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This paper deals with the problem of a mixture of hard spherical ions and central point dipoles, described within the mean-spherical approximation (MSA). In this non-primitive model, the species have different diameters (unrestricted case). The first purpose of this work is to establish clear and valid equations for this problem and present a method to solve them. Formulas for the pressure, the internal and Helmholtz energies, and the chemical potentials of the species are given and discussed. The results are illustrated by considering a binary 1-1 electrolyte solution in a water-like dipolar solvent.

Keywords: Electrolytes; non-primitive; mean-spherical approximation (MSA); unrestricted case; dipoles.

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I.   INTRODUCTION

In the last decades, numerical simulations of solutions have been developed at a rapid pace. They have reached an appreciable level of reliability, but they are generally time-consuming and not always suitable for practical applications.

The case of electrolyte solutions is challenging because it involves long- and short-range electrostatic forces, the effect of which is not easy to account for. There seems to be presently a renewed interest, and a significant demand, for analytic electrolyte models aimed at applications in various areas, such as industrial chemistry, food processing, refrigeration, oil industry, geochemistry, water treatment, and environmental chemistry.

Two types of analytic models may be distinguished, namely those that regard the solvent as a continuum ('primitive' models with implicit solvent), and those that explicitly consider the solvent ('non-primitive' models). The latter may provide more information over the former and have a higher degree of predictability, but they also represent a much more difficult task.

Explicit solvent models for ionic solutions include some chemical engineering models[1,2], such as electrolyte-NRTL[3,4] or UNIQUAC[5], and more refined descriptions based on the statistical-associated fluid theory (SAFT)[6]. In the latter case, the semi-restricted non-primitive MSA model for a mixture of ions and dipoles (MSA-ID)[7–10] has been employed in a few studies[11,12] in order to account for the effect of electrostatic interactions between all species (ion-ion, ion-solvent and solvent-solvent), and that of volume exclusion. Here, semi-restricted (denoted as SR hereafter) means that all ions have the same diameter, and it is different from that of the solvent. In the MSA-ID model, the water and the ions are represented as hard spheres bearing a central point dipole, and charged hard spheres, respectively.

An important point is that valid equations are available for the SR MSA-ID[9,10,12–14]. Thus the SR case constitutes a reference for testing equations derived in the general unrestricted case, where the ions and the solvent dipoles are all of different diameters.

The unrestricted case was first tackled by L. Blum[†15] who showed that the MSA equations could be solved by using an invariant expansion formalism[16], in order to properly account for angular correlations involving the dipoles. In subsequent work, expressions for the thermodynamic properties were obtained[8]. The derivation undertaken by L. Blum constituted a

real *tour de force*. However, the value of this achievement has not been fully recognized because the unrestricted case resulted in very numerous and cumbersome equations, for which the method of solution was not quite clear. Moreover, some printed equations contained typographical errors. It seems that these issues have deterred investigators from using these formulas subsequently.

A clear and complete solution to the original unrestricted MSA-ID model is still missing. This is a regrettable situation since most of the (very hard) work has already been done. A solution would be interesting from a fundamental point of view, and it could be used for applications, possibly in conjunction with other contributions (e.g., within the SAFT framework) so as to compensate for deficiencies of the MSA.

In the present study, the following methodology was employed. The papers published about the topic[8,15,17] were analyzed closely. Every relation was cross-examined between the available references. Misprints were identified by checking the consistency of the equations, their homogeneity, and by ensuring that the relations in the SR case[9] were recovered when the sizes of the ions were taken to be equal. The minimum set of equations to solve was determined, and dimensionless parameters were introduced for the unknowns (similarly to the SR case). The same approach was employed as regards the thermodynamic properties. This led to an expression of the electrostatic pressure, and to a discussion of the Helmholtz energy, and ion and solvent chemical potentials.

The structure of this article is as follows. The next section outlines the equations derived for an ion-dipole mixture within the MSA. A method is proposed to solve the set of equations. The thermodynamic properties of the system are described and discussed. The third section is devoted to an illustration, in which a binary electrolyte of a 1-1 salt in a dipolar solvent mimicking water is considered. The set of MSA equations is solved numerically, and the consistency of the equations is verified for this solution. Then the main features exhibited by the thermodynamic quantities are analyzed. Finally, the results are summarized and some prospects are presented in the conclusion section.

II. THE MSA-ID MODEL

Hereafter, we will denote Ref. 15 by B0, Ref. 8 by BW1, Ref. 17 by BW2, and Ref. 9 by BVF.

A. General relations

In this work we consider a mixture of hard spherical cations and anions, and hard spheres with a centrally embedded point dipole (the solvent), as a model of electrolyte solution. As in B0, BW1 and BW2 the number of ions will be $n-1$, and the solvent will be denoted by index n. The dipole moment of the solvent particles is m_n. The valence and diameter of an ion i are Z_i, and σ_i, respectively. A priori, the diameters σ_k $(k=1,\ldots,n)$ are all different. A binary 1-1 electrolyte is sketched in Figure 1.
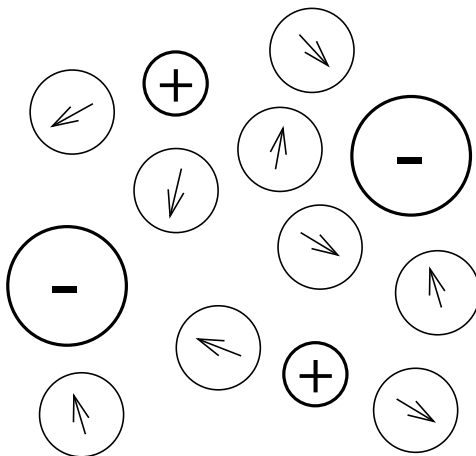

FIG. 1. Sketch of a binary ion-dipole mixture considered in this work. All species have different diameters.

The method devised by L. Blum to solve the equations of the MSA-ID model is quite involved. Its basic principles were reported in 1978 in B0. A fundamental tool was the use of the invariant expansion formalism[16,18,19] for describing the correlations involving the dipoles, which depend on their angular orientations.

The rotational invariants will be denoted as $\Phi^{mnl}(12)$, with $\{m,n,l\}$ being a set of integers, and '12' representing the vector $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. They are functions of the sole mutual orientations of the particles located at 1 and 2 (for $\{m,n,l\} \neq \{0,0,0\}$).

With this formalism, the pair potential between two particles may be written as follows[20]. For two ions i and j of charges q_i and q_j at positions 1 and 2, respectively, one has,

$$u_{ij}(12) = u_{ij}^{000}(r)\,\Phi^{000}(12), \tag{1}$$

4

in which $r = r_{12}$, and,

$$u_{ij}^{000}(r) = u_{ij}^{HS}(r) + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r}, \qquad \Phi^{000}(12) = 1, \tag{2}$$

with $u_{ij}^{HS}(r)$ the hard sphere (HS) interaction potential, $u_{ij}^{HS} = +\infty$ for $r < \sigma_{ij}$ and $=0$ otherwise, in which,

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2$$

For an ion i at position 1 and a dipole n at position 2,

$$u_{in}(12) = u_{in}^{000}(r) \, \Phi^{000}(12) + u_{in}^{011}(r) \, \Phi^{011}(12), \tag{3}$$

with $u_{in}^{000}(r) = u_{in}^{HS}(r)$ and,

$$u_{in}^{011}(r) = -\frac{1}{4\pi\epsilon_0} \frac{q_i \, m_n}{r^2}, \quad \text{and} \quad \Phi^{011}(12) = \widehat{\mathbf{r}} \cdot \widehat{\mathbf{m}}_\mathbf{n}(2), \tag{4}$$

in which $\widehat{\mathbf{m}}_\mathbf{n}(2) = \mathbf{m}_n(2)/m_n$ is the unit vector along the dipole $\mathbf{m}_n(2)$ at position 2, and $\widehat{\mathbf{r}}$ is the unit vector $\mathbf{r_{12}}/r_{12}$.

