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ON THE MEAN SPHERICAL APPROXIMATION FOR HARD IONS AND DIPOLES

by

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On the Mean Spherical Approximation for Hard Ions and Dipoles

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Abstract

The analytical solution of the Mean Spherical Approximation for the case of equal size ions and different size solvent is reexamined using only two parameters : a polarization parameter λ and a screening parameter Γ. We show that the ion dipole cross

energy parameter, which in previous work was obtained solving a cubic equation, can be obtained from a linear algebraic equation. Therefore, the inverse problem of calculating the reduced charge parameter d_0 and the reduced dipole parameter d_2 from λ and Γ is reduced to a system of two equations: a cubic for d_0, and a linear for d_2. Simpler expressions for the thermodynamic parameters are also obtained.

1 Introduction

Considerable advances have been made over tha last thirty years in the statistical mechanical description of electrolyte solutions in molecular solvents. This work has been carried out using different approaches: computer simulations,[1,2] accurate integral equations, such as the hypernetted chain equation,[3] which were applied to this case by Patey and coworkers[4,5] and simple analytical theories, based on the mean spherical approximation (MSA).[6] The last approach is attractive for chemists examining the thermodynamic properties of electrolyte solutions not only because the model gives rather simple analytical results but also because it shares with the Debye Hückel theory the remarkable simple description in terms of a single screening parameter for any arbitrary mixture of electrolytes, and has the added bonus of satisfying the large charge, large density limits of Onsager.[7,8] In the present work we consider a mixture of a salt of equal size hard sphere ions, and a solvent which is represented by a hard sphere of different size with a permanent point dipole. Early work at the non-primitive level[9,10] was restricted , for technical reasons, to the case of ions and solvent of equal diameter. The extension of the analytical result to mixtures of arbitrary size ions and solvents is considerably more complex[11-14] but the remarkable fact that the excess ionic properties depend on a single scaling, Debye-like parameter is still retained by this approximation. The equations for the most general case appear to be rather complex, but the semirestricted case of equal size ions of diameter σ_i and a different size dipole of diameter σ_s is both interesting and tractable. In recent years[15] it has become apparent that the underlying structure of the MSA consists of a number of scaling parameters which is equal to the number of independent interaction parameters of the problem. For example, for the ion-dipole mixture there are only two interaction parameters, the charge and the dipole moment, and correspondingly, there will be only two scaling parameters, Γ, for the charges, and λ for the dipoles. For the primitive model of ionic solutions in the semirestricted case[16]the parameter Γ is determined from the equation

$$\frac{4\pi e^2}{\epsilon_W k_B T}\sum_i \frac{\rho_i z_i^2}{1+\Gamma\sigma_i} = 4\Gamma^2 \tag{1}$$

where tho ionic charge is $z_i e$ and number density $\rho_i = \mathcal{N}_i/V$, where $\mathcal{N}_i$ is the number of ions and V is the volume of the system. The temperature is T and Boltzmann's constant is k_B. For the case of only one ion diameter σ_i the screening parameter Γ is related to the Debye screening parameter

$$\kappa^2 = \frac{4\pi e^2}{\epsilon_W k_B T} \sum_i \rho_i z_i^2 \tag{2}$$

by

$$(1 + 2\Gamma\sigma)^2 = (1 + 2\kappa\sigma) \tag{3}$$

For a system of spheres of diameter σ_s and a permanent dipole moment μ_s the MSA result can be expressed in terms of a single parameter λ . Following Wertheim,[17] we have

$$d_2^2 = \frac{\lambda^2(\lambda + 2)^2}{9}(1 - \frac{1}{\epsilon_W}) \tag{4}$$

where

$$d_2^2 = \frac{4\pi \rho_s \mu_s^2}{3k_B T} \tag{5}$$

and ρ_s is the solvent number density. Furthermore, the MSA dielectric constant ϵ_W of the solvent is given by

$$\epsilon_W = \frac{\lambda^2(\lambda + 1)^4}{16} \tag{6}$$

As has been often done in the literature, the parameter λ can be computed directly from the dielectric constant ϵ_W using the above cubic equation. This parametrization defines an effective polarization parameter.

