

## On the mean spherical approximation for hard ions and dipoles

L. Blum, Fernando Vericat, and W. R. Fawcett

Citation: *The Journal of Chemical Physics* **96**, 3039 (1992); doi: 10.1063/1.462001

View online: <http://dx.doi.org/10.1063/1.462001>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/96/4?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Scaling for mixtures of hard ions and dipoles in the mean spherical approximation](#)

*J. Chem. Phys.* **117**, 756 (2002); 10.1063/1.1483294

[A global phase diagram for the ion-dipole model in the mean spherical approximation](#)

*J. Chem. Phys.* **109**, 214 (1998); 10.1063/1.476553

[Erratum: On the mean spherical approximation for hard ions and dipoles \[\*J. Chem. Phys.\* 96, 3039 \(1992\)\]](#)

*J. Chem. Phys.* **101**, 10197 (1994); 10.1063/1.468516

[Generalized mean spherical approximation for a mixture of hard ions and hard dipoles against a charged hard wall](#)

*J. Chem. Phys.* **77**, 5808 (1982); 10.1063/1.443739

[Mixtures of hard ions and dipoles against a charged wall: The Ornstein–Zernike equation, some exact results, and the mean spherical approximation](#)

*J. Chem. Phys.* **74**, 1902 (1981); 10.1063/1.441282

---



# On the mean spherical approximation for hard ions and dipoles

L. Blum

*Department of Physics, P.O. Box 23343, University of Puerto Rico, Rio Piedras, Puerto Rico 00931-3343*

Fernando Vericat

*Instituto de Física de Líquidos y Sistemas Biológicos (IFL-YSIB) c.c 565 (1900), La Plata, Argentina  
and Departamento de Fisicomatemáticas, Facultad de Ingeniería, Universidad Nacional de La Plata,  
La Plata, Argentina*

W. R. Fawcett

*Department of Chemistry, University of California, Davis, California 95616*

(Received 18 September 1991; accepted 30 October 1991)

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  $\lambda$  and a screening parameter  $\Gamma$ . 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  $\lambda$  and  $\Gamma$  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.

## I. INTRODUCTION

Considerable advances have been made over the last 30 years in the statistical mechanical description of electrolyte solutions in molecular solvents. This work has been carried out using different approaches: computer simulations,<sup>1,2</sup> accurate integral equations, such as the hypernetted chain equation,<sup>3</sup> which were applied to this case by Patey and co-workers<sup>4,5</sup> and simple analytical theories, based on the mean spherical approximation (MSA).<sup>6</sup> 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.<sup>7,8</sup> 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 nonprimitive level<sup>9,10</sup> 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<sup>11-14</sup> but the remarkable fact that the excess ionic properties depend on a single scaling, Debye-type 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  $\sigma_i$  and a different size dipole of diameter  $\sigma_s$  is both interesting and tractable. In recent years<sup>15</sup> 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,  $\Gamma$ , for the charges, and  $\lambda$  for the dipoles. For the primitive model of

ionic solutions in the semirestricted case<sup>16</sup> the parameter  $\Gamma$  is determined from the equation

$$\frac{4\pi e^2}{\epsilon_w k_B T} \sum_i \frac{\rho_i z_i^2}{1 + \Gamma \sigma_i} = 4\Gamma^2, \quad (1)$$

where the 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  $\sigma_i$  the screening parameter  $\Gamma$  is related to the Debye screening parameter

$$\kappa^2 = \frac{4\pi e^2}{\epsilon_w k_B T} \sum_i \rho_i z_i^2 \quad (2)$$

by

$$(1 + 2\Gamma\sigma)^2 = (1 + 2\kappa\sigma). \quad (3)$$

For a system of spheres of diameter  $\sigma_s$  and a permanent dipole moment  $\mu_s$ , the MSA result can be expressed in terms of a single parameter  $\lambda$ . Following Wertheim,<sup>17</sup> we have

$$d_2^2 = \frac{\lambda^2(\lambda + 2)^2}{9} \left(1 - \frac{1}{\epsilon_w}\right), \quad (4)$$

where

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

and  $\rho_s$  is the solvent number density. Furthermore, the MSA dielectric constant  $\epsilon_w$  of the solvent is given by

$$\epsilon_w = \frac{\lambda^2(\lambda + 1)^4}{16}. \quad (6)$$

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

This paper is the continuation of previous work of Blum and Wei<sup>12</sup> and of Blum and Fawcett.<sup>18</sup> 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 which is also a function of the reduced charge  $d_0$ . In our previous work<sup>19,12</sup> this parameter was obtained as a solution of a cubic equation with coefficients that depend on  $\Gamma$ , the dielectric constant  $\epsilon_w$  and  $\lambda$ . 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.*<sup>20</sup> and of Blum *et al.*<sup>12</sup>