When a dipole is at position 1 and an ion j at 2 one has,

$$u_{nj}(12) = u_{nj}^{000}(r) \, \Phi^{000}(12) + u_{nj}^{101}(r) \, \Phi^{101}(12), \tag{5}$$

with $u_{nj}^{000} = u_{jn}^{000} = u_{jn}^{HS}$ and,

$$u_{nj}^{101}(r) = \frac{1}{4\pi\epsilon_0} \frac{m_n \, q_j}{r^2}, \quad \text{and} \quad \Phi^{101}(12) = \widehat{\mathbf{m}}_\mathbf{n}(1) \cdot \widehat{\mathbf{r}}, \tag{6}$$

For two dipoles located at 1 and 2,

$$u_{nn}(12) = u_{nn}^{000}(r) \, \Phi^{000}(12) + u_{nn}^{112}(r) \, \Phi^{112}(12), \tag{7}$$

with $u_{nn}^{000}(r) = u_{nn}^{HS}(r)$, and,

$$u_{nn}^{112}(r) = -\frac{1}{4\pi\epsilon_0} \frac{m_n{}^2}{r^3}, \quad \text{and} \quad \Phi^{112}(12) = 3(\widehat{\mathbf{m}}_\mathbf{n}(1) \cdot \widehat{\mathbf{r}})(\widehat{\mathbf{m}}_\mathbf{n}(2) \cdot \widehat{\mathbf{r}}) - \widehat{\mathbf{m}}_\mathbf{n}(1) \cdot \widehat{\mathbf{m}}_\mathbf{n}(2). \tag{8}$$

With these notations the radial distribution functions (RDF's) for ion-ion, ion-dipole, dipole-ion, and dipole-dipole, are formally given by[19,20],

$$g_{ij}(12) = g_{ij}^{000}(r) \, \Phi^{000}(12) = g_{ij}^{000}(r), \tag{9}$$

$$g_{in}(12) = g_{in}^{000}(r) \, \Phi^{000}(12) + h_{in}^{011}(r) \, \Phi^{011}(12), \tag{10}$$

$$g_{ni}(12) = g_{ni}^{000}(r)\,\Phi^{000}(12) + h_{ni}^{101}(r)\,\Phi^{101}(12), \tag{11}$$

$$g_{nn}(12) = g_{nn}^{000}(r)\,\Phi^{000}(12) + h_{nn}^{110}(r)\,\Phi^{110}(12) + h_{nn}^{112}(r)\,\Phi^{112}(12), \tag{12}$$

in which i and j designate ions. These relations contain functions denoted by h, rather than g, because they tend to zero when $r \to 0$[21], as the total correlation function $h = g - 1$ does in simple systems.

A $\{110\}$ contribution appears in g_{nn}, which is not present in u_{nn}, with,

$$\Phi^{110}(12) = \widehat{\mathbf{m}}_{\mathbf{n}}(1) \cdot \widehat{\mathbf{m}}_{\mathbf{n}}(2), \tag{13}$$

In the case of an ion-dipole mixture in the MSA, only the rotational invariants appearing in the above equations are involved in the expansions of the RDF's[20,22].

The functions g and h satisfy the following relations[20],

$$g_{ij}^{000} = g_{ji}^{000}, \qquad g_{in}^{000} = g_{ni}^{000}, \qquad h_{in}^{011} = -h_{ni}^{101}. \tag{14}$$

in which i and j denote ions.

B. Basic equations

Many relations are reported in references B0, BW1, and BW2. The first task was to identify the equations required to solve the problem. The notations of BW1 and BW2 will be used, except for B^{10}, Ω^{10}, and χ_1 that will be replaced by B, Ω, and χ for convenience.

The first three fundamental equations (Eqs. (1.29), (1.30) and (1.32) of BW1) are,

$$\sum_{i=1}^{n-1} \rho_i\,(a_i^0)^2 + \rho_n\,(a_n^1)^2 = \alpha_0{}^2, \tag{15}$$

$$-\sum_{j=1}^{n-1} \rho_j\,a_j^0\,K_{nj}^{10} + a_n^1\,(1 - \rho_n\,K_{nn}^{11}) = \alpha_0\,\alpha_2, \tag{16}$$

$$\rho_n \sum_{j=1}^{n-1} \rho_i\,(K_{nj}^{10})^2 + (1 - \rho_n\,K_{nn}^{11})^2 = y_1{}^2 + \rho_n\,\alpha_2{}^2, \tag{17}$$

In these expressions, ρ_i is the number density of species i ($\rho_i = N_i/V$, with N_i the number of particles i and V the volume), and,

$$\alpha_0{}^2 = \beta e^2/\epsilon_0, \qquad \alpha_2{}^2 = \beta m_n{}^2/(3\epsilon_0), \qquad y_1 = \beta_6/\beta_{12}{}^2, \tag{18}$$

6

$$\beta_6 = 1 - b_2/6, \qquad \beta_{12} = 1 + b_2/12.$$

The definitions of α_0 and α_2 are Eqs. (1.18) and (1.19) of BW1 in the SI unit system, $\beta = 1/(k_B T)$ (with T the temperature and k_B the Boltzmann constant), e is the charge of a proton, ε_0 is the permittivity of a vacuum, and b_2 is a dimensionless parameter characteristic of the dipole-dipole interaction[9].

In Eqs. (15)-(17), a_i^0 (for $i \neq n$) and a_n^1 are given by Eq. (1.39) of BW1,

$$a_i^0 = \frac{\beta_6}{\sigma_i D_a} \left(\frac{1}{2} Z_i \beta_6 - D_i^G - \frac{\pi \sigma_i^2}{2\Delta} \sum_{k=1}^{n-1} \rho_k \, \sigma_k \, D_k^G \right), \tag{19}$$

$$a_n^1 = \frac{\beta_6}{2D_a} \left(\frac{1}{2} \sigma_n B + \frac{\Omega \beta_3}{D \beta_6{}^2} \right), \tag{20}$$

with,

$$B = \sum_{k=1}^{n-1} \rho_k Z_k m_k, \qquad D = 1 + \frac{\rho_n \sigma_n{}^2}{4\beta_6{}^2} \sum_{k=1}^{n-1} \rho_k (\sigma_k m_k)^2, \tag{21}$$

$$S_m = \frac{\pi}{2\Delta} \sum_{k=1}^{n-1} \rho_k \sigma_k{}^2 m_k, \qquad \eta_i = \frac{1}{\beta_6} \left(m_i + \sigma_i S_m \right), \tag{22}$$

$$D_k^F = \frac{1}{2} \left[\beta_6 (N_k \sigma_k + Z_k) - \frac{1}{12} \rho_n \sigma_n{}^3 B \sigma_k m_k \right], \qquad \Omega = \sum_{k=1}^{n-1} \rho_k \, \sigma_k \, m_k \, D_k^F, \tag{23}$$

$$D_k^G = D_k^F - \rho_n \sigma_n{}^2 \, \Omega \, \sigma_k m_k / (4 D \beta_6{}^2), \qquad D_{ac} = \sum_{k=1}^{n-1} \rho_k (D_k^F)^2, \tag{24}$$

$$D_a = \frac{1}{D} \left\{ D_{ac} + \frac{1}{32} \rho_n \sigma_n{}^2 \sum_{\{i,j\}=1}^{n-1} \rho_i \rho_j \left[(N_i \sigma_i + Z_i) m_j \sigma_j - (N_j \sigma_j + Z_j) m_i \sigma_i \right]^2 \right\}. \tag{25}$$

In the latter expression, the summation is performed for both $\{i = i_0, j = j_0\}$ and $\{i = j_0, j = i_0\}$.

The expressions for D_a in BW1 and BW2 (Eqs. (1.40) and (2.12), respectively) are different from Eq. (25). They contain a minus sign after the term D_{ac}. This seems to be a misprint. Here this sign has been changed to a plus (+) sign. This modification ensures that Eq. (62) below is fulfilled, and it gives consistent results when numerically solving the system of equations (see Sec. III B below). It is not so if the minus sign is used.

In Eqs. (15)-(17), K_{ij}^{mn} is given by the general relation (Eq. (39) of B0 or (1.31) of BW1),

$$K_{ij}^{mn} \equiv \int_{\lambda_{ji}}^{\sigma_{ij}} Q_{ij}^{mn}(r) \, dr. \tag{26}$$

in which $\lambda_{ji} = (\sigma_j - \sigma_i)/2$, and Q_{ij}^{mn} is the Baxter factor correlation function (see, e.g., B0). Its expression is given in Eq. (1.34) of BW1,

$$Q_{ij}^{mn}(r) = \frac{1}{2}(r - \sigma_{ij})(r - \lambda_{ji})\,\alpha_{ij}^{mn} + (r - \sigma_{ij})\,\beta_{ij}^{mn}, \tag{27}$$

in which the parameters α_{ij}^{mn} and β_{ij}^{mn} will be defined below.