This paper is the continuation of previous work of Blum and Wei[12] and of Blum and Fawcett.[22] The notation of Blum and Wei will be used throughout. We show that for the semirestricted case of the ion-dipole model of ionic solutions an ion-dipole interaction parameter b_1 is obtained from a linear equation whic is also a fuction of the reduced charge d_0. In our previous work[19,12] this parameter was obtained as a solution of a cubic equation with coefficients that depend on Γ, the dielectric constant ϵ_W and λ. When $\sigma_s \rightarrow 0$ we recover the primitive model MSA equations, and the hydration thermodynamics is that of the continuum model as described by the Born equation. In the next section we discuss the new form of the MSA equations for the semirestricted case of equal size ions and a different size hard dipole. The thermodynamics for this system is derived in the final section using the expressions of Vericat et al.[18] and of Blum et al.[12]

2 Theory

We summarize the results of previous work.[11,18,12] We use the invariant expansion formalism,[20] in which the total pair correlation $h(12)$ is expanded in terms of rotational invariants

$$h(12) = \hat{h}^{000}(r_{12}) + \hat{h}^{011}(r_{12})\hat{\Phi}^{011} + \hat{h}^{101}(r_{12})\hat{\Phi}^{101} + \hat{h}^{110}(r_{12})\hat{\Phi}^{110} + \hat{h}^{112}(r_{12})\hat{\Phi}^{112} \tag{7}$$

where $\hat{h}^{mn\ell}(r_{12})$ is the coefficient of the invariant expansion, which depend only on the distance r_{12} between spheres 1 and 2. The rotational invariants $\hat{\Phi}^{mn\ell}$ depend only on the mutual orientations of the molecules. For the present case the relevant correlation functions are

- ion-ion:

$$h_{ii}(r) = (1/2)\left[\hat{h}^{000}_{++}(r) - \hat{h}^{000}_{+-}(r)\right] \tag{8}$$

- ion-dipole:

$$h_{in}(r) = (1/2)\left[\hat{h}^{011}_{+n}(r) - \hat{h}^{011}_{-n}(r)\right](\hat{\mathbf{r}}\cdot\hat{\mu}) \tag{9}$$

- dipole-dipole:

$$\begin{aligned} h_{nn}(r) &= -\sqrt{3}\hat{h}^{110}_{nn}(r)\hat{\mu}_1\cdot\hat{\mu}_2 \\ &+ \sqrt{\frac{15}{2}}\hat{h}^{112}_{nn}(r)\left[3(\hat{\mathbf{r}}\cdot\hat{\mu}_1)(\hat{\mathbf{r}}\cdot\hat{\mu}_2) - \hat{\mu}_1\cdot\hat{\mu}_2\right] \end{aligned} \tag{10}$$

where $\hat{\mu}$ is the unit vector in the direction of μ. The solution of the MSA is given in terms of the 'energy' parameters

- ion-ion:

$$b_0 = 2\pi\rho_i\int_0^\infty dr h_{ii}(r) r\sigma_i \tag{11}$$

- ion-dipole:

$$b_1 = 2\pi\sqrt{\frac{\rho_i\rho_n}{3}}\int_0^\infty dr h_{in}(r)\sigma_i\sigma_n \tag{12}$$

- dipole-dipole:

$$b_2 = 3\pi\rho_n\sqrt{\frac{2}{15}}\int_0^\infty dr\frac{\hat{h}^{112}(r)}{r}\sigma_n^3 \tag{13}$$

which, as will be shown below are proportional to the ion-ion, ion-dipole and dipole-dipole excess internal energy.[18] In the MSA they are functions of the ion charge and the solvent dipole moment, through the parameters

$$d_0^2 = \frac{4\pi e^2}{k_B T}\sigma_i^2 \sum_j \rho_j z_j^2 \tag{14}$$

and

$$d_2^2 = \frac{4\pi \rho_s \mu_s^2}{3k_B T} \tag{15}$$

These parameters are required to satisfy the following equations[12]