## II. THEORY

We summarize the results of previous work.<sup>11,20,12</sup> We use the invariant expansion formalism,<sup>21</sup> in which the total pair correlation  $h(12)$  is expanded in terms of rotational invariants

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

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

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

ion-dipole,

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

dipole-dipole,

$$h_{nn}(r) = -\sqrt{3}\hat{h}_{nn}^{110}(r)\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2 + \sqrt{15/2}\hat{h}_{nn}^{112}(r) [3(\hat{\mathbf{r}} \cdot \hat{\boldsymbol{\mu}}_1)(\hat{\mathbf{r}} \cdot \hat{\boldsymbol{\mu}}_2) - \hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2]; \quad (10)$$

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

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

ion-dipole,

$$b_1 = 2\pi\sqrt{\rho_i\rho_s/3} \int_0^\infty dr h_{in}(r)\sigma_i\sigma_s; \quad (12)$$

dipole-dipole,

$$b_2 = 3\pi\rho_s\sqrt{2/15} \int_0^\infty dr \frac{\hat{h}^{112}(r)}{r} \sigma_s^3 \quad (13)$$

which, as will be shown below are proportional to the ion-ion, ion-dipole, and dipole-dipole excess internal energy.<sup>20</sup> In the MSA they are functions of the ion charge and the solvent dipole moment, through the parameters

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

and

$$d_2^2 = \frac{4\pi\rho_s\mu_s^2}{3k_B T}. \quad (15)$$

These parameters are required to satisfy the following equations<sup>12</sup>

$$a_1^2 + a_2^2 = d_0^2, \quad (16)$$

$$d_0 d_2 = a_1 K_{10} - a_2 [1 - K_{11}], \quad (17)$$

$$K_{10}^2 + [1 - K_{11}]^2 = y_1^2 + d_2^2. \quad (18)$$

Since,

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

and

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

with

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

can be rearranged to

$$a_1^2 + a_2^2 = d_0^2, \quad (22)$$

$$\frac{a_1 b_1 \sigma_s}{2\sigma_i} - a_2 \beta_3 = d_0 \Delta \mathcal{A}, \quad (23)$$

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

where we have used the definitions

$$a_1 = \frac{1}{2D_F^2} [\Delta - 2\beta_6 D_F], \quad (25)$$

$$a_2 = -\frac{b_1}{\beta_6 2D_F^2} \left[ \Delta/2 + D_F \frac{\beta_3 \sigma_i}{\sigma_s} \right], \quad (26)$$

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

$$\Delta = \frac{b_1^2}{4} + \beta_6^2, \quad (28)$$

and

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

which can also be written<sup>12</sup>

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

where

$$\mathcal{D} = 1 + \mathcal{B}_1 \quad (31)$$

with

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

Also

$$\beta_6 = 1 - b_2/6, \quad (33)$$

$$\beta_3 = 1 + b_2/3, \quad (34)$$

$$\beta_{12} = 1 + b_2/12. \quad (35)$$

It will turn out convenient to use the parameter

$$\lambda = \frac{\beta_3}{\beta_6}. \quad (36)$$

Then,

$$b_2 = 6 \frac{\lambda - 1}{\lambda + 2}, \quad (37)$$

$$\beta_3 = 3 \frac{\lambda}{\lambda + 2}, \quad (38)$$

$$\beta_6 = \frac{3}{\lambda + 2}, \quad (39)$$

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

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

Furthermore, we have the dielectric constant<sup>17</sup>

$$\epsilon_w = \frac{y_0^2}{y_1^2} = \frac{\lambda^2(\lambda + 1)^4}{16}. \quad (42)$$

As has been previously shown<sup>19,12-14</sup> Eq. (23) can be replaced by

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

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.<sup>16,17</sup> We define  $\Gamma$  through the relation

