923 [8], namely,

\[
\ln \gamma_i^{DH} = \frac{-q_i^2}{8\pi\varepsilon_s k_B T (R_i + l_{DF})}
\]  

(45)

provided that \( R_i^{\text{Born}}(C_i^B) = R_i^0 \) (without considering the Born energy effect), \( R_i^{sh} = R_i \) (an effective ionic radius (parameter) [8]), \( l_{DF} = l_D \) (no steric effect), and \( l_c = 0 \) (no correlation effect). The reduction is shown by taking the limit of the last term in (43) as \( l_c \to 0 \), i.e.,

\[
\lim_{l_c \to 0} \frac{\Theta - 1}{R_{sh}^i} = \frac{-1}{R_i + l_D}
\]

since

\[
\Theta = \frac{\lambda_1^2 - \lambda_2^2}{\lambda_1^2 (\sqrt{\lambda_2} R_{sh}^i + 1) - \lambda_2^2 (\sqrt{\lambda_1} R_{sh}^i + 1)}
\]

\[
\Theta - 1 = \frac{(\lambda_1^2 \sqrt{\lambda_2} R_{sh}^i - \lambda_2^2 \sqrt{\lambda_1} R_{sh}^i)}{\lambda_1^2 (\sqrt{\lambda_2} R_{sh}^i + 1) - \lambda_2^2 (\sqrt{\lambda_1} R_{sh}^i + 1)}
\]

\[
\Theta - 1 = \frac{- (\lambda_1^2 \sqrt{\lambda_2} - \lambda_2^2 \sqrt{\lambda_1})}{\lambda_1^2 (\sqrt{\lambda_2} R_{sh}^i + 1) - \lambda_2^2 (\sqrt{\lambda_1} R_{sh}^i + 1)} = \frac{-1}{R_{sh}^i + G}
\]

\[
G = \frac{\lambda_1^2 - \lambda_2^2}{\lambda_1^2 \sqrt{\lambda_2} - \lambda_2^2 \sqrt{\lambda_1} = \frac{\lambda_1^2 / \lambda_2^2 - 1}{\lambda_1^2 \sqrt{\lambda_2} / \lambda_2^2 - \sqrt{\lambda_1}}}
\]

\[
\lim_{l_c \to 0} G = \lim_{l_c \to 0} \frac{1}{\sqrt{\lambda_1}} = l_D, \quad \left( \lim_{l_c \to 0} \lambda_1 = \frac{1}{l_D^2}, \lim_{l_c \to 0} \lambda_2 = \infty \right).
\]

Hückel soon realized that the DH formula (43) failed to fit experimental data at high ionic strengths and modified it in 1925 [18] by adding a linear term in \( C_i^B \) with an extra parameter \( \eta_i^1 \) to become

\[
\ln \gamma_i^{DHB} = \ln \gamma_i^{DH} + \eta_i^1 C_i^B
\]  

(46)

where the linear term is an approximation of the Born solvation energy

\[
\frac{q_i^2}{8\pi\varepsilon_0 R_i^0} \left( \frac{1}{\epsilon_w} - \frac{1}{\epsilon} \right)
\]  

(47)
as the permittivity varies from $\varepsilon_w \varepsilon_0$ in pure water to $\varepsilon_0$ in electrolyte solutions, where the dielectric constant $\varepsilon$ is unknown and changes with $C_i^B$, i.e., $\varepsilon = \varepsilon(C_i^B)$ a function of salt concentrations. Consequently, a variety of extended DH models $\gamma_i^{DHBx}$ in the form similar to

$$\ln \gamma_i^{DHBx} = \ln \gamma_i^{DH} + \sum_{k=1}^{n} \eta_k^i (C_i^B)^k$$

have been proposed in the literature to express other thermodynamic properties such as temperature and pressure by a power expansion of $C_i^B$ with more and more adjustable parameters $\eta_k^i$ that can increase combinatorially with various composition (various $i$), temperature, and pressure to a frustrating amount as mentioned above. Note that $\eta_k^i$ may also depend on ionic strength $I$ in a complicated way, see e.g. Eq. (2) in [40]. Many expressions of those parameters are rather long and tedious and do not have clear physical meaning [12, 40, 46]. Moreover, it has been reported in [11] that no improvement is found for the extended DH model (46) by changing the constants in the approximation of $\varepsilon(C_i^B)$ to reflect changes in solvent permittivity. This means that changing only $\eta_1^i$ may not improve the model to fit experimental data unless more adjustable parameters are introduced to model the Born energy more accurately as proposed in [43].