$$a_1^2 + a_2^2 = d_0^2 \tag{16}$$

$$d_0 d_2 = a_1 K_{10} - a_2[1 - K_{11}] \tag{17}$$

$$K_{10}^2 + [1 - K_{11}]^2 = y_1^2 + d_2^2 \tag{18}$$

Since

$$K_{10} = (\sigma_s/\sigma_i)\frac{b_1}{2\Delta}[1 + a_1\Lambda] \tag{19}$$

and

$$1 - K_{11} = \frac{1}{\Delta}[\beta_3 - a_2 b_1 \Lambda(\sigma_s/2\sigma_i)] \tag{20}$$

with

$$\Lambda = (1/2)(1 + b_0) + \beta_6(\sigma_s/6\sigma_i) \tag{21}$$

can be rearranged to

$$a_1^2 + a_2^2 = d_0^2 \tag{22}$$

$$\frac{a_1 b_1 \sigma_s}{2\sigma_i} - a_2\beta_3 = d_0\Delta\mathcal{A} \tag{23}$$

$$\left[\frac{b_1\sigma_s}{2\sigma_i}\right]^2 + \beta_3^2 = \Delta^2 y_1^2 + \Delta^2\mathcal{A}^2 \tag{24}$$

where we have used the definitions

$$a_1 = \frac{1}{2D_F^2}[\Delta - 2\beta_6 D_F] \tag{25}$$

$$a_2 = -\frac{b_1}{\beta_6 2D_F^2}[\Delta/2 + D_F\frac{\beta_3\sigma_i}{\sigma_s}] \tag{26}$$

$$D_F = \frac{1}{2}\left[\beta_6(1 + b_0) - \frac{b_1^2\sigma_s}{12\sigma_i}\right] \tag{27}$$

$$\Delta = \frac{b_1^2}{4} + \beta_6^2 \tag{28}$$

and

$$\mathcal{A} = d_2 - \frac{b_1 d_0 \sigma_s}{4\Delta\sigma_i}\left[1 + b_0 + \frac{\beta_6\sigma_s}{3\sigma_i}\right] \tag{29}$$

which can also be written[12]

$$\mathcal{A} = d_2 - d_0\Lambda\frac{b_1\sigma_s}{2\beta_6^2\mathcal{D}\sigma_i} \tag{30}$$

where

$$\mathcal{D} = 1 + \mathcal{B}_1 \tag{31}$$

with

$$\mathcal{B}_1 = \frac{b_1^2}{4\beta_6^2} = \frac{b_1^2(\lambda+2)^2}{36} \tag{32}$$

Also

$$\beta_6 = 1 - b_2/6 \tag{33}$$

$$\beta_3 = 1 + b_2/3 \tag{34}$$

$$\beta_{12} = 1 + b_2/12 \tag{35}$$

It will turn out convenient to use the parameter

$$\lambda = \frac{\beta_3}{\beta_6} \tag{36}$$

Then

$$b_2 = 6\frac{\lambda - 1}{\lambda + 2} \tag{37}$$

$$\beta_3 = 3\frac{\lambda}{\lambda + 2} \tag{38}$$

$$\beta_6 = \frac{3}{\lambda + 2} \tag{39}$$

$$y_0 = \frac{\beta_3}{\beta_6^2} = \frac{\lambda(\lambda+2)}{3} \tag{40}$$

$$y_1 = \frac{\beta_6}{\beta_{12}^2} = 3\frac{4(\lambda+2)}{3(\lambda+1)^2} \tag{41}$$

Futhermore we have the dielectric constant[17]

$$\epsilon_W = \frac{y_0^2}{y_1^2} = \frac{\lambda^2(\lambda+1)^4}{16} \tag{42}$$