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

or

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

and  $\lambda$  from

$$\lambda = \frac{\beta_3}{\beta_6}. \quad (46)$$

After some long but straightforward algebra we get

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

$$a_2 = -a_1 \frac{b_1}{2\beta_6\zeta_i} = -\frac{b_1\Gamma\sigma_i}{2D_F\zeta_i}, \quad (48)$$

where now

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

where we have defined the convenient parameter  $\zeta_i$

$$\zeta_i = \frac{\Gamma\sigma_i}{1 + \Gamma\sigma_i + \lambda\sigma_i/\sigma_s} = \frac{\Gamma\sigma_i}{1 + \Gamma\sigma_i + 1/\xi_i}, \quad (50)$$

where

$$\xi_i = \sigma_s/\lambda\sigma_i \quad (51)$$

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

and

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

Furthermore we get for Eq. (29)

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

Also,

$$d_0^2 = \frac{a_1^2}{\zeta_i^2} [\zeta_i^2 + \mathcal{B}_1], \quad (55)$$

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

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

With this the boundary condition

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

The MSA equation (43) reduces to

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

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

$$\mathcal{D}^2[\zeta_i^2 + \mathcal{D} - 1] = \epsilon_w[\zeta_i - (\mathcal{D} - 1)\xi_i]^2. \quad (60)$$

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

$$2\Gamma\sigma_i(1 + \Gamma\sigma_i)[1 - \mathcal{B}_1(\xi_i/\zeta_i)] = \frac{d_0(1 + \mathcal{B}_1)^2}{\sqrt{\epsilon_w}}, \quad (61)$$

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

$$(1 + \mathcal{B}_1)^2[\zeta_i^2 + \mathcal{B}_1] = \epsilon_w[\zeta_i - \mathcal{B}_1\xi_i]^2. \quad (62)$$

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

$$\mathcal{B}_1 = \zeta_i^2 \frac{[1 - v_i]}{v_i + \xi_i\zeta_i}. \quad (63)$$

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. Here

$$\nu_i = \frac{2\Gamma\sigma_i(1 + \Gamma\sigma_i)}{d_0\sqrt{\epsilon_w}}. \quad (64)$$

Furthermore,

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

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

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

$$\mathcal{D}^2 = [1 + \mathcal{B}_1]^2 = \epsilon_w \nu_i^2 \frac{(1 + \xi_i\xi_i)}{\nu_i + \xi_i\xi_i}, \quad (68)$$

so that from Eq. (61) we get

$$\begin{aligned} 2\Gamma\sigma_i(1 + \Gamma\sigma_i) \frac{\nu_i(1 + \xi_i\xi_i)}{\nu_i + \xi_i\xi_i} \\ = d_0/\sqrt{\epsilon_w} \left[ -\frac{-\nu_i - \xi_i\xi_i - \xi_i^2 + \nu_i\xi_i^2}{\nu_i + \xi_i\xi_i} \right]^2. \end{aligned} \quad (69)$$

Substituting

$$\begin{aligned} \nu_i^2\epsilon_w(1 + \xi_i\xi_i)(\nu_i + \xi_i\xi_i) \\ = (-\nu_i - \xi_i\xi_i - \xi_i^2 + \nu_i\xi_i^2)^2. \end{aligned}$$

We have that

$$1 + \xi_i\xi_i = \frac{(1 + \xi_i)(1 + \Gamma\sigma_i)\Gamma\sigma_i}{1 + \Gamma\sigma_i + 1/\xi_i}, \quad (70)$$

$$\begin{aligned} \nu_i + \xi_i\xi_i = \frac{\Gamma\sigma_i}{1 + \Gamma\sigma_i + 1/\xi_i} \\ \times \left[ \xi_i + 2 \frac{(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_i + 1/\xi_i)}{d_0\sqrt{\epsilon_w}} \right], \end{aligned} \quad (71)$$

$$\begin{aligned} \nu_i + \xi_i\xi_i + \xi_i^2 - \nu_i\xi_i^2 = \frac{(1 + \xi_i)(1 + \Gamma\sigma_i)\Gamma\sigma_i}{(1 + \Gamma\sigma_i + 1/\xi_i)^2} \\ \times \left[ 1 + \frac{2(1 + 2\Gamma\sigma_i + 1/\xi_i)}{d_0\sqrt{\epsilon_w}\xi_i} \right]. \end{aligned} \quad (72)$$

Finally, after some lengthy algebra

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

which can be written in the form

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

This is a cubic equation for the parameter  $d_0$ :

$$d_0[d_0 + c_1]^2 = c_2(d_0 + c_3) \quad (75)$$

with

$$c_1 = 2 \frac{\Gamma\sigma_i}{\sqrt{\epsilon_w}\xi_i} (1 + 1/\xi_i), \quad (76)$$

