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Inclusion of solvent polarizability in the modeling of ion-dipole mixtures within the mean spherical approximation (MSA)

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Abstract

The fluctuating polarization model of Høye and Stell [J. Chem. Phys. 72, 1597 (1980); J. Chem. Phys. 73, 461 (1980)] is introduced in the non-primitive mean spherical approximation (MSA) framework for an arbitrary mixture of hard spherical ions and polar polarizable solvent molecules. The thermodynamic properties are derived for this more realistic representation of an aqueous electrolyte. The obtained explicit formulas constitute a thermodynamically consistent set.

Keywords: Electrolytes, polarizability, non-primitive, ion-dipole, mean-spherical approximation (MSA).

1. Introduction

This article is dedicated to the memory of D. Henderson. It reports on a way of introducing the effect of solvent polarizability in the mean spherical approximation (MSA) model for a mixture of ions and dipoles [1, 2, 3, 4, 5]. D. Henderson significantly contributed to the description of such mixtures, in the bulk [6, 7], and near a charged wall [8, 9, 10, 11].

In the present work, an electrolyte solution is modeled as a collection of ions and dipolar polarizable solvent molecules (representing mostly water). The ions and the solvent particles are regarded as hard spheres, carrying a charge (positive or negative) and a central point dipole, respectively. The polarizability of the solvent is introduced by using a theory proposed by Høye and Stell [12, 13]. Within this theory, every polarizable particle is regarded as a classical

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oscillator in which electric charges of opposite signs are displaced within the molecule. In the case of solvents like water, the dipole moment of a molecule oscillates around a mean value. In Ref. [13] the model was employed to describe the polarization of a pure dipolar liquid. An expression was derived for the average magnitude of the dipole moment within the MSA, in terms of the component, $c_{\Delta}(0)$, of the direct correlation function in the notation of Wertheim [14] (for $r = 0$). However, the macroscopic thermodynamic properties of such a polarizable fluid were not given.

The effect of ion polarizabilities [15, 16] will not be addressed here. This problem would be formidably difficult to solve within the present framework because it would involve considering a mixture of at least three types of dipoles (for the solvent and two ions), all constituents having different sizes. Moreover, quantum effects would have to be taken into account [17]. Besides, it may be noticed that the effect of ion polarizabilities is often expected to be low to moderate [18] because of the spherical symmetry around ions in the bulk of ionic solutions, which results in low induced dipoles in ions. However, the onset of asymmetries in a solution, such as those met in ion pairs [18], may trigger large induced dipoles in ions, especially in big, highly polarizable, anions.

In this study, in a continued effort to make the model more realistic, the polarizability of the solvent is included in the ion-dipole MSA model that was solved recently in the general case of particles of different diameters [5]. The classical (non-quantum) version of the fluctuating polarization model is employed to account for this property. The thermodynamic properties of the system are derived, and used to ensure that the solution to the problem is fully thermodynamically consistent. The Gibbs-Duhem relation is one of the relations to be satisfied. The chemical potentials of all species are obtained, which allows one to calculate the activity coefficients of the ions and the osmotic coefficient of the solution.

2. Model for a pure fluid of dipolar particles

2.1. Solvent with permanent dipole moment

In this section, a pure solvent is considered to be comprised of hard spherical dipolar particles, of diameter σ and number density ρ . They bear a permanent central point dipole of

moment s_0 . Its Helmholtz energy per particle will be denoted as $f(\rho)$. It will be convenient to use the quantity $I = -\beta\rho f$, with $\beta = 1/(k_B T)$ the usual inverse temperature parameter.

For a reference system comprised of hard spheres of the same size, the Helmholtz energy per particle is $f_0(\rho)$, and $I_0 = -\beta\rho f_0$. The reference system pressure P_0 and chemical potential μ_0 follow from

$$\beta P_0 = I_0 - \rho \frac{\partial I_0}{\partial \rho}, \quad \beta \mu_0 = -\frac{\partial I_0}{\partial \rho}. \quad (1)$$

Now extend the hard sphere fluid to a simplified version of “polar” fluid with pair potential $(\pm s_0)(\pm s_0)\psi(r)$. The purpose with this version is to establish general properties and results due to polarizability. Next they are used when polarizability is added to the more demanding ion-dipole fluid in following sections. The simplified model is a one-dimensional version with “dipole” moment $\pm s_0$ whose average is $\langle s \rangle = \langle \pm s_0 \rangle = 0$. Within the MSA this gives a perturbing contribution to the free energy, I_1 , ($I = I_0 + I_1$) [19], with

$$I_1 = -\frac{1}{2} \frac{1}{(2\pi)^3} \int [\ln(1 - R\tilde{c}(k)) + R\tilde{c}(k)] d\mathbf{k} = -\frac{1}{2} \frac{1}{(2\pi)^3} \int \ln(1 - R\tilde{c}(k)) d\mathbf{k} - \frac{1}{2} R c(0), \quad (2)$$

with \mathbf{k} the Fourier wave vector and R given by

$$R = \rho \langle s^2 \rangle = \rho \langle (\pm s_0)^2 \rangle = \rho s_0^2. \quad (3)$$

Note that here the density ρ has been replaced by the quantity R . This rescales both the pair correlation function and the direct one. This rescaling will be convenient when the general MSA properties of polarizable particles are derived below.

With rescaled quantities the MSA direct correlation function is

$$c(r) = \begin{cases} c_0(r), & \text{when } r < \sigma, \\ -\beta\psi(r), & \text{when } r > \sigma, \end{cases} \quad (4)$$

With $\langle s \rangle = 0$ the condition on the dipolar part of the pair correlation function, that separates from the reference system, is

$$h(r) = 0, \quad r < \sigma. \quad (5)$$

The OZ (Ornstein-Zernike) equation for it is

$$\tilde{h}(k) = \tilde{c}(k) + \tilde{c}(k) R \tilde{h}(k). \quad (6)$$

Note that with this rescaling the influence of the “dipole” moment goes via R , and the core conditions (4) and (5) stay fixed. With use of proper three-dimensional dipole interaction and dipole moments the OZ equation would split into two parts. Here this is avoided by use of the simplified version.