Another quantity related to Q_{ij}^{mn} is P_{ij}^{mn}, which is defined in BW1 by Eqs. (1.35) and (1.36), but these relations are incorrect. They may be obtained instead by considering Eq. (41) of B0, which suggests that,

$$P_{ij}^{mn} = -Q_{ij}^{mn}(\lambda_{ji}) + Z_i\,a_j^0, \tag{28}$$

By virtue of Eq. (27) one has, for $j \neq n$, $Q_{ij}^{mn}(\lambda_{ji}) = -\sigma_i\,\beta_{ij}^{mn}$, so that one gets from Eq. (28),

$$P_{ij}^{mn} = \sigma_i\,\beta_{ij}^{mn} + Z_i\,a_j^0, \tag{29}$$

for any $i = 1, \ldots, n$ (but $j \neq n$). For $j = n$, one has,

$$P_{in}^{mn} = \sigma_i\,\beta_{in}^{mn} + Z_i\,a_n^1. \tag{30}$$

For any i and j, the P's should satisfy the symmetry relations,

$$P_{ij}^{mn} = P_{ji}^{nm}. \tag{31}$$

instead of Eqs. (1.35) and (1.36) of BW1.

It was mentioned in BW1 that the P's should satisfy the following relations ('sum rules'),

$$\sum_{k=1}^{n-1}(\delta_{kj} + \frac{1}{2}\,\rho_k\,\sigma_j\,P_{kj}^{00})\,D_k^F = \frac{1}{2}\,Z_j\beta_6, \tag{32}$$

for $j = 1, \ldots, n-1$, with δ_{kj} the Kronecker symbol ($\delta_{kj} = 1$ when $k = j$, and $=0$ otherwise), and,

$$\sum_{k=1}^{n-1}\rho_k\,P_{kn}^{01}\,D_k^F = \frac{1}{2}\,\sigma_n\,B. \tag{33}$$

for the solvent.

The P's are expressed explicitly by Eq. (1.38) of BW1. The expressions for the β's are then found using Eqs. (29) and (30). One has,

$$\beta_{ij}^{00} = \frac{\pi}{\Delta}\,\sigma_j - \frac{1}{2D\beta_6}\,\rho_n\sigma_n{}^2 m_i\eta_j + \left(\frac{2}{\beta_6}\,D_i^G - Z_i\right)\frac{1}{\sigma_i}\,a_j^0, \tag{34}$$

8

$$\beta_{in}^{00} = \frac{\pi}{\Delta}\,\sigma_n, \qquad \beta_{nj}^{00} = \frac{\pi}{\Delta}\,\sigma_j, \tag{35}$$

$$\beta_{in}^{01} = -\frac{\beta_3}{\beta_6{}^2}\,\frac{m_i}{D} + \left(\frac{2}{\beta_6}\,D_i^G - Z_i\right)\frac{1}{\sigma_i}\,a_n^1, \qquad \beta_{nj}^{10} = \frac{1}{D}\left(\eta_j + \frac{1}{\beta_6{}^2}\,\Omega a_j^0\right), \tag{36}$$

in which i and j designate ions, and,

$$1 + \frac{1}{2}\,\rho_n\sigma_n{}^2\beta_{nn}^{11} = \frac{1}{D}\left(\frac{\beta_3}{\beta_6} + \frac{1}{2\beta_6{}^2}\,\rho_n\sigma_n{}^2\,\Omega\,a_n^1\right), \tag{37}$$

In Eq. (34), Δ is defined by,

$$\Delta = 1 - \frac{\pi}{6}\sum_{k=1}^{n}\rho_k\,\sigma_k{}^3. \tag{38}$$

in which the summation is done on *all* species (contrary to Eq. (54) of B0; see the discussion following Eq. (60)).

It will be useful below to write,

$$\beta_{ij}^{00} = \beta_{ij}^{00,HS} + \beta_{ij}^{00,el}, \tag{39}$$

for ions i and j where,

$$\beta_{ij}^{00,HS} = \frac{\pi}{\Delta}\,\sigma_j, \tag{40}$$

is the purely HS contribution to β_{ij}^{00}, and,

$$\beta_{ij}^{00,el} = -\frac{1}{2D\beta_6}\,\rho_n\sigma_n{}^2\,m_i\eta_j + \left(\frac{2}{\beta_6}\,D_i^G - Z_i\right)\frac{a_j^0}{\sigma_i}. \tag{41}$$

is its electrostatic part.

The α's appearing in Eq. (27) may be obtained conveniently from a relation given between Eqs. (2.10) and (2.11) of Ref. 23,

$$\alpha_{ij}^{mn} = -\frac{12}{\sigma_i{}^3}\,K_{ij}^{mn} - \frac{6}{\sigma_i}\,\beta_{ij}^{mn}, \tag{42}$$

By using this relation, and Eqs. (27) and (26), one obtains,

$$\alpha_{ij}^{00} = \frac{\pi}{\Delta}\left(2 + \sum_{k=1}^{n}\rho_k\sigma_k{}^2\beta_{kj}^{00} + \chi a_j^0\right), \tag{43}$$

$$\alpha_{in}^{00} = \frac{2\pi}{\Delta}\left(1 + \frac{3}{\Delta}\,\sigma_n X_2\right) \qquad \alpha_{nj}^{00} = \frac{2\pi}{\Delta}\left(1 + \frac{3}{\Delta}\,\sigma_j X_2\right), \tag{44}$$

$$\alpha_{in}^{01} = \frac{\pi}{\Delta}\left(\sum_{k=1}^{n}\rho_k\sigma_k{}^2\beta_{kn}^{01} + \chi a_n^1\right) \qquad \alpha_{nj}^{10} = \frac{b_2}{\beta_6\sigma_n}\,\beta_{nj}^{10} + \frac{1}{\beta_6}\,Ba_j^0, \tag{45}$$

9

in which i and j designate ions, and,

$$\alpha_{nn}^{11} = 2\frac{b_2}{\beta_6 \rho_n \sigma_n{}^3}\left(1 + \frac{1}{2}\rho_n \sigma_n{}^2 \beta_{nn}^{11}\right) + \frac{1}{\beta_6}Ba_n^1, \tag{46}$$

In these equations,

$$X_2 = \frac{\pi}{6}\sum_{k=1}^{n}\rho_k \sigma_k{}^2, \qquad \chi = \sum_{k=1}^{n-1}\rho_k Z_k \sigma_k. \tag{47}$$

The summations in Eqs. (43) and (45) run over all species. This will ensure that one recovers the Percus-Yevick RDF at contact in Sec. II E below.

It stems from Eq. (27) that α_{ij}^{mn} is the second derivative of $Q_{ij}^{mn}(r)$ w.r.t. r. For this reason α_{ij}^{00} for ions was denoted by Q_j'' in B0 and in Ref. 24. It does not depend on i, as may be seen in Eqs. (43)-(44). It was checked that, if Eq. (43) is taken in the case of the primitive model ($\rho_n = 0$), it yields the expression for Q_j'' reported in Eq. (2.12) of Ref. 24 (by using the relation $\sum_k \rho_k \sigma_k(N_k \sigma_k + z_k) = P_n{}^{25}$).

It was also found that the first 2 equations of Eq. (1.50) of BW1 for K_{ij}^{00} and K_{in}^{01} contain a minus sign after the term δ_{ik}. They must be changed to a plus (+) sign. This modification yields the relations for α_{ij}^{00} and α_{in}^{01} above.

In the next section we will need the value of the derivative of $Q_{ij}^{mn}(r)$ w.r.t. r at contact $(r = \sigma_{ij})$, denoted by Q'^{mn}_{ij}. It stems from Eq. (27) that,

$$Q'^{mn}_{ij} = \beta_{ij}^{mn} + \frac{1}{2}\alpha_{ij}^{mn}\sigma_i. \tag{48}$$

C. Introduction of dimensionless energy parameters

In the above equations, the m_i's, N_i's and b_2 are the unknowns to be determined. These parameters correspond to ion-ion (N_i), ion-solvent (m_i) and solvent-solvent (b_2) interactions, as shown by their definition in Eq. (1.40) of BW1. There is one N_i and one m_i for every ion in solution. Thus, for a solution comprised of n_C cations and n_A anions, this makes $2(n_C + n_A) + 1$ unknown parameters to determine.