The $R_i^{Born}$ term in (43) differs significantly from the last term in (48) as they are inverse of each other in terms of $C_i^B$ and parameters. Therefore, the generalized $\gamma_i^{DHPF}$ is not a $\gamma_i^{DHBx}$ for which the empirical nature of extended DH models requires a great deal of efforts to extract parameters (without physical hints) from existent thermodynamic databases by regression analysis [40, 46, 47].

**Remark 3.5.** Same as the classical $\gamma_i^{DH}$, the generalized activity coefficient also satisfies the DH limiting law [23], i.e., $\gamma_i^{DHPF} = \gamma_i^{DH} = 1$ as $C_i^B \to 0$ for infinite dilute (ideal) solutions. The DH limiting law is useful for calculating the activity coefficient of an ion in very dilute solutions to compare with experimental measurements that are especially important for highly charged electrolytes [13].

The formula (43) shows that the principal determinant of ionic activity is the concentration-dependent Born radius $R_i^{Born}(C_i^B)$ since $\gamma_i^{DHPF}$ is very sensitive to $R_i^{Born}(C_i^B)$ that is an atomic distance from the singular charge $q_i \delta(r - 0)$ of the ion, which is infinite at $0$ and thus critically affects $\gamma_i^{DHPF}$. The secondary determinant is the hydration shell radius $R_i^{sh}$ that lumps short-range ion-water interactions into a single physical length. The
last part of ionic activity is extracted to the symbol $\Theta$ that accounts for ion-ion correlations ($l_c$) and long-range electrostatics ($l_{DFP}$) via the eigenvalues $\lambda_1$ and $\lambda_2$ in (21) and (39).

4. NUMERICAL RESULTS

We now report numerical results obtained by the extended (16) and generalized (43) DH models for fitting the experimental data of individual ionic activity by Wilczek-Vera et al. in [48] for eight 1:1 electrolytes and six 2:1 electrolytes as shown in Figs. 4.1 and 4.2, respectively. The corresponding adjustable parameters are $\{R_i, \eta_i\}$ (in (45) and (46) for DHB) and $\{\alpha_i^1, \alpha_i^2, \alpha_i^3\}$ (in (42) for DHPF), whose values are given in Tables 4.1 and 4.2. The fitting method for both models is the same, i.e., for each pair of DHB and DHPF curves (either cation or anion) in Figs. 4.1 and 4.2, we chose the same first two data points (squares or circles in the figures) for both models while one more data point is chosen for the DHPF model. Once the data points are chosen, the two $\{R_i, \eta_i\}$ or three $\{\alpha_i^1, \alpha_i^2, \alpha_i^3\}$ unknown parameters are determined uniquely by two or three algebraic equations. The data points are indexed by $j_{DHB}$ and $j_{PF} = 1, 2, 3, ...$ from low to high concentrations for the DHB and DHPF models, respectively. The values of $j_{DHB}$ or $j_{PF}$ for each curve are given in Table 4.3. The physical values of the remaining notations in our model systems are given in Table 4.4, which are all fixed throughout the calculation.
FIG. 2: Individual activity coefficients of 1:1 electrolytes. Comparison of DHB and DHPF results with experimental data [48] on $i = C^+$ (cation) and $A^-$ (anion) activity coefficients $\gamma_i$ in various [CA] from 0 to 1.6 M.
FIG. 3: Individual activity coefficients of 2:1 electrolytes. Comparison of DHB and DHPF results with experimental data [48] on $i = C^{2+}$ (cation) and $A^-$ (anion) activity coefficients $\gamma_i$ in various $[CA_2]$ from 0 to 1.5 M.
Table 4.1. Values of \(R_i, \eta_i^1\) and \(\alpha_i^1, \alpha_i^2, \alpha_i^3\) for Fig. 4.1