By differentiation and use of the OZ equation and the conditions on $c(r)$ and $h(r)$ one finds

$$\begin{aligned}
\frac{\partial I_1}{\partial \rho} &= \frac{1}{2} \frac{1}{(2\pi)^3} \int \frac{R\tilde{c}(k)}{1 - R\tilde{c}(k)} \left[\frac{\partial R}{\partial \rho} \tilde{c}(k) + R \frac{\partial \tilde{c}(k)}{\partial \rho} \right] \mathbf{dk} \\
&= \frac{1}{2} \frac{1}{(2\pi)^3} \int \left\{ \left[\frac{\tilde{c}(k)}{1 - R\tilde{c}(k)} - \tilde{c}(k) \right] \frac{\partial R}{\partial \rho} + \frac{R\tilde{c}(k)}{1 - R\tilde{c}(k)} R \frac{\partial \tilde{c}(k)}{\partial \rho} \right\} \mathbf{dk} \\
&= \frac{1}{2} \left[(h(0) - c(0)) \frac{\partial R}{\partial \rho} + \int R h(r) R \frac{\partial c(r)}{\partial \rho} \mathbf{dr} \right] = -\frac{1}{2} c(0) \frac{\partial R}{\partial \rho}.
\end{aligned} \tag{7}$$

Thus altogether with fixed dipole moment s_0

$$\frac{\partial I_1}{\partial \rho} = -\frac{1}{2} \frac{\partial R}{\partial \rho} c(0) = -\frac{1}{2} c(0) s_0^2, \tag{8}$$

and the contributions to the pressure and chemical potential become

$$\begin{aligned}
\beta P_1 &= I_1 - \rho \frac{\partial I_1}{\partial \rho} = -\frac{1}{2} \frac{1}{(2\pi)^3} \int \ln(1 - R\tilde{c}(k)) \mathbf{dk} \\
\beta \mu_1 &= \frac{\partial I_1}{\partial \rho} = \frac{1}{2} c(0) s_0^2.
\end{aligned} \tag{9}$$

2.2. Solvent with fluctuating dipole moment

The principles of the model were presented by Høye and Stell [13]. The dipole moment of a solvent particle is assumed to fluctuate in a harmonic potential that turns out to read

$$\varphi(\mathbf{s}) = \frac{1}{2\alpha} (\mathbf{s} - \mathbf{s}_0)^2. \tag{10}$$

where α is the polarizability of the particle, \mathbf{s} is the dipole moment, and \mathbf{s}_0 is the permanent dipole on a molecule (\mathbf{s} and \mathbf{s}_0 are vectors). We will consider in this work that, as it is approximately the case for water, the polarizability of the molecule is isotropic. Then α is a scalar, not a tensor (this approximation may be dropped without fundamental difficulty [13]).

For the simplified polarizable fluid with fluctuating dipole moment s the fluid may be regarded as a polar fluid mixture with density distribution ρ_s and “dipolar” pair interaction $s_1 s_2 \psi(r)$. Based on the simplified version of a “polar” fluid the OZ equation will be as before except that R changes into

$$R = \rho \langle s^2 \rangle = \sum_s \rho_s s^2, \tag{11}$$

with

$$\rho = \sum_s \rho_s s^2. \quad (12)$$

Note that for the general treatment below it is not required for the potential $\varphi(s)$ to be harmonic. The MSA contribution I_1 to I is still given by expression (2) ($I_1 = -\beta\rho f_1$, with f_1 the Helmholtz energy per particle).

The dipole moment \mathbf{s} fluctuates in the potential φ of Eq. (10) inside each particle. This adds an internal energy to each particle. Further the density ρ splits into a density distribution ρ_s of hard spheres with equal diameters. This gives an additional entropy term that corresponds to an ideal mixture. Altogether, for this mixture of hard spheres, the free energy function I_0 changes into I_r for this new reference system, which reads,

$$I_r = I_0 + I_m \quad \text{with} \quad I_m = - \sum_s \rho_s \ln \left(\frac{\rho_s}{\rho} \right) - \sum_s \rho_s \beta \varphi(s), \quad \sum_s \rho_s = \rho. \quad (13)$$

With this one finds

$$\frac{\partial I_r}{\partial \rho} = \frac{\partial I_0}{\partial \rho} - \ln \left(\frac{\rho_s}{\rho} \right) - \beta \varphi(s). \quad (14)$$

and the pressure for this mixture reference system becomes

$$\beta P_r = I_r - \sum_s \rho_s \frac{\partial I_r}{\partial \rho_s} = I_0 - \rho \frac{\partial I_0}{\partial \rho} = \beta P_0, \quad (15)$$

since the additional terms cancel (with $\partial I_0 / \partial \rho_s = \partial I_0 / \partial \rho$ and $I_0 = I_0(\rho)$). So one has, $P_r = P_0$.

With R modified from expression (3) to (11) the MSA expression (2) for I_1 remains unchanged. Expression (8) is modified to

$$\frac{\partial I_1}{\partial \rho_s} = -\frac{1}{2} \frac{\partial R}{\partial \rho_s} c(0) = -\frac{1}{2} c(0) s^2, \quad (16)$$

which is the MSA contribution to the chemical potentials

$$\beta \mu_{1,s} = \frac{1}{2} c(0) s^2. \quad (17)$$

The MSA contribution to the pressure, $\beta P_1 = I_1 - \sum_s \rho_s \partial I_1 / \partial \rho_s$, will still be given by Eq. (9), but now with R given by Eq. (11). Altogether, by adding this to result (15) the resulting expression for the pressure remains unchanged.

This result can be given a physical interpretation as follows. The average dipole moment squared $\langle s^2 \rangle$ for a given temperature and density may be regarded as a permanent dipole

moment from which the pressure follows. Internal states and energies of the particles have no direct influence upon the pressure, only via the average $\langle s^2 \rangle$.

Adding expressions (14) and (17) one finds the resulting chemical potentials (with $\beta\mu_0 = -\partial I_0/\partial\rho$),

$$\beta\mu_s = \beta\mu_0 + \ln\left(\frac{\rho_s}{\rho}\right) + \beta\varphi(s) + \frac{1}{2}c(0)s^2. \quad (18)$$

Here it can be mentioned that in Refs. [12, 13] the chemical potentials were defined without the term $\varphi(\mathbf{s})$. There this term was viewed mainly as an external potential by which the μ_s and then the density ρ_s at “position” s should decrease with increasing $\varphi(s)$. By that, μ_s was like a local chemical potential in an external field, like the gravity field. However, here we need the proper thermodynamic chemical potential by which they all should be equal since they all belong to the same basic particles, except for different values of the parameter s . Thus one has,

$$\mu_s = \mu. \quad (19)$$

Together with Eq. (18) this gives the density distribution

$$\rho_s = C \exp\left[-\beta\varphi(s) - \frac{1}{2}c(0)s^2\right], \quad C = \rho \exp(\beta\mu - \beta\mu_0). \quad (20)$$

This equation used for different values of s gives equations of chemical equilibria for particle densities

$$\ln\left(\frac{\rho_{s_1}}{\rho}\right) + \beta\varphi(s_1) + \frac{1}{2}c(0)s_1^2 = \ln\left(\frac{\rho_{s_2}}{\rho}\right) + \beta\varphi(s_2) + \frac{1}{2}c(0)s_2^2, \quad (21)$$

$$\frac{\rho_{s_1}}{\rho_{s_2}} = K_{12}, \quad K_{12} = \exp\left[-\beta(\varphi(s_1) - \varphi(s_2)) - \frac{1}{2}c(0)(s_1^2 - s_2^2)\right]. \quad (22)$$