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

$$c_3 = 2 \frac{\Gamma\sigma_i(1 + \Gamma\sigma_i)}{\xi_i\xi_i\sqrt{\epsilon_w}}. \quad (78)$$

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

$$\begin{aligned} \frac{y_0^2}{\mathcal{D}^2} \left[ 1 + (\mathcal{D}/2)\mathcal{M}_i \left[ \frac{1}{1 + \Gamma\sigma_i} + \frac{\beta_6\sigma_s}{3\sigma_i} \right] \right]^2 \\ + \frac{y_0\sigma_s}{2\beta_6\sigma_i} \mathcal{M}_i \frac{(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_i\beta_6\sigma_s/3\sigma_i)^2}{1 + 1/\xi_i + \Gamma\sigma_i} \\ = y_1^2 + d_2^2, \end{aligned} \quad (79)$$

where

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

$$y_0 = \beta_3/\beta_6^2. \quad (81)$$

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

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

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

$$2\Gamma\sigma(1 + \Gamma\sigma) = \kappa\sigma \quad (83)$$

with the MSA Wertheim dielectric constant  $\epsilon_w$ .

### III. THERMODYNAMICS

The excess internal energy for the semirestricted case of equal size ions and a different size solvent is similar to the completely restricted case of all equal size spheres. The thermodynamic relations for the completely restricted case were first derived by Vericat and Blum.<sup>20</sup> The generalization of the thermodynamic expressions to the completely general case and the semirestricted case were obtained later by Wei and Blum.<sup>12</sup> We use the reduced quantities of the second work. The internal energy is

$$\begin{aligned} \sigma^3 E / (Vk_B T) \\ = \frac{1}{4\pi} \left[ d_0^2 b_0 - 2 \left( \frac{\sigma_i}{\sigma_s} \right) d_0 d_2 b_1 - 2 \left( \frac{\sigma_i}{\sigma_s} \right)^3 d_2^2 b_2 \right] \end{aligned} \quad (84)$$

the Helmholtz free energy is obtained using the method of Høye and Stell<sup>22</sup>

$$\sigma^3 A / (Vk_B T) = \frac{1}{12\pi} (2d_0^2 b_0 - 2d_0 d_2 b_1 - J'), \quad (85)$$

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

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

$$A/(Vk_B T) = E/(Vk_B T) - S/(Vk_B T), \quad (87)$$

where

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

Using the results of Wei and Blum,<sup>12</sup> Eqs. (16)–(20) and

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

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

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

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

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

After some lengthy calculations we get

$$-S/(Vk_B) = \frac{1}{3\pi} \left\{ \Gamma^3 + \frac{\lambda^3}{\sigma_s^3} \left[ \left( 1 + \frac{(1 + 1/\lambda)}{\epsilon_w} \right) - 3 \right] \right\} - T'/\sigma_i^3, \quad (93)$$

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

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

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<sup>23–25</sup> 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.*<sup>26</sup>

We have

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

with

$$T_b = T_{b0} + T_{b1} + T_{b2}, \quad (96)$$

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

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

$$T_{b2} = \left(\frac{\sigma_i}{\sigma_s}\right)^3 6b_2 [d_2^2 + y_1^2 - y_0^2] = 6b_2 \left(\frac{\sigma_i}{\sigma_s}\right)^3 \left[ \frac{\mathcal{B}_1}{\mathcal{D}^2} \right] \left[ \left( \frac{(1 + \Gamma \sigma_i)(1 + \Gamma \beta_6 \sigma_s/3)}{\beta_6} \right)^2 + y_0^2 \gamma_i [2\mathcal{D} + \mathcal{B}_1 \gamma_i] \right], \quad (99)$$

where

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

Furthermore

$$T_J = T_{J0} + T_{J1} + T_{J2}, \quad (100)$$

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

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

$$T_{J2} = \left(\frac{\sigma_i}{\sigma_s}\right)^3 [[\mathcal{Q}'_{dd}]^2 - 4(\lambda^2 - 1)^2] = -4 \left(\frac{\sigma_i}{\sigma_s}\right)^3 \left[ \frac{\mathcal{B}_1}{\mathcal{D}^2} \right] [\lambda^2 - (\Gamma \sigma_i/\xi_i)^2] \times [(\lambda^2 - 1)(1 + \mathcal{D}) - \mathcal{B}_1 (1 - (\Gamma \sigma_i/\xi_i)^2)]. \quad (103)$$

The excess pressure can also be computed.<sup>22</sup> The expression is<sup>12</sup>

$$P/k_B T = -S/Vk_B T. \quad (104)$$

Then,

$$G = E \quad (105)$$

still holds.