As has been previously shown[19,12-14] Eq.(23) can be replaced by

$$\frac{a_2 b_1 \sigma_s}{2\sigma_i} + a_1\beta_3 = d_0 \Delta y_1 \tag{43}$$

which together with Eqs.(22) and (24) form a system of three equations for the three unknowns b_0, b_1, b_2. However these equations are still complex. A much simpler set of equations is obtained when we use the proper scaling lengths.[16,17] We define Γ through the relation

$$b_0 = \frac{-\Gamma\sigma_i}{1+\Gamma\sigma_i} + \frac{b_1^2}{4\beta_6^2}\left[\frac{1}{1+\Gamma\sigma_i} + \frac{\beta_6\sigma_s}{3\sigma_i}\right] = \frac{-\Gamma\sigma_i}{1+\Gamma\sigma_i} + \frac{2\mathcal{B}_1\Lambda}{\mathcal{D}} \tag{44}$$

or

$$\Gamma\sigma_i = -\frac{b_0 - \mathcal{B}_1(1+\frac{\beta_6\sigma_s}{3\sigma_i})}{(1+b_0-\frac{\mathcal{B}_1\beta_6\sigma_s}{3\sigma_i})} \tag{45}$$

and λ from

$$\lambda = \frac{\beta_3}{\beta_6} \tag{46}$$

After some long but straightforward algebra we get

$$a_1 = \frac{2}{\mathcal{D}}\Gamma\sigma_i(1+\Gamma\sigma_i) = \frac{\beta_6\Gamma\sigma_i}{D_F} \tag{47}$$

$$a_2 = -a_1\frac{b_1}{2\beta_6\zeta_i} = -\frac{b_1\Gamma\sigma_i}{2D_F\zeta_i} \tag{48}$$

where now

$$D_F = \frac{\beta_6\mathcal{D}}{2(1+\Gamma\sigma_i)} \tag{49}$$

where we have defined the convenient parameter ζ_i

$$\zeta_i = \frac{\Gamma\sigma_i}{1+\Gamma\sigma_i+\frac{\lambda\sigma_i}{\sigma_s}} = \frac{\Gamma\sigma_i}{1+\Gamma\sigma_i+\frac{1}{\xi_i}} \tag{50}$$

where

$$\xi_i = \frac{\sigma_s}{\lambda\sigma_i} \tag{51}$$

$$\Lambda = (1/2)\left[1+b_0+\frac{\beta_6\sigma_s}{3\sigma_i}\right] = (\mathcal{D}/2)\left[\frac{1}{1+\Gamma\sigma_i}+\frac{\beta_6\sigma_s}{3\sigma_i}\right] \tag{52}$$

and

$$\mathcal{D} = 1 + \frac{b_1^2}{4\beta_6^2} = 1 + \frac{b_1^2(\lambda+2)^2}{36} \tag{53}$$

Furthermore we get for Eq.(29)

$$\mathcal{A} = d_2 - d_0\left(\frac{\sigma_s}{\sigma_i}\right)\left(\frac{b_1}{12\beta_6}\right)\left(\frac{2+\Gamma\sigma_s/\zeta_i}{1+\Gamma\sigma_i}\right) \tag{54}$$

Also

$$d_0^2 = \frac{a_1^2}{\zeta_i^2}\left[\zeta_i^2 + \mathcal{B}_1\right] \tag{55}$$

$$1 - K_{11} = (y_0/\mathcal{D})\left[1 + \mathcal{B}_1(\xi_i/\zeta_i)\Gamma\sigma_i\left(1 + (1+\Gamma\sigma_i)\frac{\beta_6\sigma_s}{3\sigma_i}\right)\right] \tag{56}$$

$$K_{10} = \frac{b_1}{2\mathcal{D}\beta_6^2}(1+\Gamma\sigma_i)\left(1 + \frac{\Gamma\sigma_i\beta_6\sigma_s}{3\sigma_i}\right) \tag{57}$$