With Eqs. (18) and (19) the “common” chemical potential μ or Gibbs free energy per particle becomes

$$\rho\beta\mu = \rho\beta\mu_0 + \frac{1}{2}Rc(0) + \sum_s \rho_s \ln\left(\frac{\rho_s}{\rho}\right) + \sum_s \rho_s \beta\varphi(s). \quad (23)$$

By summation on both sides the chemical potential can be determined explicitly from Eq. (20)

$$\begin{aligned} \rho &= CZ, \quad \beta\mu = \beta\mu_0 - \ln Z, \\ Z &= \sum_s \exp\left[-\beta\varphi(s) - \frac{1}{2}c(0)s^2\right]. \end{aligned} \quad (24)$$

Here Z is the one-particle partition function for the internal fluctuations inside particles. Usually the density distribution will be continuous in s by which sums will be integrals. Then the question may be how to normalize or make small steps ds . But such normalization will only give a constant factor to Z and by that a constant added to the entropy. Otherwise it has no physical significance. Since entropy can be interpreted in terms of the logarithm of the number of micro-states, as established by Boltzmann, this constant of the entropy cannot be settled in classical physics. However, quantum mechanics with discrete eigenstates resolves this problem of entropy.

Some further relations are provided in Appendix A, and fulfillment of the Gibbs-Duhem relation is also examined formally in Appendix B.

The simplified model considered in this section forms a basis that easily extends itself to the much more demanding polarizable ion-dipole fluid and its MSA solution. An immediate extension is the polar/polarizable fluid of Ref. [13] where the OZ equation splits into two parts. There the general form of the chemical potential remains the same with $c(0)$ replaced by the quantity $c_{\Delta}(0)/m_e^2$ of the polar fluid, where m_e is defined in Eq. (26). The extension to the ion-dipole case modifies $c(0)$ further where the dipolar chemical potential splits into two parts, one with $s^2 \rightarrow m^2$ dependence connected to the internal energy and another without this dependence. Apart from this, the ions do not interfere with the properties of the simplified model by which properties of this model can also be applied to the polarizable ion-dipole fluid considered below in this work.

3. Inclusion of polarizability effects for electrolytes

In the case of electrolytes, for commodity, we will employ a slightly different notation to distinguish the solvent from the ions. Quantities related to the dipolar solvent will be denoted with subscript n , and the dipole on a molecule by the symbol \mathbf{m} .

3.1. Further relations

A few useful relations in the case of electrolytes are exposed now.

It was shown in Ref. [13] that the excess chemical potential of a dipole in pure solvent is

given, within the MSA, by

$$\mu_n^E(\mathbf{m}) = \frac{m^2}{\langle m^2 \rangle} u_n. \quad (25)$$

where superscript E denotes an excess quantity, $\langle m^2 \rangle$ is the mean square dipole moment of the solvent molecules, and u_n is the mean configurational internal energy of the dipoles. In this equation, this energy is used in the case of electrolyte solutions, instead of $c_\Delta(0)/(2\beta)$, where c_Δ is the component of the direct correlation function in the notation of Wertheim [14], equivalently, to express μ_n^E . Thus, Eq. (25) follows from Eq. (17) with $c(0) = c_\Delta(0)/\langle m^2 \rangle$. It represents the mean internal energy per particle by considering that the dipoles bear a mean *effective* dipole moment, m_e , given explicitly by the formula derived in Ref. [13],

$$m_e^2 = \langle m^2 \rangle = 3 \frac{\alpha}{\beta} a + m_0^2 a^2, \quad (26)$$

with

$$a = \frac{1}{1 + 2\alpha u_n/m_e^2}. \quad (27)$$

This is also result (C.4) from the evaluation of Z made in Appendix C.

3.2. Case of ions of equal diameters within the MSA

We now consider the problem of an electrolyte comprised of ions and polarizable dipolar particles. We first particularize to the semi-restricted (SR) case in which all ions have the same diameter. The general case is addressed below in a second stage.

With polarization the expression for the pressure will not change compared to the basic situation with permanent dipole moment, except that the permanent dipole moment is replaced by the effective one. This follows from Eq. (15) where the mixing term does not contribute and Eq. (9), which is the MSA term as before. This is mentioned below Eq. (17).

Let us consider a particular dipole of moment \mathbf{m} that is present in the electrolyte. It is expected that the relations presented in the previous subsection still hold when ions are added to a pure dipolar solvent. Furthermore, it may be thought that the ions simply experience the *effective* solvent dipole moments, m_e , of Eq. (26). This follows from the analysis of the MSA solution made in Ref. [5]. Then, the individual internal energy and chemical potential of the ions (which are equal in the SR case of the MSA) are expected to be expressed by the classic

formulas derived in the non-polarizable case, that is,

$$\beta\mu_i^E = \beta u_i = \frac{L_0}{\sigma_i} b_0 - \frac{L_0 d_2}{\sigma_n d_0} b_1, \quad (28)$$

with $L_0 = \beta e^2 / (4\pi\epsilon_0)$, ϵ_0 the permittivity of a vacuum, σ_i the diameter of an ion, σ_n that of a solvent molecule, and e the charge of a proton. Moreover, the dimensionless parameters d_0 and d_2 were defined by Blum et al. [20] as, $d_0^2 = 2\rho_S\sigma_i^2\beta e^2 / \epsilon_0$ (with ρ_S the number density of the salt S) and

$$d_2^2 = \beta\rho_n m_e^2 / (3\epsilon_0). \quad (29)$$

in which the solvent dipole moment is identified with the *effective* dipole moment m_e of Eq. (26), and b_0 , b_1 and b_2 are MSA parameters to be determined by solving a set of equations [20, 21].

In the SR case, the expression of u_n is given by Eq. (23) of Ref. [21] (similarly to u_i , u_n is equal to the electrostatic contribution to the solvent chemical potential [4]), which yields

$$\beta u_n = -d_2 \left[2d_2 b_2 + d_0 \left(\frac{\sigma_n}{\sigma_i} \right)^2 b_1 \right] / (4\pi\rho_n\sigma_n^3). \quad (30)$$

Then by using Eqs. (29) and (30), one gets for a [Eq. (27)] in the SR case,

$$a^{-1} = 1 - \frac{\alpha}{3\pi\epsilon_0\sigma_n^3} \left[b_2 + \frac{1}{2} \frac{d_0}{d_2} \left(\frac{\sigma_n}{\sigma_i} \right)^2 b_1 \right], \quad (31)$$

In the case of pure solvent (absence of ions: $d_0 = 0$), this relation simplifies to give,

$$a_0^{-1} = 1 - \frac{\alpha}{3\pi\epsilon_0\sigma_n^3} b_2. \quad (32)$$

As was seen in Eq. (20), the distribution law of dipole moments, $\rho_n(\mathbf{m})$, may be written,

$$\rho_n(\mathbf{m}) = C \exp[-\beta\varphi(\mathbf{m}) - \frac{m^2}{m_e^2} u_n], \quad \text{with} \quad C = \rho_n \exp(\beta\mu_n^E). \quad (33)$$