| Fig. | i  | \(R_i\)  | \(\eta_i^1\) | \(\alpha_i^1\) | \(\alpha_i^2\) | \(\alpha_i^3\) |
|------|----|----------|--------------|----------------|----------------|----------------|
| 1a   | Li\(^+\) | 5.1455   | 0.75856      | 0.00302        | -0.04841       | 0.00636        |
| 1a   | Cl\(^-\) | 0.1569   | 0.97392      | 0.04697        | -0.01146       | -0.00092       |
| 1b   | Li\(^+\) | 4.8267   | 0.47995      | -0.00499       | -0.01112       | -0.00395       |
| 1b   | Br\(^-\) | 4.2063   | 0.36348      | 0.02923        | -0.05870       | 0.01005        |
| 1c   | Na\(^+\) | 5.1715   | -0.09639     | -0.00261       | 0.00622        | -0.00164       |
| 1c   | F\(^-\)  | 2.7945   | 0.10815      | 0.03438        | -0.00538       | -0.00164       |
| 1d   | Na\(^+\) | 6.5954   | 0.16037      | -0.02792       | 0.00078        | 0.0164         |
| 1d   | Cl\(^-\) | 2.7558   | 0.16531      | 0.05789        | -0.01740       | 0.0164         |
| 1e   | Na\(^+\) | 6.1983   | 0.04359      | -0.03594       | 0.03406        | -0.01262       |
| 1e   | Br\(^-\) | 3.8671   | 0.13065      | 0.02077        | -0.00879       | -0.00082       |
| 1f   | K\(^+\)  | 3.4093   | -0.10042     | 0.00195        | 0.05044        | -0.01416       |
| 1f   | F\(^-\)  | 1.8246   | 0.61888      | 0.03120        | -0.02623       | 0.00245        |
| 1g   | K\(^+\)  | 2.3934   | 0.04967      | 0.02531        | 0.02938        | -0.00736       |
| 1g   | Cl\(^-\) | 4.1267   | 0.18771      | 0.01399        | -0.01849       | 0.00268        |
| 1h   | K\(^+\)  | 0.0006   | 2.14260      | 0.03405        | -0.06265       | 0.01587        |
| 1h   | Br\(^-\) | 3.5540   | -0.33142     | 0.00237        | 0.07132        | 0.00453        |

The purposes of data fitting are to show how well these two models can fit the data, to describe the physical meaning of these parameters, and to explore predictive or verifiable features of the DHPF model for future experimental studies of ion activities. The DHPF model is obviously better as shown in Figs. 1 and 2 because it has one more parameter to fit the data. Nevertheless, the DHB model can fit 14 out of 28 data sets quite well as shown in Figs. 4.1a, 1c, 1d, 1e, 1g, 1h, 2a, 2b, 2c, 2d, and 2e. However, the numerical values of \(R_i\) and \(\eta_i^1\) in Tables 4.1 and 4.2 do not reflect any physical meanings of these two parameters, see e.g. the three values of \(R_{K^+}\) in Table 4.1. If \(R_i\) in (45) is chosen to be an effective ionic radius as originally proposed by Debye and Hückel, it is then not adjustable and thus incurs a worse fitting that consequently led to numerous extended DHBx (48) with more parameters in the literature.