With this the boundary condition

$$b_1 d_0 d_2 = \frac{2\mathcal{B}_1}{\mathcal{D}}\left[d_0^2(\sigma_s/\sigma_i)\Lambda + (\lambda/\zeta_i)(1+\zeta_i\xi_i)\right]. \tag{58}$$

the MSA equation (43)reduces to

$$2\Gamma\sigma_i(1+\Gamma\sigma_i)\left[1 - (\mathcal{D}-1)(\xi_i/\zeta_i)\right] = \frac{d_0\mathcal{D}^2}{\sqrt{\epsilon_W}} \tag{59}$$

together with the cubic equation for the ion-dipole parameter b_1

$$\mathcal{D}^2[\zeta_i^2 + \mathcal{D} - 1] = \epsilon_W[\zeta_i - (\mathcal{D}-1)\xi_i]^2 \tag{60}$$

These can be written in a more convenient form using Eq.(59)

$$2\Gamma\sigma_i(1+\Gamma\sigma_i)\left[1 - \mathcal{B}_1(\xi_i/\zeta_i)\right] = \frac{d_0(1+\mathcal{B}_1)^2}{\sqrt{\epsilon_W}} \tag{61}$$

Eq.(60) is a cubic equation in $\mathcal{B}_1$

$$(1+\mathcal{B}_1)^2\left[\zeta_i^2 + \mathcal{B}_1\right] = \epsilon_W\left[\zeta_i - \mathcal{B}_1\xi_i\right]^2 \tag{62}$$

Eliminating $(1+\mathcal{B}_1)^2$ between these two equations, we get a linear expression in $\mathcal{B}_1$ (in place of the cubic[19]), which is easily solved to yield

$$\mathcal{B}_1 = \zeta_i^2\frac{[1-\nu_i]}{\nu_i + \xi_i\zeta_i} \tag{63}$$

This is one of our main results: The parameter b_1 is now explicitly obtained as a function of the other parameters of the problem. where

$$\nu_i = \frac{2\Gamma\sigma_i(1+\Gamma\sigma_i)}{d_0\sqrt{\epsilon_W}} \tag{64}$$

Furthermore

$$1 + \mathcal{B}_1 = \frac{-(-\nu_i - \xi_i\zeta_i - \zeta_i^2 + \nu_i\zeta_i^2)}{\nu_i + \xi_i\zeta_i} \tag{65}$$

$$\zeta_i^2 + \mathcal{B}_1 = \frac{\zeta_i^2(1+\xi_i\zeta_i)}{\nu_i + \xi_i\zeta_i} \tag{66}$$

$$1 - (\xi_i/\zeta_i)\mathcal{B}_1 = \frac{\nu_i(1+\xi_i\zeta_i)}{\nu_i + \xi_i\zeta_i} \tag{67}$$

$$\mathcal{D}^2 = [1+\mathcal{B}_1]^2 = \epsilon_W \nu_i^2 \frac{(1+\xi_i\zeta_i)}{\nu_i + \xi_i\zeta_i} \tag{68}$$

so that from eq.(61) we get

$$2\Gamma\sigma_i(1+\Gamma\sigma_i)\frac{\nu_i(1+\xi_i\zeta_i)}{\nu_i+\xi_i\zeta_i} = d_0/\sqrt{\epsilon_W}\left[-\frac{-\nu_i - \xi_i\zeta_i - {\zeta_i}^2 + \nu_i{\zeta_i}^2}{\nu_i+\xi_i\zeta_i}\right]^2 \tag{69}$$

Substituting

$$\nu_i^2\epsilon_W(1+\xi_i\zeta_i)(\nu_i+\xi_i\zeta_i) = (-\nu_i - \xi_i\zeta_i - \zeta_i^2 + \nu_i\zeta_i^2)^2$$