The one-particle partition function is,

$$Z = \int_{\mathbf{m}} \exp[-\beta\varphi(\mathbf{m}) - \frac{m^2}{m_e^2} u_n] d^3m, \quad (34)$$

and the sum of the distribution function $\rho_n(\mathbf{m})$ over the dipole moments \mathbf{m} must give ρ_n , that is, by combining the latter two equations,

$$\rho_n = \int_{\mathbf{m}} \rho_n(\mathbf{m}) d^3m = C Z, \quad (35)$$

By taking \mathbf{m}_0 along the x axis one can explicitly perform the integration in Eq. (34) by using Eqs. (10), (33), and (35). More details are given in Appendix C. One gets,

$$\ln Z = -a \frac{m_0^2}{m_e^2} \beta u_n + \frac{3}{2} \ln \left(\frac{2\pi\alpha a}{\beta} \right), \quad (36)$$

From this relation one obtains using the definition of C in Eqs. (33) and (35) (from which $\beta\mu_n^E = -\ln Z$),

$$\beta\mu_n^E = a \frac{m_0^2}{m_e^2} \beta u_n - \frac{3}{2} \ln a = \frac{1}{a + 3\alpha/(\beta m_0^2)} \beta u_n - \frac{3}{2} \ln a. \quad (37)$$

after removing a term involving β and α which may be inserted in the chemical potential of the reference system of apolar particles. The last expression of $\beta\mu_n^E$ in Eq. (37) was obtained by using Eq. (26) for m_e .

Eq. (37) represents the excess chemical potential of the solvent dipoles. As required, it vanishes for apolar molecules ($m_0 = 0$ and $\alpha = 0$) because then $u_n = 0$ in Eq. (27) and therefore $a = 1$. It also vanishes at infinite dilution of the dipoles and ions (in which case one also has $a = 1$). It is also noticed that the non-polarizable result ($\alpha = 0$) for μ_n is recovered, that is $\mu_n^E = u_n$ [4] because then $a = 1$ by virtue of Eq. (27).

By again taking \mathbf{m}_0 along the x axis, one can likewise calculate the mean value of the dipole moment,

$$\langle \mathbf{m} \rangle = \int_{\mathbf{m}} \mathbf{m} \rho_n(\mathbf{m}) d^3 m, \quad (38)$$

which yields

$$\langle m_x \rangle = a m_0, \quad \langle m_y \rangle = \langle m_z \rangle = 0. \quad (39)$$

which means that the mean dipole moment is stretched by a factor of a in the direction of \mathbf{m}_0 .

In contrast with the solvent, the chemical potential of the ions coincides with their individual internal energy per ion, u_i , in which the solvent dipole moment is taken to be the effective dipole moment. Their expression may be found in Eq. (19) of Ref. [21].

3.3. General case of ions of arbitrary diameters within the MSA

In the general case where all species have different diameters, following the result of our previous work [5], the solvent chemical potential will be given by,

$$\begin{aligned} \beta\mu_n^E &= a \frac{m_0^2}{m_e^2} \beta u_n - \frac{3}{2} \ln a + \beta\delta\mu_n \\ &= \frac{1}{a + 3\alpha/(\beta m_0^2)} \beta u_n - \frac{3}{2} \ln a + \beta\delta\mu_n. \end{aligned} \quad (40)$$

the latter form resulting from Eq. (37), and in which $\delta\mu_n$ is the additional contribution expressing the effect of ion size asymmetry.

Note here the different use of u_n and $\delta\mu_n$. For the pure polarizable fluid the term m^2u_n/m_e^2 is the excess chemical potential of the mixture problem as given by Eq. (25) in accordance with the s^2 term of Eq. (18). For this situation $2\beta u_n = c_\Delta(0)$ as mentioned below Eq. (25). With ions present, u_n will have additional contributions, but for polarizable particles they will keep their m^2 dependence. However, for the more general situation, dipolar particles will have a third contribution $\delta\mu_n$ to their chemical potential. But $\delta\mu_n$ does not have the m^2 dependence. It is due to the ion asymmetry and does not depend upon m , only indirectly via $\langle m^2 \rangle$ [5].

The formal expression for the excess chemical potential of the ions remains unchanged as compared to the non-polarizable case, that is [5],

$$\mu_i^E = u_i + \delta\mu_i. \quad (41)$$

in which u_i and $\delta\mu_i$ are calculated for the effective solvent dipole moment. Again this follows from the analysis of the MSA in Ref. [5]. Dipole moments can be distributed in various ways on particles with the same hard core diameter while the solution remains the same. Polarization leads to such a distribution where the average $\langle m^2 \rangle$ is equivalent to the m_0^2 of a permanent dipole moment.

The expressions of the chemical potentials of the solvent and the ions were established in Ref. [5]. They will not be reproduced here because they are quite involved.

3.4. Internal energy

We now want to calculate the excess internal energy U^E of the electrolyte. The excess Helmholtz energy per volume unit is,

$$\frac{A^E}{V} = \sum_{k=i,n} \rho_k \mu_k^E - P^E. \quad (42)$$

in which V is the volume of solution and the sum runs on all ions i and on n . The energy U^E per volume unit may be obtained from the relation,

$$\frac{U^E}{V} = \frac{\partial(\beta A^E/V)}{\partial\beta}, \quad (43)$$

It will be useful to write this relation alternatively as,

$$\frac{U^E}{V} = \left. \frac{\partial(\beta A^E/V)}{\partial\beta} \right|_{m_e} + \left. \frac{\partial(\beta A^E/V)}{\partial m_e} \right|_{\beta} \frac{\partial m_e}{\partial\beta}, \quad (44)$$

in which it turns out that,

$$\left. \frac{\partial(\beta A^E/V)}{\partial m_e} \right|_{\beta} = 0. \quad (45)$$

This follows from the differentiations given by Eq. (A.6) in Appendix A. As commented below Eq. (A.9), partial differentiations of I_{1m} and then Helmholtz free energy with respect to changes in $\langle s^2 \rangle$, i.e. m_e , do not contribute.