On the other hand, the numerical values of \(\alpha_i^1, \alpha_i^2, \alpha_i^3\) imply that the Born radius \(R_{i}^{Born}(C_i^B)\) in (42) deviates slightly from \(R_i^0 = R_{i}^{Born}(0)\) in the ranges of salt concentrations...
shown in these figures. The small deviation is consistent with the derivation of the PF model since the Green function \( \phi^*(r) = q_i/(4\pi\varepsilon_iR_i^{\text{Born}}(C_i^B)) \) on \( \partial\Omega_i \) in (36) with variable \( C_i^B \) is an approximation of the singular charge \( q_i\delta(r - 0) \) that is infinite at the center of the ion. In other words, the numerical value of \( \gamma_i^{\text{DHPF}} \) in (43) (or the experimental activity of ions) is very sensitive to the change of \( R_i^{\text{Born}}(C_i^B) \) with \( C_i^B \) up to five decimal places of numerical \( \alpha_i^1, \alpha_i^2, \) and \( \alpha_i^3 \) as shown in Tables 1 and 2, which also show the significant order of these parameters, i.e., \( |\alpha_i^1| > |\alpha_i^2| > |\alpha_i^3| \) in general cases. We postulate that particular cases that violate this order are due to either our fitting method or our selection of experimental data that are subject to measurement errors. We shall investigate this issue more closely in the future with more data sets of same conditions from other sources. The numerical values of \( \alpha_i^1, \alpha_i^2, \) and \( \alpha_i^3 \) also suggest that further investigations of existing data are needed in order to develop predictive DHPF models which are of great importance for experimental use.

| Fig. | \( i \) | \( R_i \) | \( \eta_i^1 \) | \( \alpha_i^1 \) | \( \alpha_i^2 \) | \( \alpha_i^3 \) |
|------|------|------|------|------|------|------|
| 2a   | \( \text{Mg}^{2+} \) | 6.9897 | 1.70210 | -0.03693 | -0.01041 | -0.00251 |
| 2a   | \( \text{Cl}^- \)  | 2.7952 | 0.42762 | 0.07188  | -0.02097 | -0.00409 |
| 2b   | \( \text{Mg}^{2+} \) | 6.6512 | 2.76310 | -0.02960 | -0.03228 | 0.00210  |
| 2b   | \( \text{Br}^- \)  | 2.6151 | 0.55346 | 0.08516  | -0.02744 | -0.00745 |
| 2c   | \( \text{Ca}^{2+} \) | 4.4415 | 2.25920 | 0.02018  | -0.05156 | 0.00632  |
| 2c   | \( \text{Cl}^- \)  | 3.0224 | 0.29788 | 0.07575  | -0.02165 | -0.00418 |
| 2d   | \( \text{Ca}^{2+} \) | 7.5098 | 2.65970 | -0.05217 | -0.03003 | 0.00226  |
| 2d   | \( \text{Br}^- \)  | 2.2732 | 0.11472 | 0.07343  | 0.09949  | -0.03810 |
| 2e   | \( \text{Ba}^{2+} \) | 3.1112 | 2.83130 | 0.08775  | -0.10621 | 0.02114  |
| 2e   | \( \text{Cl}^- \)  | 3.6080 | 0.03419 | 0.05037  | -0.00185 | -0.00110 |
| 2f   | \( \text{Ba}^{2+} \) | 6.3477 | 1.19380 | -0.05366 | 0.00354  | -0.00438 |
| 2f   | \( \text{Br}^- \)  | 3.8487 | 0.01850 | 0.02336  | 0.04326  | -0.01925 |
Table 4.3. Values of the indices $j_{DHB}$ and $j_{PF}$ of data points