The thermodynamic expressions for the infinite dilution limit<sup>11</sup> was discussed by Chan and colaborators,<sup>27</sup> and in a more comprehensive way by Garisto *et al.*<sup>28</sup> 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.

## ACKNOWLEDGMENT

We acknowledge support from the Office of Naval Research and from the National Science Foundation through Grants Nos. NSF-CHE-89-01597 and Epscor RII-86-10677.

- <sup>1</sup> M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford Science Publications, Oxford, 1987).
- <sup>2</sup> J. M. Caillol, D. Levesque, and J. J. Weis, *J. Chem. Phys.* **91**, 5544, 5555 (1989).
- <sup>3</sup> H. L. Friedman and W. D. T. Dale, in *Modern Theoretical Chemistry*, Vol. 5 of *Statistical Mechanics*, edited by B. J. Berne (Plenum, New York, 1976).
- <sup>4</sup> P. G. Kusalik and G. Patey, *J. Chem. Phys.* **88**, 7715 (1988); **89**, 5843 (1988).
- <sup>5</sup> D. Levesque, J. J. Weis, and G. Patey, *J. Chem. Phys.* **72**, 1887 (1980).
- <sup>6</sup> L. Blum and F. Vericat, in *The Chemical Physics of Solvation*, edited by R. R. Dogonadze, E. Kalman, A. A. Kornyshev, and J. Ulstrup (Elsevier, Amsterdam, 1985).
- <sup>7</sup> L. Onsager, *J. Phys. Chem.* **63**, 189 (1939).
- <sup>8</sup> Y. Rosenfeld and L. Blum, *J. Phys. Chem.* **89**, 5149 (1985); *J. Chem. Phys.* **85**, 1556 (1986).
- <sup>9</sup> L. Blum, *Chem. Phys. Lett.* **26**, 200 (1974); *J. Chem. Phys.* **61**, 2129 (1974).
- <sup>10</sup> S. A. Adelman and J. M. Deutch, *J. Chem. Phys.* **60**, 3935 (1974).
- <sup>11</sup> L. Blum, *J. Stat. Phys.* **18**, 451 (1978).
- <sup>12</sup> L. Blum and D. Q. Wei, *J. Chem. Phys.* **87**, 555 (1987).
- <sup>13</sup> D. Q. Wei and L. Blum, *J. Chem. Phys.* **87**, 2999 (1987).
- <sup>14</sup> D. Q. Wei and L. Blum, *J. Chem. Phys.* **89**, 1091 (1988).
- <sup>15</sup> L. Blum and Y. Rosenfeld, *J. Stat. Phys.* **63**, 1177 (1991).
- <sup>16</sup> L. Blum, *Mol. Phys.* **30**, 1529 (1975).
- <sup>17</sup> M. S. Wertheim, *J. Chem. Phys.* **55**, 4291 (1971).
- <sup>18</sup> L. Blum and W. R. Fawcett, *J. Phys. Chem.* (to be published).
- <sup>19</sup> W. Pérez-Hernández and L. Blum, *J. Stat. Phys.* **24**, 451 (1981).
- <sup>20</sup> F. Vericat and L. Blum, *J. Stat. Phys.* **22**, 593 (1980).
- <sup>21</sup> L. Blum and A. J. Torruella, *J. Chem. Phys.* **56**, 303 (1972), L. Blum and A. H. Narten, *Adv. Chem. Phys.* **34**, 203 (1976).
- <sup>22</sup> J. S. Høye and G. Stell, *J. Chem. Phys.* **67**, 439 (1977).
- <sup>23</sup> L. Blum, *Mol. Phys.* **30**, 1529 (1975).
- <sup>24</sup> L. Blum and J. S. Høye, *J. Phys. Chem.* **81**, 1311 (1977).
- <sup>25</sup> K. Hiroike, *Mol. Phys.* **33**, 1195 (1977).
- <sup>26</sup> G. S. Rushbrooke, G. Stell, and J. S. Høye, *Mol. Phys.* **26**, 1199 (1973).
- <sup>27</sup> D. Y. C. Chan, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **70**, 2946 (1979).
- <sup>28</sup> F. Garisto, P. Kusalik, and G. N. Patey, *J. Chem. Phys.* **79**, 6294 (1983).