We have that

$$1+\xi_i\zeta_i = \frac{(1+\xi_i)(1+\Gamma\sigma_i)\Gamma\sigma_i}{1+\Gamma\sigma_i+1/\xi_i} \tag{70}$$

$$\nu_i+\xi_i\zeta_i = \frac{\Gamma\sigma_i}{1+\Gamma\sigma_i+1/\xi_i}\left[\xi_i + 2\frac{(1+\Gamma\sigma_i)(1+\Gamma\sigma_i+1/\xi_i)}{d_0\sqrt{\epsilon_W}}\right] \tag{71}$$

$$\nu_i+\xi_i\zeta_i+\zeta_i^2-\nu_i\zeta_i^2 = \frac{(1+\xi_i)(1+\Gamma\sigma_i)\Gamma\sigma_i}{(1+\Gamma\sigma_i+1/\xi_i)^2}\left[1+\frac{2(1+2\Gamma\sigma_i+1/\xi_i)}{d_0\sqrt{\epsilon_W}\xi_i}\right] \tag{72}$$

Finally, after some lengthy algebra

$$\begin{aligned} &d_0(1+\xi_i)(2+2\xi_i+4\Gamma\sigma_i\xi_i+d_0\sqrt{\epsilon_W}\xi_i^2)^2 \\ &= 4\Gamma\sigma_i\sqrt{\epsilon_W}(1+\Gamma\sigma_i\xi_i)(1+\xi_i+\Gamma\sigma_i\xi_i)^2 \\ &(2+2\Gamma\sigma_i+2\xi_i+4\Gamma\sigma_i\xi_i+2\Gamma^2\sigma_i^2\xi_i+d_0\sqrt{\epsilon_W}\xi_i^2) \end{aligned} \tag{73}$$

which can be written in the form

$$\begin{aligned} &d_0\left[\frac{d_0+2(1+1/\xi_i+2\Gamma\sigma_i)/(\sqrt{\epsilon_W}\xi_i)}{(1+1/\xi_i+\Gamma\sigma_i)}\right]^2 \\ &= 4\Gamma\sigma_i\frac{(1+\Gamma\sigma_i\xi_i)}{1+\xi_i}[d_0+2(1+\Gamma\sigma_i)(1+1/\xi_i+\Gamma\sigma_i)/(\xi_i\sqrt{\epsilon_W})] \end{aligned} \tag{74}$$

This is a cubic equation for the parameter d_0.

$$d_0[d_0+c_1]^2 = c_2(d_0+c_3) \tag{75}$$

with

$$c_1 = 2\frac{\Gamma\sigma_i}{\sqrt{\epsilon_W}\xi_i}(1 + 1/\zeta_i) \tag{76}$$

$$c_2 = 4\frac{(\Gamma\sigma_i)^3}{\zeta_i^2(1+\xi_i)}(1 + \Gamma\sigma_i\xi_i) \tag{77}$$

$$c_3 = 2\frac{\Gamma\sigma_i(1+\Gamma\sigma_i)}{\zeta_i\xi_i\sqrt{\epsilon_W}} \tag{78}$$

A second equation is laboriously obtained from Eq.(18)

$$\frac{y_0^2}{\mathcal{D}^2}\left[1 + (\mathcal{D}/2)\mathcal{M}_i\left[\frac{1}{1+\Gamma\sigma_i} + \frac{\beta_6\sigma_s}{3\sigma_i}\right]\right]^2$$

$$+ \frac{y_0\sigma_s}{2\beta_6\sigma_i}\mathcal{M}_i\frac{(1+\Gamma\sigma_i)(1+\Gamma\sigma_i\frac{\beta_6\sigma_s}{3\sigma_i})^2}{1 + 1/\xi_i + \Gamma\sigma_i} = y_1^2 + d_2^2 \tag{79}$$

where

$$\mathcal{M}_i = \frac{2\Gamma\sigma_i(1+\Gamma\sigma_i)}{\mathcal{D}^2} - \frac{d_0}{\sqrt{\epsilon_W}} \tag{80}$$

$$y_0 = \frac{\beta_3}{\beta_6^2} \tag{81}$$

From these two equations the inverse problem can be solved explicitly, that is, to compute the parameters d_0 and d_2 from Γ and λ. When the solvent diameter σ_s goes to zero we recover the correct primitive model result

$$2\Gamma\sigma_i(1+\Gamma\sigma_i) = \frac{d_0}{\sqrt{\epsilon_W}} \tag{82}$$

which is equal to the primitive model MSA Eq.(3) in the form

$$2\Gamma\sigma(1+\Gamma\sigma) = \kappa\sigma \tag{83}$$

with the MSA Wertheim dielectric constant ϵ_W.