| Fig. | $i$  | $j_{DHB}$ | $j_{PF}$ | Fig. | $i$  | $j_{DHB}$ | $j_{PF}$ |
|------|------|-----------|----------|------|------|-----------|----------|
| 1a   | Li$^+$| 2,7,13    |          | 2a   | Mg$^{2+}$| 3,6,10    |          |
| 1a   | Cl$^-$| 3,10,13   |          | 2a   | Cl$^-$  | 3,6,10    |          |
| 1b   | Li$^+$| 3,7,11    |          | 2b   | Mg$^{2+}$| 3,6,10    |          |
| 1b   | Br$^-$| 3,7,11    |          | 2b   | Br$^-$  | 3,6,10    |          |
| 1c   | Na$^+$ | 3,6,10    |          | 2c   | Ca$^{2+}$| 3,6,10    |          |
| 1c   | F$^-$  | 3,6,10    |          | 2c   | Cl$^-$  | 3,6,10    |          |
| 1d   | Na$^+$ | 5,12,14   |          | 2d   | Ca$^{2+}$| 3,6,10    |          |
| 1d   | Cl$^-$ | 5,12,14   |          | 2d   | Br$^-$  | 3,6,10    |          |
| 1e   | Na$^+$ | 3,6,10    |          | 2e   | Ba$^{2+}$| 3,6,9     |          |
| 1e   | Br$^-$ | 3,6,10    |          | 2e   | Cl$^-$  | 3,6,9     |          |
| 1f   | K$^+$  | 2,6,11    |          | 2f   | Ba$^{2+}$| 6,7,11    |          |
| 1f   | F$^-$  | 2,6,11    |          | 2f   | Br$^-$  | 3,7,11    |          |
| 1g   | K$^+$  | 3,7,13    |          | 1h   | K$^+$  | 2,4,8     |          |
| 1g   | Cl$^-$ | 3,7,13    |          | 1h   | Br$^-$ | 2,4,8     |          |
Table 4.4. Values of model notations

| Symbol | Meaning | Value | Unit |
|--------|---------|-------|------|
| $k_B$  | Boltzmann constant | $1.38 \times 10^{-23}$ | J/K  |
| $T$    | temperature      | 298.15 | K    |
| $e$    | proton charge   | $1.602 \times 10^{-19}$ | C    |
| $\epsilon_0$ | permittivity of vacuum | $8.85 \times 10^{-14}$ | F/cm |
| $\epsilon_{\text{ion}}, \epsilon_w$ | dielectric constants | 1, 78.45 |
| $O_i^w$ | in Eq. (44) | 18 [36, 41] |
| $a_{\text{Li}^+, \text{Na}^+, \text{K}^+}$ | radii Eq. (1) | 0.6, 0.95, 1.33 | Å |
| $a_{\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}}$ | radii | 0.65, 0.99, 1.35 | Å |
| $a_{\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{H}_2\text{O}}$ | radii | 1.36, 1.81, 1.95, 1.4 | Å |
| $R_{\text{Li}^+, \text{Na}^+, \text{K}^+}^0, R_{\text{Br}^-}^0$ | Born radii in Eq. (43) | 1.3, 1.618, 1.95 | Å |
| $R_{\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}}^0$ | Born radii | 1.424, 1.708, 2.03 | Å |
| $R_{\text{F}^-, \text{Cl}^-, \text{Br}^-}^0$ | Born radii | 1.6, 2.266, 2.47 | Å |

Another important feature of the DHPF model is that the electric potential and other physical properties of ionic activity can be studied in detail according to the partitioned domain in Fig. 3.1 characterized by $R_i^{\text{Born}}(C_i^B)$ and $R_i^{\text{sh}}$. For example, for the case of $[\text{LiBr}] = [\text{KBr}] = 2 \text{ M}$ in Fig. 4.3a, it is interesting to observe that the electric potential and the Born radius ($\phi^{PF}(0) = 2.4744 \ k_B T/e, \ R_{\text{Br}^-}^{\text{Born}}(2 \text{ M}) = 2.0637 \ \text{Å}$) generated by Br$^-$ in LiBr solution are significantly different from that ($\phi^{PF}(0) = 0.6860 \ k_B T/e, \ R_{\text{Br}^-}^{\text{Born}}(2 \text{ M}) = 4.2578 \ \text{Å}$) of KBr at the same salt concentration. The only difference between these two solutions is the size of cations, i.e., the size of different monocations changes significantly the activity of the same monoanion at high concentrations. Note that the difference in $\phi^{PF}(0)$ generated by Li$^+$ and K$^+$ is mainly due to their sizes not by the size of Br$^-$. Similar properties can be observed for the 2:1 electrolytes at 2 M in Fig. 4.3b.