The dimension of N_i is L^{-1}, that of m_i is L (with L denoting a length), and b_2 is dimensionless. It is useful to introduce new dimensionless parameters. This may be done by first considering the SR case for a binary 1-1 electrolyte (cation 1 and anion 2), for which $\sigma_1 = \sigma_2 = \sigma$. In that case, the use of Eqs. (1.26) and (1.40) of BW1 leads to, $N_1 = -N_2 = N$

10

and $m_1 = -m_2 = m$. From Eq. (2.2) of BW1 one has,

$$N = \frac{1}{\sigma} b_0, \qquad (49)$$

with b_0 the dimensionless ion-ion energy parameter in the SR case (see BVF). This relation results from the definition of N_i and B_i in Eq. (1.40) of BW1, and of b_0 in Eq. (11) of BVF.

Besides, the definition of B in Eq. (1.40) of BW1 gives $B = 2\rho m$, and Eq. (2.5) of BW1 gives a relation between B and b_1 (the dimensionless ion-solvent energy parameter; see Eq. (12) of BVF). From these two relations we get,

$$m = \frac{1}{\sqrt{2\rho\rho_n}} \frac{1}{\sigma\sigma_n} b_1, \qquad (50)$$

Eqs. (49) and (50) suggest the introduction of new dimensionless parameters, $b_0^{(k)}$ and $b_1^{(k)}$, for each ion k, as,

$$N_k = \frac{Z_k}{\sigma_k} b_0^{(k)}, \qquad (51)$$

$$m_k = \frac{1}{\sqrt{2\rho\rho_n} \, \sigma_n} \frac{Z_k}{\sigma_k} b_1^{(k)}. \qquad (52)$$

These definitions will be used in Sec. III for an application of the model.

D. RDF's at contact

The contact values of the RDF's will be required in the next section. They can be obtained from Eq. (3.3) in BW2 (Eq. (3.7) of BW1 contains misprints in the superscripts),

$$g_{ij,c}^{000} = Q'^{00}_{ij}/(2\pi\sigma_{ij}) \quad (\{i,j\} = 1,\ldots,n), \qquad h_{in,c}^{011} = -\sqrt{3}\,Q'^{01}_{in}/(2\pi\sigma_{in}) \quad (i = \text{ion}), \quad (53)$$

$$h_{nn,c}^{110} = (Q'^{11}_{nn} + 2q')/(2\sqrt{3}\pi\sigma_n), \qquad h_{nn,c}^{112} = \sqrt{10}(Q'^{11}_{nn} - q')/(2\sqrt{3}\pi\sigma_n), \qquad (54)$$

in which subscript c indicates that the RDF is taken at contact of the species, Q' is given by Eq. (48), the sign of $h_{in,c}^{011}$ in BW1 has been reversed so that it is positive for a cation and negative for an anion (see the example in Sec. III B 2), and q' is defined by,

$$q' = -\frac{b_2}{\rho_n\sigma_n{}^2} \frac{\beta_{24}}{\beta_{12}{}^2}. \qquad (55)$$

with $\beta_{24} = 1 - b_2/24$.

This expression is different from Eq. (3.10) of BW1. The term $\rho_n\sigma_n{}^2$ was added to the denominator of q' so as to recover the corresponding term in the SR case (note that q' does

not have exactly the same definition in BVF). The presence of this term ensures that Eq. (55) is homogeneous. Indeed q' has the same dimension as Q', as seen Eq. (54), which is that of a length since g and h are dimensionless.

One has,

$$h_{ni,c}^{101} = -h_{in,c}^{011}. \tag{56}$$

which stems from Eq. (14). It was verified analytically that this relation is indeed satisfied by using Eqs. (19)-(25), (36), and (48). This type of verification brings support to the validity and consistency of the set of equations involved in the test.

It will be useful to break down the ion-ion RDF's, $g_{ij,c}^{000}$, into HS and electrostatic contributions. This may be done by using Eqs. (34), (43), and (48), which yields,

$$Q'_{ij}^{00} = \beta_{ij}^{00} + \frac{\pi\sigma_i}{\Delta} + \frac{\pi\sigma_i}{2\Delta} \sum_{k=1}^{n} \rho_k \sigma_k{}^2 \beta_{kj}^{00} + \frac{\pi}{2\Delta} \sigma_i \chi a_j^0, \tag{57}$$

In this relation, β_{kj}^{00} may be split into HS and electrostatic parts (Eqs. (40) and (41)). This way, and by virtue of Eq. (53), one gets,

$$g_{ij,c}^{000} = g_{ij,c}^{000,HS} + g_{ij,c}^{000,el}, \tag{58}$$

where,

$$g_{ij,c}^{000,HS} = \frac{1}{\Delta} + \frac{3}{\Delta^2} \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} X_2, \tag{59}$$

and,

$$g_{ij,c}^{000,el} = \frac{1}{2\pi\sigma_{ij}} \left(\beta_{ij}^{00,el} + \frac{\pi\sigma_i}{2\Delta} \sum_{k=1}^{n} \rho_k \sigma_k{}^2 \beta_{kj}^{00,el} + \frac{\pi}{2\Delta} \sigma_i \chi a_j^0 \right), \tag{60}$$

An alternative symmetric expression may be found from Eq. (67) of B0,

$$g_{ij,c}^{000,el} = -\frac{1}{4\pi\sigma_{ij}} \left(D_\Omega\, a_i^0 a_j^0 + \frac{1}{D} \rho_n \sigma_n{}^2 \eta_i \eta_j \right), \tag{61}$$

in which,

$$D_\Omega = 4D_a/\beta_6^2. \tag{62}$$

In Eq. (59), one notices that $g_{ij,c}^{000,HS}$ coincides with the contact value of the RDF in the Percus-Yevick (PY) approximation[26], as is usual within the MSA[24]. This result confirms the fact that the expression of Δ in Eq. (38) must include the solvent in the summation.

As regards the other RDF's $g_{in,c}^{000}$, $g_{ni,c}^{000}$ and $g_{nn,c}^{000}$, it is found from Eqs. (35), (44), (48), and (53), that they are purely HS RDF's, given by the PY expression (Eq. (59)),

$$g_{in,c}^{000} = g_{ni,c}^{000} = g_{in,c}^{HS,000}. \tag{63}$$

12

E.   Expression for the pressure

The pressure of the system may be derived in the MSA from the work of Høye and Stell[27]. The expression given in BW1 is partly incorrect.

From Eqs. (41) and (43) of Ref. 27 one obtains the relation,

$$\beta P^{el} = J + J', \tag{64}$$

in which J is given by Eq. (42) of this reference and Eq. (3.4) of BW1. By using Eqs. (3.2), (3.3), and (3.11) of BW1, one gets,

$$J = \frac{1}{12\pi} \left(\alpha_0^2 \sum_i \rho_i Z_i N_i - 4\alpha_0\,\alpha_2\,\rho_n\,B - \frac{6}{\sigma_n^3}\,\alpha_2^2\rho_n b_2 \right), \tag{65}$$

An expression for J' (replacing Eq. (3.5) of BW1) is obtained from Eqs. (41) and (43) of Høye and Stell[27], which reads,

$$J' = \frac{\pi}{3} \sum_{\{i,j\}=1}^{n} \rho_i\rho_j\sigma_{ij}^{\,3} \left\langle \left[(g_{ij,c})^2 - (g_{ij,c}^{HS})^2 \right] \right\rangle, \tag{66}$$

in which the brackets indicate that the quantity is averaged over the orientations[20,28], and the superscript HS means that $g_{ij,c}$ is evaluated in the case of neutral hard spheres.