It will be convenient to rewrite Eq. (42) as,

$$\frac{A^E}{V} = \left[\sum_{k=i,n} \rho_k (u_k + \delta\mu_k) - P^E \right] + \rho_n [\mu_n^E - (u_n + \delta\mu_n)], \quad (46)$$

in which Eqs. (40) and (41) were utilized. In this relation, the first term in brackets is the Helmholtz energy for the system of ions and *permanent dipoles* of moment m_e . Therefore, one obtains from Eqs. (44), (45), and (46),

$$\frac{U^E}{V} = \sum_{k=i,n} \rho_k u_k + \rho_n \left. \frac{\partial\{\beta [\mu_n^E - (u_n + \delta\mu_n)]\}}{\partial\beta} \right|_{m_e}, \quad (47)$$

By setting

$$f = a \frac{m_0^2}{m_e^2} - 1, \quad (48)$$

which is a function of m_e , one has from Eq. (40),

$$\beta [\mu_n^E - (u_n + \delta\mu_n)] = f \beta u_n - \frac{3}{2} \ln a, \quad (49)$$

Insertion of this relation into Eq. (47) leads to,

$$\frac{U^E}{V} = \sum_{k=i,n} \rho_k u_k + \rho_n f u_n + \rho_n \left\{ \beta \left. \frac{\partial(f u_n)}{\partial\beta} \right|_{m_e} - \frac{3}{2} \left. \frac{\partial(\ln a)}{\partial\beta} \right|_{m_e} \right\}, \quad (50)$$

It is shown in Appendix D that the last term in curly braces turns out to be nought. Consequently one obtains the simple result for the internal energy,

$$\frac{U^E}{V} = \sum_{k=i,n} \rho_k u_k + \rho_n f u_n, \quad (51)$$

Equation (C.5) of Appendix C shows that this result is consistent with Eq. (A.8) which in the present context reads, $u_n^{tot} = u_n + \langle \varphi(\mathbf{m}) \rangle$, in which u_n^{tot} is the total internal energy per solvent particle. Then an extra term of $3/2$ appears in it, i.e. in $\beta u = \beta u_n^{tot}$. It comes from the term $3/2 \times \ln \beta$ that was subtracted from $-\ln Z$ in Eq. (36), and inserted into the reference chemical potential, to yield the excess chemical potential of Eq. (37). Further, this corresponds to the potential energy of a classical three-dimensional harmonic oscillator where each degree of freedom has an energy $k_B T/2 = 1/(2\beta)$.

Consequently, the internal energy of the system is not only the sum of the individual electrostatic interaction energies of the ions and the solvent. It also comprises a contribution from the self-energy of the dipoles (the last term of Eq. (51)), which corresponds to the work needed to induce the dipoles in the solvent molecules. This energy is equal to $f u_n$ per solvent particle. By virtue of Eqs. (26) or (37) and (48) one has,

$$f = a \frac{m_0^2}{m_e^2} - 1 = \frac{1}{a + 3\alpha/(\beta m_0^2)} - 1. \quad (52)$$

It stems from this relation that f is negative because $a \geq 1$, and so is u_n . Consequently, this extra energy $f u_n$ is always positive as expected for this induced-dipole energy.

3.5. Thermodynamic consistency checks

As in Ref. [5], it was verified numerically by using the symbolic calculation program Maple (with 50 digit numbers), that the thermodynamic quantities obtained in this work fulfill some fundamental relations. The test was done in the case of a binary solution of a one molar 1-1 salt at 25°C in a water-like solvent comprised of polarizable dipolar molecules. The diameters of the cation and the anion were identical to those employed in previous work [5], namely 2 Å and 4 Å, respectively, for which results for the case of permanent dipole were reported. The choice of the parameters for the solvent is described in the next section.

The thermodynamic relations are summarized in Table 1 together with the accuracy to which they are satisfied for values of a parameter ε that represents the relative increment by which the densities or the temperature are varied.

The accuracies reported in this Table are the absolute values of the relative differences between the two sides of the relations. Fulfilment of the Gibbs-Duhem relation was checked at

constant temperature by verifying that the equality,

$$\rho_S \frac{\partial \mu_S}{\partial \rho_k} + \rho_n \frac{\partial \mu_n}{\partial \rho_k} = \frac{\partial P}{\partial \rho_k}. \quad (53)$$

was satisfied for $k = n$ and $k = S$, with subscript S designating the salt. The two corresponding relations are called GDn and GDs in Table 1.

Table 1: Accuracies observed in the thermodynamic consistency checks as a function of increment ε .

Relation	$\varepsilon = 10^{-2}$	$\varepsilon = 10^{-3}$	$\varepsilon = 10^{-4}$
GDn	1.52×10^{-5}	1.52×10^{-7}	1.52×10^{-9}
GDs	1.03×10^{-6}	1.03×10^{-8}	1.03×10^{-10}
$\mu_S^E = \partial(A^E/V)/\partial\rho_S$	5.90×10^{-8}	5.90×10^{-10}	5.90×10^{-12}
$\mu_n^E = \partial(A^E/V)/\partial\rho_n$	3.87×10^{-6}	3.87×10^{-8}	3.87×10^{-10}
$\partial\mu_S^E/\partial\rho_n = \partial\mu_n^E/\partial\rho_S$	2.51×10^{-5}	2.51×10^{-7}	2.51×10^{-9}
$P^E = -\partial A^E/\partial V$	4.70×10^{-5}	4.70×10^{-7}	4.70×10^{-9}
$U^E/V = \partial(\beta A^E/V)/\partial\beta$	4.29×10^{-6}	4.29×10^{-8}	4.29×10^{-10}
$\partial(U^E/V)/\partial\rho_S = \partial(\beta\mu_S^E)/\partial\beta$	1.72×10^{-6}	1.72×10^{-8}	1.72×10^{-10}
$\partial(U^E/V)/\partial\rho_n = \partial(\beta\mu_n^E)/\partial\beta$	8.41×10^{-7}	8.41×10^{-9}	8.41×10^{-11}
$\partial(\beta P^E)/\partial\beta = -\partial U^E/\partial V$	4.78×10^{-4}	4.78×10^{-6}	4.78×10^{-8}

As was shown in Ref. [5] the fact that an accuracy in Table 1 varies as ε^2 for a given relation, shows that this relation is accurately fulfilled, and that the analytic expressions of the quantities involved in this relation are consistent and valid.

4. Illustration in the case of a binary 1-1 electrolyte with polarizable water-like solvent

4.1. Parameter values for the solvent

The model employed here to represent a water-like solvent is rather simple, because in particular it does not include hydrogen bonding. So it cannot be expected that the use of experimental values for the permanent dipole moment and the polarizability of water account accurately for the physical properties of water.

Therefore the values to be taken for these parameters first require some discussion.

The experimental values for the permanent dipole moment and the average polarizability of the water molecule *in vacuum* are $m_0 = 1.855$ Debye [22] and $\alpha/(4\pi\epsilon_0) \sim 1.47 \text{ \AA}^3$ [23]. If these values are used as inputs in the present model, and if it is required that the density of the pure solvent be that of water at a pressure of 1 atm and a temperature of 25°C, then one gets a diameter $\sigma_n \sim 4.8 \text{ \AA}$ and a dielectric constant $\epsilon_n \sim 55$, respectively too large and too small as compared to expectations. It was found in previous work [21] that a fluid comprised of molecules of diameter $\sigma_n \simeq 2.4805 \text{ \AA}$, and permanent dipole moment $m \simeq 2.2203$ Debye (incidentally close to the value of 2.27 Debye for the permanent dipole moment in SPC simulations [24]) has a dielectric constant and a density in agreement with experiment ($\epsilon_n \sim 78.4$, $d_n = 0.997047 \text{ kg dm}^{-3}$) in the MSA.