From Figs. 4.3a and 4.3b, we also observe that the electric potential is decreasing inversely with $r$ in $\Omega_{sh}$ and exponentially in $\Omega_s$ as implied by the exact formula in (10). This means that the exact value of $R_i^{\text{sh}}$ (or the exact value of $O_i^w$ in (41)) does not significantly affect the electric potential profile that is primarily determined by the Born radius $R_i^{\text{Born}}(C_i^B)$.
FIG. 4: Electric potential $\phi^{PF}(r)$ profiles by the DHPF model near the solvated ions Li$^+$ and Br$^-$ at [LiBr] = 2, K$^+$ and Br$^-$ at [KBr] = 2, Mg$^{2+}$ and Cl$^-$ at [MgCl$_2$] = 2, and Ba$^{2+}$ and Cl$^-$ at [BaCl$_2$] = 2 M, where $r$ is the distance from the center of the respective ion.

Experimental data have been fitted in similar agreement (not shown) using different values, $O_i^ω = 16$ for example, resulting in slight differences in $R_{i}^{\text{Born}}(C^B_i)$. Nonetheless, if more experimental data on $O_i^ω$ are available as given in [36, 41] for more ions, the DHPF model may provide more accurate description of physical properties as illustrated in these figures.

We make a note on the generalized $l_{D\text{PF}}$ and original $l_D$ Debye length in these results. The only difference between $l_{D\text{PF}}$ and $l_D$ is due to the term $-C^B_i \Lambda q^2_i$ in (16). Note that $\lim_{C^B_i \to \infty} l_D = 0$ and $\lim_{C^B_i \to \infty} \Lambda = \text{constant}$, which imply that $l_{D\text{PF}}$ deviates more from $l_D$ at higher concentrations. However, for [NaCl] = 2 M for instance, we obtained $l_{D\text{PF}} - l_D = 2.201 - 2.157 = 0.044$ Å, i.e., the difference is not significant in the range of salt concentrations considered in this study.

Finally, we remark on some future applications of the DHPF model (43) to fit or study experimental data of various ionic activities as summarized in [20, 37, 40, 45, 46, 47, 48] to name a few. As seen from Tables 4.1 and 4.2, our model requires only three adjustable parameters $\alpha_i^1$, $\alpha_i^2$, and $\alpha_i^3$ that are based solely on the crucial Born radius $R_{i}^{\text{Born}}(C^B_i)$, which is unknown and depends in a very complex and complicated way on physical interactions between ions and water molecules at variable concentration, composition, temperature, and pressure etc. Since our model includes the temperature $T$ and the steric effect $S_{\text{strc}}(r)$ that is equivalent the pressure effect, the same Born radius $R_{i}^{\text{Born}}(C^B_i)$ formula in (12) can be applied to experimental data with variable temperature, pressure, and mixtures of different salts as...
5. CONCLUSION

A generalized Debye-Hückel equation has been derived and analyzed from the Poisson-Fermi theory that accounts for the steric, correlation, and polarization effects of ions and water in aqueous electrolyte solutions at variable composition, concentration, temperature, and pressure. A new Debye length is proposed to include the size effect of ions and water. The new equation and length have been shown to reduce to their classical counterparts when these three effects are ignored. We have also shown that the generalized DH model is not an extended Debye-Hückel model since their approximations of the Born solvation energy are inversely different in salt concentration. Numerical results have been given to show the difference between an extended DH model by Hückel and the generalized DH model with two and three adjustable parameters, respectively. A detailed description regarding to the results of these models and parameters is also provided. We have shown with numerical evidence that classical extended DH models fail to describe properly the physical meaning of their parameters. By contrast, numerical results illustrate the significant order of our parameters that are based on the Born solvation energy with an unknown Born radius that varies with variable concentration, composition, temperature, and pressure in a complex and complicated way.

Acknowledgement. This work was supported by the Ministry of Science and Technology, Taiwan (No. MOST 105-2115-M-007-016-MY2 to J.L.L.).