The expression of J' may be expanded by using Eqs. (9)-(12), taking into account the fact that the rotational invariants constitute an orthogonal set of functions w.r.t. to orientation average, that is $\left\langle \Phi^{mnl}\, \Phi^{m'n'l'} \right\rangle = 0$ if $\{m,n,l\} \neq \{m',n',l'\}$). Furthermore, as mentioned at the end of the previous section, $g_{in,c}^{000}$, $g_{ni,c}^{000}$ and $g_{nn,c}^{000}$ are purely HS RDF's. At the same time, $h_{kn,c}^{011}$, $h_{nk,c}^{101}$, $h_{nn,c}^{110}$, and $h_{nn,c}^{112}$ are purely electrostatic (see Eqs. (45)-(46) and (53)-(56)). By combining these properties, and using Eq. (14) for $h_{ni,c}^{101}$, one obtains,

$$J' = J'_{ion-ion} + 2J'_{ion-n} + J'_{n-n}, \tag{67}$$

where,

$$J'_{ion-ion} = \frac{\pi}{3} \sum_{\{i,j\}=1}^{n-1} \rho_i\rho_j\sigma_{ij}^{\,3} \left[(g_{ij,c}^{000})^2 - (g_{ij,c}^{HS,000})^2 \right], \tag{68}$$

$$J'_{ion-n} = \frac{\pi}{3} \sum_{i=1}^{n-1} \rho_i\rho_n\sigma_{in}^{\,3} \frac{1}{3}\,(h_{in,c}^{011})^2, \tag{69}$$

where in which i and j designate ions, and,

$$J'_{n-n} = \frac{\pi}{3}\,\rho_n^{\,2}\sigma_n^{\,3} \left[(h_{nn,c}^{110})^2 + \frac{1}{5}\,(h_{nn,c}^{112})^2 \right], \tag{70}$$

13

Eq. (68) for $J'_{ion-ion}$ differs from Eqs. (3.5) of BW1 and (3.3) of BW2, in which the term $(g_{ij,c}^{HS,000})^2$ is absent (note that in BW1 and BW2, the term $h_{ij}^{000}(\sigma_{ij})$ is $g_{ij,c}^{000}$ of the present work). It can be shown that these HS terms containing $g_{ij,c}^{HS,000}$ cancel out in the SR case (see supplementary material), which allows one to recover the expression for $J'_{ion-ion}$ in BVF (Eq. (90)).

In Eqs. (69) and (70), the factors 1/3 and 1/5 originate from the angle averages of the squares of the rotational invariants, $\left\langle \left(\Phi^{mnl}\right)^2 \right\rangle = 1/(2l+1)$ (note that Blum's definition of the rotational invariants differs slightly[28] from that of Eqs. (4), (6), (8), and (13)).

By inserting Eq. (54) into Eq. (70) one obtains,

$$J'_{n-n} = \frac{1}{12\pi} \rho_n{}^2 \sigma_n \left[\left(Q'^{11}_{nn}\right)^2 + 2q'^2 \right]. \tag{71}$$

This expression has the same form as the last term of Eq. (86) in BVF in the SR case.

An important verification was done regarding the expression for the pressure. Namely, it was checked that Eq. (64), together with Eqs. (55) and (67)-(71), leads exactly to the relation for P^{el} in the SR case (see BVF). This is a valuable result because it has been shown that the SR expression for the pressure is valid[14] (see also supplementary material). It does not seem to be the case of an alternative expression for P^{el} that contains a different ion-dipole contribution $(l=1)$ to J'[29,30].

F.   Internal and Helmholtz energies

The expression for the electrostatic contribution to the internal energy may be found in Eq. (3.2) of BW1,

$$\frac{\beta E^{el}}{V} = \frac{1}{4\pi} \left(\alpha_0{}^2 \sum_i \rho_i Z_i N_i - 2\alpha_0 \alpha_2 \rho_n B - 2\alpha_2{}^2 \frac{1}{\sigma_n{}^3} \rho_n b_2 \right). \tag{72}$$

with V the volume. It was verified that this equation leads to the correct expression for this quantity in the SR case (Eq. (84) of BVF).

Regarding the Helmholtz energy, A^{el}, it could be proposed to use the following relation presented in Eq. (3.16) of BW1,

$$\beta P^{el} \stackrel{?}{=} \frac{\beta E^{el}}{V} - \frac{\beta A^{el}}{V}, \tag{73}$$

However, it is easy to show that this relation is valid only in the SR case (Eqs. (87) and (104) of BVF), not in the general case of ions of different size. This may be seen in the case

14

of the primitive model (PM), in the absence of explicit solvent ($\rho_n = 0$), for which the MSA gives, by using Eqs. (3.4) and (3.7) of Ref. 24 (with $\beta P^{el} = \xi_0 \, \Delta\Phi$),

$$\beta P^{el,PM} = \frac{\beta E^{el,PM}}{V} - \frac{\beta A^{el,PM}}{V} - \frac{\alpha_0^2}{8} \left(\frac{P_n}{\Delta}\right)^2, \tag{74}$$

where P_n is a quantity that vanishes when the ions have equal diameters. This result shows that Eq. (73) is not satisfied in the the general case of the primitive model. However, the term in $(P_n)^2$ in this relation is generally small and has been sometimes neglected in the literature[24].

Therefore Eq. (73) cannot be expected to be satisfied either in the general case of the MSA-ID model. One may write instead for A^{el},

$$A^{el} = A^{el,app} + \delta A^{el}, \tag{75}$$

where,

$$\frac{\beta A^{el,app}}{V} = \frac{\beta E^{el}}{V} - \beta P^{el}, \tag{76}$$

and $\delta A^{el} = 0$ in the SR case. By virtue of Eqs. (64), (72), and (76), one gets,

$$\frac{\beta A^{el,app}}{V} = \frac{1}{6\pi} \left(\alpha_0{}^2 \sum_{i=1}^{n-1} \rho_i Z_i N_i - \alpha_0 \alpha_2 \, \rho_n \, B\right) - J'. \tag{77}$$

which is Eq. (3.11) of BW1. In the PM, it stems from Eq. (74) that $\beta \delta A^{el,PM}/V = -(\alpha_0^2/8)\,(P_n/\Delta)^2$, which brings a small contribution to $\beta A^{el,PM}/V$[24,25]. Similarly, it is likely that δA^{el} is small as compared to A^{el} in the MSA-ID framework.

As for A^{el}, the formulas proposed in BW1 for the chemical potentials (Eqs. (3.13 and 3.14)) must be modified as,

$$\mu_k^{el} = \mu_k^{el,app} + \delta\mu_k^{el}, \tag{78}$$

for all species, with $\delta\mu_k^{el}$ an expectedly small contribution. In this relation, the approximate chemical potentials read,

$$\beta\mu_i^{el,app} = Z_i \frac{1}{4\pi} \left(\alpha_0{}^2 N_i - \alpha_0\alpha_2 \, \rho_n \, m_i\right), \tag{79}$$

for the ions, and,

$$\beta\mu_n^{el,app} = -\frac{1}{4\pi} \left(\alpha_0\alpha_2 \, B + 2\alpha_2{}^2 \frac{1}{\sigma_n{}^3} b_2\right), \tag{80}$$

15

for the solvent. These contributions were determined in BW1 according to the method of Høye and Stell[27] (Eq. (39) of this reference in particular), which is the only way to obtain them. They correspond to the mean electrostatic interaction energies per particle, that is,

$$\mu_k^{el,app} = u_k^{el}, \tag{81}$$

Expressions for $\delta\mu_i^{el}$ and $\delta\mu_n^{el}$ may also be obtained, in principle, from the work of Høye and Stell[27]. However, the derivation requires expressions for the direct correlation functions, which is a difficult task in the MSA-ID. The calculation of these corrective terms will be addressed in subsequent work.

As a consequence of Eq. (81) one may write that,

$$\sum_{k=1}^{n} \rho_k \, \mu_k^{el,app} = \frac{E^{el}}{V}, \tag{82}$$

Then it stems from the general relation, $A/V = \sum_k \rho_k \mu_k - P$, and Eqs. (75) and (82), that the corrective terms are related by,

$$\frac{\delta A^{el}}{V} = \sum_{k=1}^{n} \rho_k \, \delta\mu_k. \tag{83}$$

The contributions $\delta\mu_i^{el}$ and $\delta\mu_n^{el}$ vanish in the SR case, and the resulting equations for $\beta\mu_i^{el}$ and $\beta\mu_n^{el}$ are valid in that case[14]. It is shown in Sec. III B 4 below that the terms $\delta\mu_i^{el}$ indeed seem to bring a rather small, albeit not negligible, contribution to μ_i^{el} in moderately concentrated solutions.

III. APPLICATION TO THE CASE OF A BINARY 1-1 ELECTROLYTE

In this section we will specialize to the case of a binary 1-1 electrolyte of number density $\rho_s = \rho_1 = \rho_2$, in which the cation and the anion have different diameters σ_1 and σ_2, and valencies $Z_1 = +1$ and $Z_2 = -1$, respectively.

A. Handling of the equations

As mentioned in Sec. II C, there are 5 unknowns in this case, namely $b_0^{(1)}$, $b_0^{(2)}$, $b_1^{(1)}$, $b_1^{(2)}$, and b_2. We now examine in which way these parameters may be determined in practice.