3 Thermodynamics

The excess internal energy for the semirestricted case of equal size ions and a different size solvent is similar to the completely resticted case of all equal size spheres. The thermodynamic relations for the completely restricted case were first derived by Vericat and Blum.[18] The generalization of the thermodynamic expressions to the completely general case and the semiresticted case were obtained later by Wei and Blum.[12] We use the reduced quantities of the second work. The internal energy is

$$\sigma_i^3 E/(V k_B T) = \frac{1}{4\pi}\left[d_0^2 b_0 - 2\left(\frac{\sigma_i}{\sigma_s}\right) d_0 d_2 b_1 - 2\left(\frac{\sigma_i}{\sigma_s}\right)^3 d_2^2 b_2\right] \tag{84}$$

the Helmholtz free energy is obtained using the method of Høye and Stell[21]

$$\sigma_i^3 A/(V k_B T) = \frac{1}{12\pi}\left(2 d_0^2 b_0 - 2 d_0 d_2 b_1 - J'\right) \tag{85}$$

$$J' = [Q'_{ii}]^2 + \left[1 + \left(\frac{\sigma_i}{\sigma_s}\right)\right]\left(\frac{\sigma_i}{\sigma_s}\right)[Q'_{id}]^2 + \left(\frac{\sigma_i}{\sigma_s}\right)^3\left[[Q'_{dd}]^2 + 2(q')^2\right] \tag{86}$$

It will be convenient to write the Helmholtz free energy as the sum of a internal energy and an entropy term

$$A/(V k_B T) = E/(V k_B T) - S/(V k_B) \tag{87}$$

where

$$-\sigma_i^3 S/(V k_B) = \frac{1}{12\pi}\left[-d_0^2 b_0 + 4\left(\frac{\sigma_i}{\sigma_s}\right) d_0 d_2 b_1 + 6\left(\frac{\sigma_i}{\sigma_s}\right)^3 d_2^2 b_2 - J'\right] \tag{88}$$

Using the results of Wei and Blum,[12] Eqs.(16-20) and

$$q' = b_2\frac{1 - b2/24}{(1 + b_2/12)^2} = 2\frac{(\lambda - 1)(\lambda + 3)}{(\lambda + 1)^2} \tag{89}$$

$$Q'_{ii} = -a_1 - 2 + \beta_6/D_F = -\frac{2}{\mathcal{D}}[\Gamma^2\sigma_i^2 + \mathcal{B}_1] \tag{90}$$

$$Q'_{id} = \frac{b_1}{\beta_6^2\mathcal{D}}[\beta_3 + a_1(3\Lambda - 2D_F)]$$

$$Q'_{id} = \frac{b_1\beta_3}{\beta_6^2\mathcal{D}}(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_i\xi_i) \tag{91}$$

$$\begin{aligned} Q'_{dd} &= 2\left[(1/\Delta)\left(\beta_3^2 - \left(\frac{\sigma_i}{2\sigma_s}\right) b_1 a_2(3\Lambda - 2D_F)\right) - 1\right] \\ &= \left[\frac{2}{\mathcal{D}}\right]\left[\lambda^2 - 1 - \mathcal{B}_1\left(1 - \frac{(\Gamma\sigma_i)^2}{\zeta_i^2}\right)\right] \end{aligned} \tag{92}$$

After some lenghty calculations we get

$$-S/(V k_B) = \frac{1}{3\pi}\left[\Gamma^3 + \frac{\lambda^3}{\sigma_s^3}\left([1 + \frac{(1 + 1/\lambda)}{\epsilon_W}] - 3\right)\right] + T'/\sigma_i^3 \tag{93}$$

where the coefficients T' is a second order polynomial in the variable

$$\frac{\mathcal{B}_1}{\mathcal{D}^2} = \frac{\mathcal{M}_i}{2(1 + \Gamma\sigma_i)(1 + (1 + \Gamma\sigma_i)\xi_i)} \tag{94}$$

where $\mathcal{M}_i$ has been defined in eq.(80). When this variable is zero then the system behaves like a sum of a primitive model electrolyte and a dipolar fluid. Our expressions reproduce the known results[23–25] for the ionic part. For the dipolar part we get a new and simple expression, which, however, is in full agreement with the result of Rushbrooke et al.[26]