The m_0 and α values in the present framework must be such that they lead to an effective dipole moment that coincides with this value, that is $m_e = 2.2203$ Debye. The diameter of the molecule must also be the same, $\sigma_n \sim 2.4805 \text{ \AA}$, for the pressure to be 1 atm.

The values of m_0 and α were determined as follows. The dielectric constant of the pure solvent obeys the equation [20],

$$\epsilon_n = \left[\frac{\lambda(\lambda + 1)^2}{4} \right]^2. \quad (54)$$

in which λ is a classic polarization parameter. With $\epsilon_n = 78.4$ this gives $\lambda \sim 2.653$. The value of b_2 is obtained from the relation [20],

$$b_2 = 6(\lambda - 1)/(\lambda + 2). \quad (55)$$

which yields $b_2 \sim 2.132$. By inserting Eq. (32) with this value of b_2 , and the diameter $\sigma_n \sim 2.4805 \text{ \AA}$ in Eq. (26) where $m_e = 2.2203$ Debye, one gets a quadratic equation relating m_0 and α .

[It may be noted that another common parametrization of the MSA solution is $\epsilon_n = q(2\xi)/q(-\xi)$ with $q(x) = (1 + 2x)^2/(1 - x)^4$. Connections between ξ and λ are: $\lambda = (1 + 4\xi)/(1 - 2\xi)$, $\lambda + 1 = 2(1 + \xi)/(1 - 2\xi)$, and $b_2 = 12\xi$ [13, 14].]

A choice for the value of m_0 imposes the value for α , and vice-versa. Taking $m_0 = 1.855$ Debye yields $\alpha/(4\pi\epsilon_0) \sim 0.828 \text{ \AA}^3$, which is much lower than the experimental value of 1.47 \AA^3 for water in vacuum. Conversely, taking the simulation result, $\alpha/(4\pi\epsilon_0) \sim 1.45 \text{ \AA}^3$ [25], imposes taking $m_0 \sim 1.58$ Debye.

In this study, it was chosen to employ the latter set, for which the polarizability is higher than in the first set. As for the ions, the following sizes were used: $\sigma_1 = 2 \text{ \AA}$ for the cation and $\sigma_2 = 4 \text{ \AA}$ for the anion as an example of asymmetric case.

4.2. Results

As in previous work [5], the following ion sizes were used: $\sigma_1 = 2 \text{ \AA}$ for the cation and $\sigma_2 = 4 \text{ \AA}$ for the anion. The formulas of this former report were utilized.

In what follows, it must be noticed that the total pressure (hard sphere [26] plus electrostatic) was kept constant, which introduced an additional equation to be solved. This condition about the pressure was ensured by employing a solvent density ρ_n that varied with salt concentration. The unknowns of the problem for a binary solution (solvent + one salt) were: $b_0^{(1)}, b_0^{(2)}, b_0^{(n)}, b_1^{(1)}, b_1^{(2)}, b_1^{(n)}, b_2, a$, and $\theta_n = \rho_n/\rho_{n,0}$ where $\rho_{n,0}$ is the density of pure solvent at 1 atm, and $b_0^{(1)}, b_0^{(2)}, b_0^{(n)}, b_1^{(1)}, b_1^{(2)}, b_1^{(n)}$, and b_2 are MSA parameters. This made a total number of parameters of 9 for this binary solution. As in Ref. [5], there was one equation more than unknowns. After the solution for the 9 MSA parameters was determined, it was checked that this extra equation was indeed satisfied for this solution.

The set of MSA equations was solved numerically by employing Maple. The complexity of these equations imposed to first determine the solution at a low salt concentration of 0.02M (by using an initial guess found in the non-polarizable case), and then by slowly increasing the concentration by increments of 0.02M.

The variation of the parameter a is plotted in Figure 1. It starts from $a_0 = 1.37$ in pure solvent [Eq. (32)]. As expected its value increases with salt concentration. The relative change in a at 2M is of the order of 4%.

Its variation influences the value of the solvent dipole moment as shown in Figure 2, where the ratio $m_e/m_{e,0}$ is plotted as a function of concentration (where $m_{e,0} \sim 2.22$ Debye is the effective dipole moment in pure solvent).

It is noticed that the relative change in m_e is modest, of only $\sim 4\%$ at 2M, similarly to the change in a in that range. This is because the value of m_e is averaged over the dipoles, most of them not being in the close vicinity of an ion.

The mean salt activity and osmotic coefficients were computed (at constant pressure). The

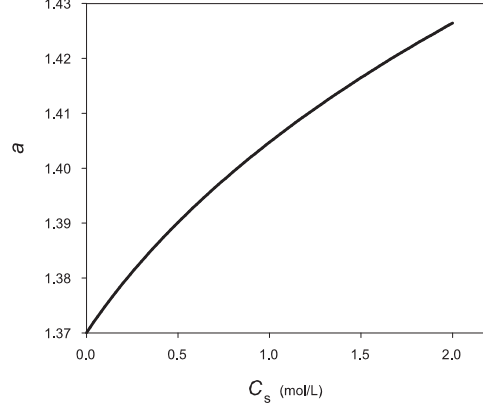


Figure 1: Plot of parameter a as a function of salt concentration (at constant pressure).

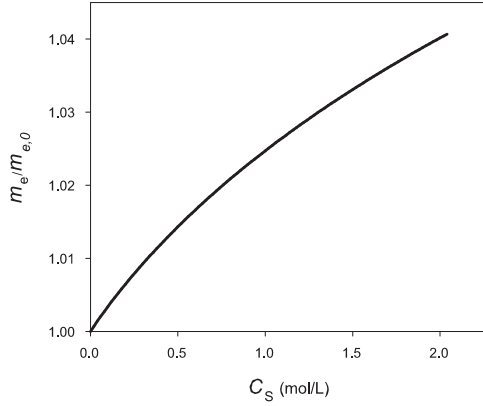


Figure 2: Relative variation of the effective solvent dipole moment as a function of salt concentration (at constant pressure).

former was calculated on molality scale as indicated in Ref. [21] from the formula,

$$\ln \gamma_S = \beta \Delta \mu_S^E + \ln \theta_n, \quad (56)$$

where $\Delta \mu_i^E = \beta \mu_i^E - \beta \mu_i^E(\rho_S \rightarrow 0)$, $\mu_i^E(\rho_S \rightarrow 0)$ is the excess chemical potential of ion i at infinite dilution of the salt, $\mu_S = \mu_1 + \mu_2$ (1=cation, 2=anion), and $\theta_n = \rho_n / \rho_{n,0}$.