First, as in the SR case, one has the 3 fundamental equations of the MSA-ID model, Eqs. (15)-(17). These equations will be denoted as E1, E2, and E3, respectively.

Next, one may use the symmetry property of P_{ij}^{mn}, for which Eq. (31) gives the three relations,

$$P_{12}^{00} = P_{21}^{00}, \qquad P_{1n}^{01} = P_{n1}^{10}, \qquad P_{2n}^{01} = P_{n2}^{10}. \tag{84}$$

which will be numbered E4, E5, and E6, respectively.

Consequently, we have 6 equations and 5 unknowns. This suggests that one of the equations may be derived from the others. Here E6 ($P_{2n}^{01} = P_{n2}^{10}$) was left aside in the search of a solution. When the latter was obtained it was verified that E6 was also satisfied. This verification served as a severe test for the validity of the equations being used in this process.

All equations were handled within the symbolic calculus software Maple.

First, it was found that b_2 can be expressed as a function of the other parameters, $b_0^{(1)}$, $b_0^{(2)}$, $b_1^{(1)}$, $b_1^{(2)}$, of the salt density ρ, and of the sizes σ_i. The explicit expression of b_2 is given in the supplementary material addendum. The replacement of b_2 by this expression in one of the relations obeyed by the parameters gives a relation between the other 4 parameters, $b_i^{(k)}$ (i= 0,1; k=1,2).

For an optimal use of Maple in the numerical calculations, equations E1, E2, and E3 were divided by $\alpha_0{}^2$, $\alpha_0\alpha_2$ and $\rho_n\,\alpha_2{}^2$, respectively, so that every term in these equations had a suitable order of magnitude for the solver to find the numerical solution easily. In the same way, E4 and E5 were entered in the form, $1 - P_{12}^{00}/P_{21}^{00} = 0$, and $1 - P_{1n}^{01}/P_{n1}^{10} = 0$. It was observed that the use of the equation giving b_2 (Eq. (S5)), or the relation between the other energy parameters, instead of, e.g., E5, generally made the determination of the solution more difficult. Therefore the 5 original equations were retained and solved numerically within Maple.

B.   Example

To illustrate, let us further consider in this section a solution of a 1-1 salt at 25°C, comprised of ions of diameter $\sigma_1 = 2$ Å and $\sigma_2 = 4$ Å, in a 'water-like' solvent. The dipolar solvent was modeled as in previous work[14] by taking, $m_n \simeq 2.2203$ D, and $\sigma_n \simeq 2.4805$ Å. With these values the model gives a dielectric constant and a pressure for pure solvent that mimic experimental data for pure water at 25°C, that is $\varepsilon_W = 78.4$, and $P = 1$ atm for the

17

density of water, $d_W = 0.99705$ kg L^{-1}.

The salt concentration is C. The case of moderately concentrated solutions ($C \leq 2$ M) will be considered. The number density of the solvent, ρ_n, was kept constant, equal to 0.95 times that of pure water.

1.   Energy parameters

The set of dimensionless energy parameter values, $S_b = \{b_0^{(1)}, b_0^{(2)}, b_1^{(1)}, b_1^{(2)}, b_2\}$, was determined in the first place. To begin with, it was verified that the solution to the SR case was recovered numerically in the case $\sigma_1 = \sigma_2 = 3.33$ Å^{14}. This check was fulfilled with a very high precision.

The values of the energy parameters were obtained by starting from a rather low value of C (e.g., $C = 0.01$ M) with typical values for the energy parameters, viz., $b_0^{(1)} = -0.05, b_0^{(2)} = -0.05, b_1^{(1)} = 0.1, b_1^{(2)} = 0.1, b_2 = 2$, in the case of a solvent mimicking water. Then the concentration was increased gradually, in small increments of 0.1 M. At each step, the solution for the set of parameters obtained at the previous step was used as an initial guess. In all cases the parameters satisfied the following conditions: $b_0^{(k)} < 0, b_1^{(k)} > 0, b_2 < b_2^{(0)}$, for $k = 1, 2$, and with $b_2^{(0)}$ the value of b_2 when $C = 0$ (see Ref. 9 for its determination). These inequalities are similar to the SR case (as regards b_0, b_1, and b_2).

When, for a given salt concentration, the value of a set of energy parameters, S_b, was used as an input in the 5 fundamental equations, E1 to E5, it was found that the latter were satisfied to a very high precision. If for instance all numbers were expressed with 50 digits in Maple, the 5 equations were found to be satisfied to a precision better than 10^{-48}. At the same time, it was observed that equation E6 for P_{2n} ($1 - P_{2n}^{01}/P_{n2}^{10} = 0$), which was not employed in the search of the solution, was satisfied to a precision of $\sim 2 \times 10^{-49}$. This outcome was observed in all calculations with different values of the solvent and salt concentration, and of the ion sizes. Similarly, it was observed that in all cases the sum rules (Eqs. (32) and (33)) were verified with a comparable precision.

In contrast, when a slight change was made randomly in one of the equations, it was found that E6 was not satisfied anymore. For example, replacing the plus sign in Eq. (25) by a minus just before the 1/32 factor resulted in E6 being satisfied with a precision of 0.02 instead of 10^{-49} at $C = 1$ M. Furthermore, the sum rules were satisfied with precisions of

~ 0.002, 0.002, and 0.008, respectively. Hence, these 4 relations were not fulfilled when the minus sign was used in Eq. (25).

One may conclude from this stringent test that the basic equations of the MSA-ID given above in Sec. II B constitute a consistent, and therefore valid, set of relations. This represents the first important result of this work.

The result for the energy parameters is shown in Figures 2-4. The solution for b_0, b_1, and b_2 in the SR case for ions of diameter $(\sigma_1 + \sigma_2)/2$ is also plotted in these figures. It is seen in Figure 2 that $b_0^{(1)}$ and $b_0^{(2)}$ are negative, and in Figure 3 that $b_1^{(1)}$ and $b_1^{(2)}$ are positive and very close to each other up to $C = 0.4$ M. As in the SR case, they vanish in the absence of salt. Fortuitously in the present case, b_1 is nearly equal to $b_1^{(1)}$ on the whole range of C. After a rapid variation at low concentration, $b_1^{(1)}$ and $b_1^{(2)}$ increase slowly with C. The value of b_2 (Figure 4) starts from a value of $b_2^{(0)} \sim 2.1$ for $C = 0$ (which value depends on the density of dipoles), and then decreases smoothly with C.
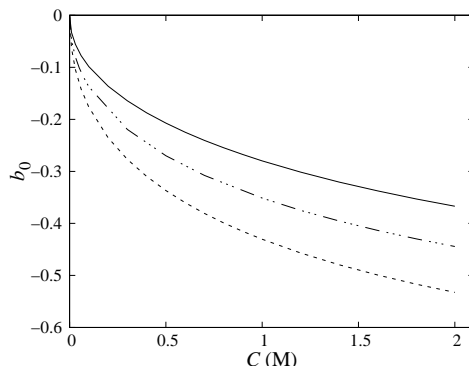

FIG. 2. Energy parameters $b_0^{(k)}$ as a function of C. Solid line $= b_0^{(1)}$, dashed line $= b_0^{(2)}$, dashed-triple-dotted line $= b_0$ in the SR case for cation and anion of diameter 3 Å.

2. *Distribution functions*

The ion-ion RDF's at contact are plotted in Figure 5, and the dipole-ion and dipole-dipole RDF's at contact are shown in Figure 6.