We have

$$T' = (1/12\pi)[T_b + T_J] \tag{95}$$

with

$$T_b = T_{b0} + T_{b1} + T_{b2} \tag{96}$$

$$T_{b0} = -\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right] 4(\Gamma\sigma_i)^3(1+\Gamma\sigma_i)\left[2 - 1/\zeta_i^2 + \mathcal{B}_1 + (1/\Gamma\sigma_i)(1+\mathcal{B}_1/\zeta_i^2)\left(1 + (1+\Gamma\sigma_i)\frac{\beta_6\sigma_s}{3\sigma_i}\right)\right] \tag{97}$$

$$T_{b1} = 16\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right]\Gamma\sigma_i(1+\Gamma\sigma_i)\left[1 + \frac{1}{\xi_i\zeta_i} + \Gamma\sigma_i(1+\mathcal{B}_1/\zeta_i^2)\left(1 + (1+\Gamma\sigma_i)\frac{\beta_6\sigma_s}{3\sigma_i}\right)\right] \tag{98}$$

$$T_{b2} = \left(\frac{\sigma_i}{\sigma_s}\right)^3 6b_2[d_2^2 + y_1^2 - y_0^2]$$

$$= 6b_2\left(\frac{\sigma_i}{\sigma_s}\right)^3\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right]\left[\left(\frac{(1+\Gamma\sigma_i)\left(1+\frac{\beta_6\sigma_s}{3\sigma_i}\right)}{\beta_6}\right)^2 + y_0^2\gamma_i[2\mathcal{D} + \mathcal{B}_1\gamma_i]\right] \tag{99}$$

where

$$\gamma_i = -1 + (\xi_i/\zeta_i)\Gamma\sigma_i\left(1 + (1+\Gamma\sigma_i)\frac{\beta_6\sigma_s}{3\sigma_i}\right)$$

Furthermore

$$T_J = T_{J0} + T_{J1} + T_{J2} \tag{100}$$

$$T_{J0} = 4\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right](1 - \Gamma^2\sigma_i^2)[2\Gamma^2\sigma_i^2 + \mathcal{B}_1(1+\Gamma^2\sigma_i^2)] \tag{101}$$

$$T_{J1} = 4\left[1 + \left(\frac{\sigma_i}{\sigma_s}\right)\right]\left(\frac{\sigma_i}{\sigma_s}\right)\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right]\lambda^2(1+\Gamma\sigma_i)^2(1+\Gamma\sigma_i\xi_i)^2 \tag{102}$$

$$T_{J2} = \left(\frac{\sigma_i}{\sigma_s}\right)^3\left[[Q'_{dd}]^2 - 4(\lambda^2 - 1)^2\right]$$

$$= -4\left(\frac{\sigma_i}{\sigma_s}\right)^3\left[\frac{\mathcal{B}_1}{\mathcal{D}^2}\right]\left[\lambda^2 - (\Gamma\sigma_i/\zeta_i)^2\right]\left[(\lambda^2-1)(1+\mathcal{D}) - \mathcal{B}_1\left(1 - (\Gamma\sigma_i/\zeta_i)^2\right)\right] \tag{103}$$

The excess pressure can also be computed.[21] The expression is[12]

$$P/k_BT = S/Vk_BT \tag{104}$$

Then,

$$G = E \tag{105}$$

still holds.

The thermodynamic expressions for the infinite dilution limit[11] was discussed by Chan and colaborators,[27] and in a more comprehensive way by Garisto et al.[28] Our expressions agree with these works in that limit. A more detailed discussion of the applications of these results will be published in future work.

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