The osmotic coefficient was determined from the classic formula,

$$\Phi = -\frac{x_n}{x_S} \ln a_n, \quad (57)$$

with x_n and x_S being the solvent and total solute mole fractions ($x_S = x_1 + x_2$; $x_n/x_S = \rho_n/2\rho_S$

for a 1-1 salt), and a_n the solvent activity which is obtained from,

$$\ln a_n = \mu_n - \mu_{n,0} = \beta \Delta \mu_n^E + \ln \theta_n. \quad (58)$$

in which the second contribution comes from the ideal part of the total chemical potential μ_n .

It was verified numerically that these expressions for $\ln \gamma_S$ and Φ satisfy the Gibbs-Duhem relation (the pressure being held constant),

$$d[m_S(1 - \Phi)] + m_S d(\ln \gamma_S) = 0. \quad (59)$$

The activity and osmotic coefficients are represented in Figures 3 and 4 up to a molality of 1 mol kg⁻¹. The plots are limited to this molality value because, above it, γ_S and Φ decrease monotonically to very low values.

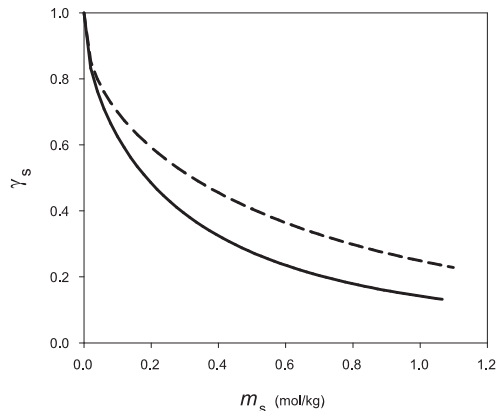


Figure 3: Mean salt activity coefficient as a function of salt molality. Dashed line: result with permanent dipole moment of 2.22 D ($=m_{e,0}$); Solid line: result with polarizability (varying dipole moment).

It is seen in these figures that the inclusion of solvent polarizability induces an appreciable drop of γ_S and Φ as compared to the case where the dipole moment does not vary ($\alpha = 0$). This effect may be explained by the increase in ion-dipole and dipole-dipole attraction caused by the rise of the solvent dipole moment.

5. Conclusion

In a continued effort to build a more realistic model, solvent polarizability effects have been introduced in the MSA for mixtures of ions and dipoles of arbitrary size. The classical

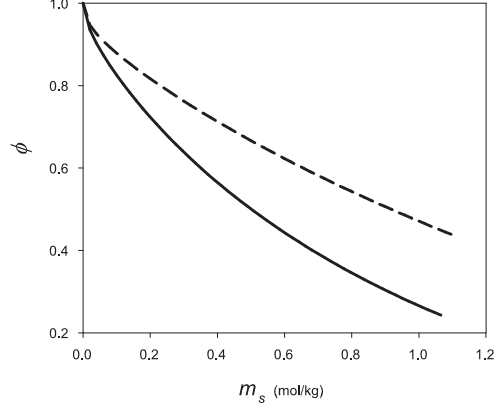


Figure 4: Osmotic coefficient as a function of salt molality. Dashed line: result with permanent dipole moment of 2.22 D ($=m_{e,0}$); Solid line: result with polarizability (varying dipole moment).

fluctuating polarization model of Høye and Stell allows one to represent a water-like solvent in a tractable way.

In the future, it will be attempted to include other features in this model, such as hydrogen bonding and van der Waals forces. However it is clear that the former in particular will require significant efforts to be accounted for in the present framework. Some possible avenues might be found in previous studies in which the hydrogen bond was modeled in terms of directional sticky interactions [27, 28, 29, 30].

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have influenced the work reported in this paper.

Appendix A. Some further relations in the case of pure solvent

By substitution of Eqs. (23) and (24) in Eq. (13) one finds

$$I_m = -\rho\beta(\mu - \mu_0) + \frac{1}{2} c(0)R = \rho \ln Z + \frac{1}{2} c(0)R. \quad (\text{A.1})$$

Adding this to the MSA contribution (2) gives

$$I_{1m} = I_1 + I_m = -\frac{1}{2} \frac{1}{(2\pi)^3} \int \ln(1 - R\tilde{c}(k)) \, dk + \rho \ln Z. \quad (\text{A.2})$$

With changes $\delta\rho$, δR , and $\delta\beta$ one first finds from Eq. (16) and its derivation

$$\delta I_1 = -\frac{1}{2} \frac{c(0)}{\beta} \delta(\beta R) = -\frac{1}{2} c(0) \delta R - \frac{1}{2} \frac{c(0)}{\beta} R \delta\beta. \quad (\text{A.3})$$

The $\delta\beta$ dependence follows from the same derivation since $Rc(r) = -\beta R\psi(r)$ for $r > \sigma$. The change in δZ follows from changes in β and $c(0)$. With integral (24) one finds

$$\frac{\delta Z}{Z} = -\langle\varphi(s)\rangle \delta\beta - \frac{1}{2} \langle s^2 \rangle \delta c(0), \quad (\text{A.4})$$

by which

$$\begin{aligned} \delta I_m &= \ln Z \delta\rho - \rho \langle\varphi(s)\rangle \delta\beta - \frac{1}{2} R \delta c(0) + \frac{1}{2} \delta[c(0)R] \\ &= \ln Z \delta\rho - \rho \langle\varphi(s)\rangle \delta\beta + \frac{1}{2} c(0) \delta R. \end{aligned} \quad (\text{A.5})$$

Adding together one finds

$$\delta I_{1m} = \delta I_1 + \delta I_m = \ln Z \delta\rho - \frac{1}{2} \frac{c(0)}{\beta} R \delta\beta - \rho \langle\varphi(s)\rangle \delta\beta. \quad (\text{A.6})$$

From this one finds the excess chemical potential

$$\beta(\mu - \mu_0) = -\frac{\partial I_{1m}}{\partial \rho} = -\ln Z, \quad (\text{A.7})$$

in agreement with Eq. (24). For the internal energy per particle u one further finds

$$\beta\rho u = -\beta \frac{\partial I_{1m}}{\partial \beta} = \frac{1}{2} c(0)R + \beta\rho \langle\varphi(s)\rangle. \quad (\text{A.8})$$

This is the MSA energy plus the average (classical) potential energy due to internal oscillations of each particle. Via the $c(0)$ the latter is influenced by the dipolar interactions.

For the pressure one finds

$$\beta P_{1m} = I_{1m} - \rho \frac{\partial I_{1m}}{\partial \rho} = -\frac{1}{2} \frac{1}{(2\pi)^3} \int \ln(1 - R\tilde{c}(k)) \, \text{d}\mathbf{k}, \quad (\text{A.9})$$

which is the same as the MSA pressure P_1 alone, i.e. the mixing term does not contribute to the pressure. This was also concluded from Eq. (15).

It can be noted that the variation $\delta R = \langle s^2 \rangle \delta\rho + \rho \delta \langle s^2 \rangle$ does not appear in the resulting variations of Eq. (A.6). This implies that partial differentiation of I_{1m} with respect to changes in $\langle s^2 \rangle$ is zero and thus does not contribute. Thus, in this respect, the effective dipole moment, for a given temperature and density, can be regarded as a fixed dipole moment.