A striking feature observed in Figure 5 is that $g_{11,c}^{000}$ and $g_{22,c}^{000}$ are negative, which is clearly unphysical. Moreover, $g_{11,c}^{000}$ is of large magnitude, of the order of -30. The fact that the like-
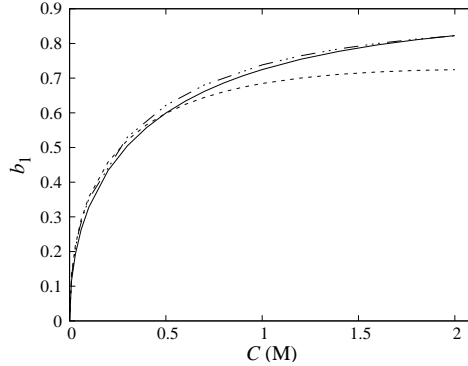
FIG. 3. Energy parameters $b_1^{(k)}$ as a function of C. Solid line $= b_1^{(1)}$, dashed line $= b_1^{(2)}$, dashed-triple-dotted line $= b_1$ in the SR case for cation and anion of diameter 3 Å.
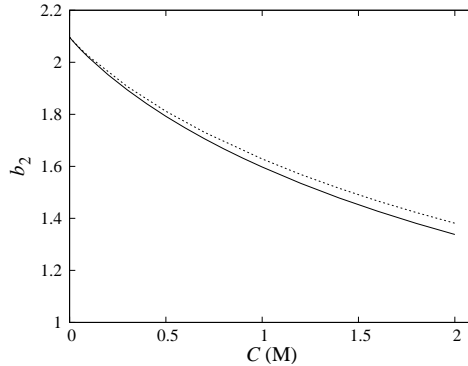

FIG. 4. Plot of b_2 as a function of C, compared to the SR case for ions of diameter 3 Å. Solid line $= b_2$, dotted line $= b_2$ when $\sigma_1 = \sigma_2 = 3$ Å.

ion RDF's can take negative values in the MSA is a well-known peculiarity that has been underscored in the literature, e.g. in Refs. 25 and 31 in the case of the primitive model, and in BW2 in the MSA-ID. This unsatisfactory outcome originates from the fact that, similarly to the Debye-Hückel theory, the MSA is a linearized theory[25]. In the MSA, the approximation on the direct correlation function c_{ij}, namely $c_{ij}(r) = -\beta u_{ij}(r)$, is asymptotically correct at large distances[25,32], but it fails in general at short distance[31]. This shortcoming manifests itself in the behavior of the contact RDF. At large dilution (of all components) one has $g_{ij,c} = 1 - \beta u_{ij,c}$ in the MSA (which can take large negative values in the case of like ions)
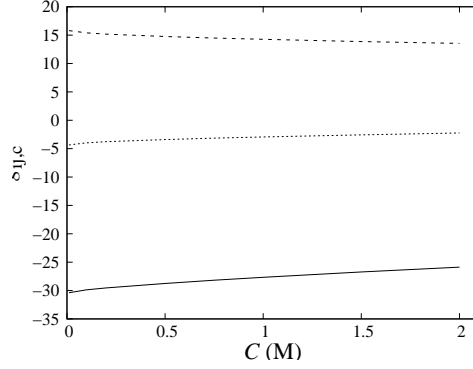
20

FIG. 5. Contact ion-ion radial distribution functions vs. concentration. Solid line = $g_{11,c}^{000}$, dashed line = $g_{12,c}^{000}$, dotted line = $g_{22,c}^{000}$.
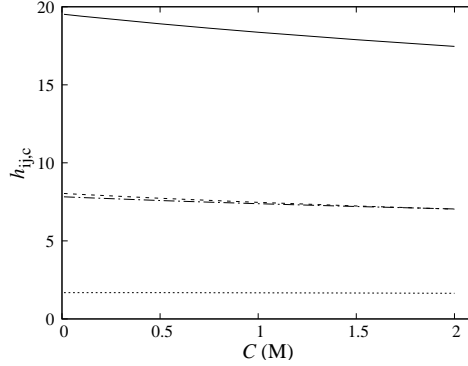

FIG. 6. Contact dipole-ion and dipole-dipole radial distribution functions vs. concentration. Solid line = $h_{1n,c}^{011} = -h_{n1,c}^{101}$, dashed line = $h_{n2,c}^{101} = -h_{2n,c}^{011}$, dotted line = $h_{nn,c}^{110}$, dash-dotted line = $h_{nn,c}^{112}$.

instead of $\exp(-\beta u_{ij,c})$ which is the correct low density limit[31]. The values of $\beta u_{ij,c}$ (Eqs. (2), (6), and (8)) in the present case are given in Table I.

We note moreover that, if one makes a comparison with what happens in the primitive model (PM) of aqueous solutions, the background medium is a vacuum in the MSA-ID model, with a permittivity that is nearly 80 times smaller than that of water in the PM. This makes the direct interaction potentials much larger in the non-primitive model, and the g_{ii}'s at contact much more negative, than in the PM (see Table I for the values of the ion-ion potentials at contact in the PM; they are of a few $k_B T$). As an example, one finds for

21

TABLE I. Absolute values of $\beta u_{ij,c}$ at contact for the present system, in the MSA-ID model, and in the primitive model (PM).

	MSA-ID	PM
$\beta u_{11,c}^{000}$	280	3.6
$\beta u_{22,c}^{000}$	140	1.8
$\beta u_{12,c}^{000}$	187	2.4
$\beta u_{1n,c}^{101}$	64.8	
$\beta u_{2n,c}^{101}$	16.2	
$\beta u_{nn,c}^{112}$	7.8	

the present system in the PM (with a dielectric constant of 78.4) that the typical orders of magnitude of $g_{11,c}$, $g_{12,c}$, and $g_{22,c}$ below 0.1 M are -2, +3, and -0.4, respectively, as compared to -30, +15, and -5 in the MSA-ID as seen in Figure 5.

It was suggested in BW2 that the deficiency observed in the contact RDF values could be corrected by using the exponential approximation[31,33]. The corrected like-ion RDF's g_{ii} would then be positive, and small, as observed in more accurate calculations (e.g., HNC or simulations), but the unlike-ion RDF could be very large (as in the case of $g_{12,c}^{000}$ here). Application of this correction to a condensed phase like the one considered here might be uncertain. The accuracy of the corrected RDF's would remain to be investigated.

One notices in Figure 6 that $h_{1n,c}^{011} > h_{n2,c}^{101}$ for any value of C. As noted in BW2, the solvent (orientational) polarization density at a distance r from the ion is proportional to the function $h_{in}^{011}(r)$. Therefore the observation that the function $h_{1n,c}^{011}$ for the cation-solvent interaction at contact is larger than that for anion-solvent may be interpreted by the fact that the smaller cation (1) is more strongly solvated than the anion (2).

Coincidentally, the functions $h_{n2,c}^{101}$ and $h_{nn,c}^{112}$ nearly cannot be distinguished from one another in this example.

3. Pressure

The electrostatic pressure P^{el}, and its contributions, computed from Eqs. (64), (65), and (67), are plotted in Figure 7. In this figure, βP_{ii}, βP_{in}, and βP_{nn}, are defined as the ion-ion, ion-solvent and solvent-solvent contributions to J in Eq. (65). Because of Eqs. (64) and

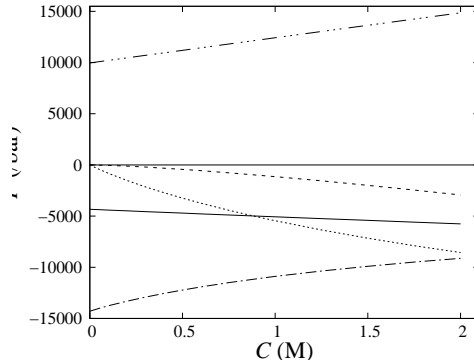(65), one has $\beta P^{el} = \beta P_{ii} + \beta P_{in} + \beta P_{nn} + J'$.

FIG. 7. Contributions to electrostatic pressure, P^{el}, vs. concentration. Solid line = P^{el}, dashed line = P_{ii}, dotted line = P_{in}, dash-dotted line = P_{nn}, dashed-triple-dotted line = J'/β.

It is seen in Figure 7 that P^{el} is negative, as a result of the dominant effect of attractive forces, it is nearly constant vs. concentration, and it takes high values. The total pressure, which would be the sum of P^{el} plus the HS pressure P^{HS}, would be much smaller because P^{HS} is positive and would counterbalance P^{el}.

The contributions P_{ii}, P_{in}, and P_{nn}, are also negative, and J'/β is positive. The 'ion-ion pressure', P_{ii}, is the minor contribution in this concentration range.

Let us now break down the contributions to J'. Table II reports the values of $J'_{ion-ion}/\beta$, $2J'_{ion-n}/\beta$, and J'_{n-n}/β that appear in Eq. (67). The values of $J'^{(0)}_{ion-ion}$ yielded by the removal of the HS RDF's, $g^{HS,000}_{ij,c}$, in Eq. (68) for $J'_{ion-ion}$ (see the remark following Eq. (70)) are also collected in this table.

TABLE II. Contributions to J'/β (in bars; 1 bar = 10^5 Pa).