[1] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions, Adv. Coll. Interf. Sci. 152, 48-88 (2009).
[2] M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, Double layer in ionic liquids: Overscreening versus crowding, Phys. Rev. Lett. 106, 046102 (2011).
[3] D. Bashford and D. A. Case, Generalized Born models of macromolecular solvation effects, Annu. Rev. Phys. Chem. 51, 129-152 (2000).
[4] H. M. Berman et al., The protein data bank, Nucleic Acids Res. 28, 235-242 (2000).
[5] M. Born, Volumen und hydratationswärme der ionen, Z. Phys. 1, 45-48 (1920).
[6] D. L. Chapman, A contribution to the theory of electrocapillarity, Phil. Mag. 25, 475-481 (1913).
[7] I-L. Chern, J.-G. Liu, and W.-C. Wang, Accurate evaluation of electrostatics for macromolecules in solution, Methods Appl. Anal. 10, 309-328 (2003).
[8] P. Debye and E. Hückel, Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen (The theory of electrolytes. I. Lowering of freezing point and related phenomena), Phys. Zeitschr. 24, 185-206 (1923).
[9] B. Eisenberg, Interacting ions in Biophysics: Real is not ideal, Biophys. J. 104, 1849-1866 (2013).
[10] W. R. Fawcett, Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details (Oxford University Press, New York, 2004).
[11] W. R. Fawcett and A. C. Tikanen, Role of solvent permittivity in estimation of electrolyte activity coefficients on the basis of the mean spherical approximation, J. Chem. Phys. 100, 4251-4255 (1996).
[12] D. Fraenkel, Simplified electrostatic model for the thermodynamic excess potentials of binary strong electrolyte solutions with size-dissimilar ions, Mol. Phys. 108, 1435 (2010).
[13] D. Fraenkel, Negative deviations from the Debye-Hückel limiting law for high-charge polyvalent electrolytes: Are they real?, J. Chem. Theory Comput. 14, 2609-2620 (2018).
[14] W. Geng, S. Yu, and G. Wei, Treatment of charge singularities in implicit solvent models, J. Chem. Phys. 127, 114106 (2007).
[15] M. Gouy, Sur la constitution de la charge électrique à la surface d’un électrolyte (Constitution of the electric charge at the surface of an electrolyte), J. Phys. 9, 457-468 (1910).
[16] L. Gross, et al., The chemical structure of a molecule resolved by atomic force microscopy, Science 325, 1110-1114 (2009).
[17] B. Hille, Ionic Channels of Excitable Membranes (Sinauer Associates Inc., Sunderland, MA, 2001).
[18] E. Hückel, Zur Theorie konzentrierterer wässeriger Lösungen starker Elektrolyte, Phys. Z. 26, 93-147 (1925).
[19] G. M. Kontogeorgis and G. K. Folas, Thermodynamic Models for Industrial Applications:
From Classical and Advanced Mixing Rules to Association Theories (John Wiley & Sons, 2009).

[20] G. M. Kontogeorgis, B. Maribo-Mogensen, and K. Thomsen, The Debye-Hückel theory and its importance in modeling electrolyte solutions, Fluid Phase Equil. 462, 130-152 (2018).

[21] E. Kreyszig, Advanced Engineering Mathematics (Wiley, 1st ed. 1962, 10th ed. 2011).

[22] W. Kunz, Specific Ion Effects (World Scientific, Singapore 2010).

[23] K. J. Laidler, J. H. Meiser, and B. C. Sanctuary, Physical Chemistry (Houghton Mifflin Co., Boston, 2003).

[24] G. Lebon, D. Jou, and J. Casas-Vázquez, Understanding Non-equilibrium Thermodynamics: Foundations, Applications, Frontiers (Springer, 2008).

[25] B. P. Lee and M. E. Fisher, Density fluctuations in an electrolyte from generalized Debye-Hueckel theory, Phys. Rev. Lett. 76, 2906 (1996).

[26] J.-L. Liu, Numerical methods for the Poisson-Fermi equation in electrolytes, J. Comput. Phys. 247, 88-99 (2013).