Appendix B. Gibbs-Duhem relation for pure solvent

For a mixture the pressure P is

$$\beta P = I + \sum_s \rho_s \beta \mu_s, \quad \beta \mu_s = -\frac{\partial I}{\partial \rho_s}. \quad (\text{B.1})$$

Differentiation of it and use of $dI = -\sum_s \beta \mu_s d\rho_s$ gives

$$\beta dP = dI + \sum_s (\beta \mu_s d\rho_s + \rho_s \beta d\mu_s) = \sum_s \rho_s \beta d\mu_s, \quad (\text{B.2})$$

which is Gibbs-Duhem relation for a mixture. For polarizable particles, the μ_s for different dipole moments of a particle are all equal to the common ‘‘thermodynamic’’ chemical potential μ for the particle [Eq. (19)]. Then the Gibbs-Duhem relation becomes the usual one for a one component system

$$dP = \rho d\mu. \quad (\text{B.3})$$

We now see that this relation is also fulfilled for the polarizable fluid. For the hard sphere part I_0 this is clearly so. For the contribution I_1 from the MSA solution the derivation of P_1 and μ_1 from I_1 is given by Eq. (2). This together with Eqs. (8) and (17) gives

$$\begin{aligned} \beta dP_1 &= dI_1 + \frac{1}{2} d(Rc(0)) = -\beta \mu_1 d\rho + \frac{1}{2} \left[c(0) dR + \frac{\partial c(0)}{\partial R} R dR \right] \\ &= \frac{1}{2} \frac{\partial c(0)}{\partial R} R dR = \rho \beta d\mu_1. \end{aligned} \quad (\text{B.4})$$

With fixed dipole moment one has $R = \rho s_0^2$. Then $dR = s_0^2 d\rho = (R/\rho) d\rho$. With polarizability $R = \rho \langle s^2 \rangle$ where $\langle s^2 \rangle$ will vary.

For the mixing term I_m given by Eq. (13) the contribution to the pressure was found to be zero by which

$$dP_m = 0. \quad (\text{B.5})$$

The corresponding contributions to the chemical potentials are

$$\begin{aligned} \beta d\mu_{ms} &= -\sum_s \frac{\partial}{\partial \rho_{s_1}} \left(\frac{\partial I_m}{\partial \rho_s} \right) d\rho_{s_1} = \sum_s \frac{\partial}{\partial \rho_{s_1}} \left[\ln \left(\frac{\rho_s}{\rho} \right) + \beta \varphi(s) \right] d\rho_{s_1} \\ &= \sum_s \left(\frac{\delta_{s_1 s}}{\rho_s} - \frac{1}{\rho} \right) d\rho_s = \frac{d\rho_s}{\rho_s} - \frac{d\rho}{\rho}, \end{aligned} \quad (\text{B.6})$$

by which ($\mu_{m,s} = \mu_m$)

$$\begin{aligned}\rho\beta\mu_m &= \sum_s \rho_s \beta d\mu_{ms} = \sum_s d\rho_s - \frac{d\rho}{\rho} \sum_s \rho_s = 0, \\ dP_m &= \rho d\mu_m = 0.\end{aligned}\tag{B.7}$$

Appendix C. One-particle partition function Z .

The quantity Z given by Eq. (24) is a useful one for the polarizable ion-dipole system. For the situation with ($s \rightarrow \mathbf{m}$, $c(0)s^2 \rightarrow (m^2/me^2)\beta u_n$) one may set for commodity

$$\begin{aligned}\beta\varphi(m) &= \frac{1}{2} b (\mathbf{m} - \mathbf{m}_0)^2, \quad \text{with } b = \frac{\beta}{\alpha}, \\ \frac{m^2}{m_e^2} \beta u_n &= \frac{1}{2} c m^2, \quad \text{with } c = \frac{2\beta u_n}{m_e^2},\end{aligned}\tag{C.1}$$

One gets,

$$\begin{aligned}\rho_n &= CZ, \\ \ln Z &= -\frac{1}{2} \frac{bc}{b+c} m_0^2 - \frac{3}{2} \ln \frac{b+c}{2\pi} \\ &= -a \frac{m_0^2}{m_e^2} \beta u_n + \frac{3}{2} \ln \left(\frac{2\alpha a}{\beta} \right), \quad \text{with } a = \frac{b}{b+c}.\end{aligned}\tag{C.2}$$

By differentiations of the integrand of the integral Z with respect to b and c , one gets the averages

$$\langle (\mathbf{m} - \mathbf{m}_0)^2 \rangle = -2 \frac{\partial \ln Z}{\partial b} = \left(\frac{c}{b+c} \right)^2 m_0^2 + \frac{3}{b+c}.\tag{C.3}$$

$$\langle m^2 \rangle = -2 \frac{\partial \ln Z}{\partial c} = \left(\frac{b}{b+c} \right)^2 m_0^2 + \frac{3}{b+c} = a^2 m_0^2 + \frac{3\alpha}{\beta} a.\tag{C.4}$$

Thus with Eq. (A.8) the total internal energy per particle becomes

$$\beta u_n^{tot} = \frac{1}{2} c \langle m^2 \rangle + \frac{1}{2} b \langle (\mathbf{m} - \mathbf{m}_0)^2 \rangle = \frac{bc}{2(b+c)} m_0^2 + \frac{3}{2} = a \frac{m_0^2}{\langle m^2 \rangle} \beta u_n + \frac{3}{2}.\tag{C.5}$$

Appendix D. Proof of Eq. (51)

Let us denote by Q the quantity appearing in Eq. (50),

$$Q = \beta \frac{\partial (f u_n)}{\partial \beta} \Big|_{m_e} - \frac{3}{2} \frac{\partial (\ln a)}{\partial \beta} \Big|_{m_e},\tag{D.1}$$

From Eq. (27) one has,

$$u_n = \frac{1}{2\alpha} m_e^2 (a^{-1} - 1), \quad (\text{D.2})$$

Since m_e is kept constant in Q , the f and u_n are functions of the lone a in the differentiations, so that one gets using Eqs. (48) and (D.2) in Eq. (D.1),

$$Q = \left[\frac{\beta}{2\alpha} \left(\frac{m_e^2}{a^2} - m_0^2 \right) - \frac{3}{2a} \right] \times \frac{\partial a}{\partial \beta} \Big|_{m_e}, \quad (\text{D.3})$$

or, by utilizing Eq. (26),

$$Q = \left(\frac{\beta}{2\alpha} \frac{1}{a^2} - \frac{3\alpha a}{\beta} - \frac{3}{2a} \right) \times \frac{\partial a}{\partial \beta} \Big|_{m_e} = 0. \quad (\text{D.4})$$

Therefore one finds that $Q = 0$, which is used in Eq. (50).

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