C (/M)	$J'_{ion-ion}/\beta$	$J'^{(0)}_{ion-ion}/\beta$	$2J'_{ion-n}/\beta$	J'_{n-n}/β
0.1	3	3	351	9858
0.5	72	75	1659	9466
1	265	276	3119	9039
2	923	975	5605	8334

It is observed that $J'_{ion-ion}$ brings a rather small contribution to J' for moderate salt

23

concentrations below 2 M. At 2 M, it represents ~ 6 % of the total value of J'. It would contribute more significantly at higher concentrations.

The values of the incorrect $J'^{(0)}_{ion-ion}$ are close to those of $J'_{ion-ion}$ because $g^{HS,000}_{ij,c}$ is significantly smaller than $g^{000}_{ij,c}$ (the maximum value of $g^{HS,000}_{ij,c}$ is $g^{HS,000}_{22,c} \sim 2.8$ at 2 M, and the value of $J'_{ion-ion}$ is dominated by $g^{000}_{11,c}$ and $g^{000}_{12,c}$). The removal of $g^{HS,000}_{ij,c}$ in Eq. (68) has a small effect on the value of J' in the present example.

In contrast, the effect of correcting Eq. (55) is found to be huge. Without the presence of the term $\rho_n \sigma_n{}^2$ in the denominator of q' the result for the pressure is in error by orders of magnitude. For example, at 2 M, one gets a large and positive value, $P^{el} \sim 6 \times 10^{20}$ bar (when using the SI unit system), instead of -5759 bar.

4. Test of approximate Helmholtz energy and chemical potentials

The degree of accuracy of the approximate Helmholtz energy, $A^{el,app}$ (Eq. (76)), and of the approximate chemical potentials, $\mu^{el,app}_i$ (Eqs. (79) and (80)), was examined.

In the first case, this was done by comparing the derivative, $P^{el,app} \equiv -\partial A^{el,app}/\partial V$, with the pressure obtained from Eq. (64). The derivative was computed numerically from the relation,

$$\frac{\partial A^{el,app}}{\partial V} = V \frac{\partial (A^{el,app}/V)}{\partial V} + \frac{A^{el,app}}{V}.$$

by computing the values of the 2 terms of the r.h.s. and using Eq. (77) for $A^{el,app}/V$.

In the second case, the relation,

$$\left. \frac{\partial \mu^{el}_i}{\partial V} \right|_{N_j} = - \left. \frac{\partial P^{el}}{\partial N_i} \right|_{V,N_j, j \neq i}, \tag{85}$$

with N_i the number of species of type i, was tested numerically by replacing μ^{el}_i by $\mu^{el,app}_i$ (Eq. (79) or (80)) in the l.h.s. and comparing the result with that for the r.h.s., which was computed numerically from Eq. (64). In the case of the salt, the relations for the two ions were added and the following relation was used,

$$\left. \frac{\partial P^{el}}{\partial N_1} \right|_{V,N_2,N_n} + \left. \frac{\partial P^{el}}{\partial N_2} \right|_{V,N_1,N_n} = \left. \frac{\partial P^{el}}{\partial N_s} \right|_{V,N_n}.$$

in which the subscript s designates the salt.

For a given value of the salt concentration, the degree to which the relations were fulfilled was quantified by computing the relative deviations between the approximate and the 'exact'

results. They are denoted by $D_P = (P^{el,app} - P^{el})/P^{el}$ in the first case, and D_n (in the test of Eq. (85) for $i = n$) and D_s (for the salt) in the second. The results are shown in Figure 8 for the system considered in this section.
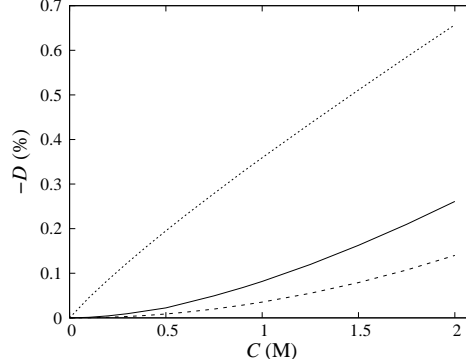

FIG. 8. Relative deviations, D_P, D_n, and D_s (all in %). Solid line $= -D_P$, dashed line $= -D_n$, dotted line $= -D_s$ (see text).

The main comments about the results of Figure 8 are as follows. All deviations are negative. The deviation on the pressure, D_P, is rather small (~ 0.25 % at 2 M). The deviation in the case of the salt, D_s, is more than 5 times larger than that for the solvent, D_n, which suggests that Eq. (79) for the approximate ion chemical potential is less accurate than Eq. (80) for that of the solvent.

Some further insight can be gained in the case where $\rho_n = 0$, which corresponds to the primitive model of ionic solutions if the background is taken to be a dielectric continuum. Interestingly, in that case, an expression for the term $\beta \delta \mu_i^{el}$ can be found explicitly. This derivation is detailed in the supplementary material.

The value of the ratio, $R_i = \delta \mu_i^{el}/\mu_i^{el}$, was computed for each ion in the case of the 1-1 salt considered above. A relative permittivity of 78.4 for the dielectric continuum was included in the parameter α_0^2 so as to mimic water as the solvent.

The result for $-R_1$ and R_2 is plotted in Figure 9.

It was found that the 2 chemical potentials μ_1^{el} and μ_2^{el} are negative (not shown). The additional contributions are of opposite signs: $\delta \mu_1^{el} > 0$ for the smaller ion, and $\delta \mu_2^{el} < 0$ for the bigger. Figure 9 shows that the two ratios $-R_1$ and R_2 are increasing functions of the salt concentration. Their values at 2 M are of a few percent. The corrective terms $\delta \mu_i^{el}$
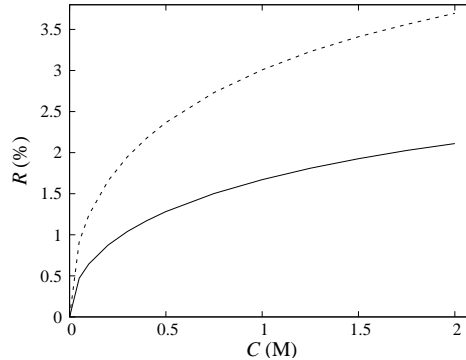
FIG. 9. Variation of $R_i = \delta\mu_i^{el}/\mu_i^{el}$ with salt concentration (with $\sigma_1 = 2$ Å and $\sigma_2 = 4$ Å). Solid line = $-R_1$ for the cation 1; Dashed line = R_2 for the anion 2.

therefore make a rather small, though not negligible, contribution to μ_i^{el}.

A similar behavior of these terms is likely in the MSA-ID model.

IV. CONCLUSION

In this work, the equations for the ion-dipole mixture within the MSA have been analyzed. A valid set of relations has been established and dimensionless energy parameters introduced in the spirit of the SR case[9]. A method to solve the set of equations has been proposed.

An expression for the electrostatic contribution to the pressure has been obtained. This expression is 'exact' within the MSA. This is not so as regards the Helmholtz energy, and the ion and solvent chemical potentials, for which approximate expressions are available at present. Corrective terms will have to be determined in subsequent work. Nonetheless the approximate relations seem to provide estimations of reasonable accuracy.

An inherent deficiency of the MSA is observed in the like-ion radial distribution functions at contact, which were found to be negative and of appreciable magnitude in the example considered here. This behavior is amplified in the non-primitive MSA by the fact that the ion-ion interaction potentials are much stronger than in the primitive model. In the latter the dielectric constant of the solvent reduces greatly the amplitude of the negative like-ion contact RDF's.

The inaccuracy of the contact RDF's casts some doubt on the accuracy of the electrostatic

26

pressure. However the effect on the latter seems rather small at low and moderate salt concentration. The exponential approximation could be employed in principle to correct the RDF's, but the accuracy of the result is uncertain. This point would have to be studied more in depth.

In future work, it is planned to reconsider the approximate version of the MSA-ID model proposed in BW2 in the light of the present work, and see if other approximations could be developed. It will also be possible to examine the results obtained from the present framework for the deviations from ideality in the case of 'real' electrolytes for which experimental data are available. The description could be improved by combining it with suitable models that would mitigate the main deficiencies of the MSA and/or account for additional effects such as association or hydrogen bonding as has been done sometimes in the literature with SAFT-like formulas combined with other versions of the non-primitive MSA[11,12,34].

SUPPLEMENTARY MATERIAL

See supplementary material for more details on the recovery of the expression for the pressure in the SR case, on the relation between the energy parameters b_i in the case of a binary 1-1 electrolyte, and on the calculation of the corrective term $\delta\mu_i^{el}$ for the ions in the primitive model.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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