[27] J.-L. Liu and B. Eisenberg, Correlated ions in a calcium channel model: a Poisson-Fermi theory, J. Phys. Chem. B 117, 12051-12058 (2013).

[28] J.-L. Liu and B. Eisenberg, Poisson-Nernst-Planck-Fermi theory for modeling biological ion channels, J. Chem. Phys. 141, 22D532 (2014).

[29] J.-L. Liu and B. Eisenberg, Analytical models of calcium binding in a calcium channel, J. Chem. Phys. 141, 075102 (2014).

[30] J.-L. Liu and B. Eisenberg, Numerical methods for a Poisson-Nernst-Planck-Fermi model of biological ion channels, Phys. Rev. E 92, 012711 (2015).

[31] J.-L. Liu and B. Eisenberg, Poisson-Fermi model of single ion activities in aqueous solutions, Chem. Phys. Lett. 637, 1-6 (2015).

[32] J.-L. Liu and B. Eisenberg, Poisson-Fermi modeling of ion activities in aqueous single and mixed electrolyte solutions at variable temperature, J. Chem. Phys. 148, 054501 (2018).

[33] J.-L. Liu, H.-j. Hsieh, and B. Eisenberg, Poisson-Fermi modeling of the ion exchange mechanism of the sodium/calcium exchanger, J. Phys. Chem. B 120, 2658-2669 (2016).

[34] J.-L. Liu, D. Xie, and B. Eisenberg, Poisson-Fermi formulation of nonlocal electrostatics in electrolyte solutions, Mol. Based Math. Biol. 5, 116-124 (2017).

[35] J. Newman, Electrochemical Systems (Prentice-Hall, NJ, 1991).
[36] J. Mähler and I. Persson, A study of the hydration of the alkali metal ions in aqueous solution, Inorg. Chem. **51**, 425 (2011).

[37] K. S. Pitzer, *Thermodynamics* (McGraw Hill, New York, 1995).

[38] A. A. Rashin and B. Honig, Reevaluation of the Born model of ion hydration, J. Phys. Chem. **89**, 5588-5593 (1985).

[39] R. Robinson and R. Stokes, *Electrolyte Solutions* (Butterworths Scientific Publications, London, 1959); (Dover Publications, New York, 2002).

[40] D. Rowland, E. Königsberger, G. Hefter, and P. M. May, Aqueous electrolyte solution modelling: Some limitations of the Pitzer equations, Appl. Geochem. **55**, 170 (2015).

[41] W. W. Rudolph and G. Irmer, Hydration of the calcium(II) ion in an aqueous solution of common anions (ClO$_4^-$, Cl$^-$, Br$^-$, and NO$_3^-$), Dalton Trans. **42**, 3919 (2013).

[42] C. D. Santangelo, Computing counterion densities at intermediate coupling, Phys. Rev. E **73**, 041512 (2006).

[43] I. Y. Shilov and A. K. Lyashchenko, The role of concentration dependent static permittivity of electrolyte solutions in the Debye–Hückel theory, J. Phys. Chem. B **119**, 10087-10095 (2015).

[44] M. Valiskó, D. Boda, Unraveling the behavior of the individual ionic activity coefficients on the basis of the balance of ion-ion and ion-water interactions, J. Phys. Chem. B **119**, 1546 (2015).

[45] J. H. Vera and G. Wilczek-Vera, *Classical Thermodynamics of Fluid Systems: Principles and Applications* (CRC Press, 2016).

[46] W. Voigt, Chemistry of salts in aqueous solutions: Applications, experiments, and theory, Pure Appl. Chem. **83**, (2011) 1015-1030.

[47] W. Voigt, et al., Quality assurance in thermodynamic databases for performance assessment studies in waste disposal, Pure and applied chemistry **79**, 883-894 (2007).

[48] G. Wilczek-Vera, E. Rodil, and J. H. Vera, On the activity of ions and the junction potential: Revised values for all data, AIChE. J. **50**, 445 (2004).