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Explicit Solution of the Mean Spherical Model for Ions and Dipoles

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It is shown that the solution of the mean spherical approximation for the ion–dipole mixtures obtained by Blum, Adelman, and Deutch has an explicit closed form solution which is one of the roots of a cubic equation.

KEY WORDS: Mean spherical approximation; ionic solutions; molecular solvents; ion–dipole mixtures.

The mean spherical approximation (MSA) was introduced by Lebowitz and Percus.[1] The solution of the MSA for the restricted primitive model of electrolytes (equal-size ions in a continuum dielectric) was first obtained by Waisman and Lebowitz,[2] and soon after, Wertheim[3] obtained a solution for a system of hard spheres with point dipoles. In both cases, the solution involves an algebraic equation for an integral of the pair correlation function which is proportional to the excess internal energy for the ionic (or dipolar) system.

In the first case, the equation is a simple quadratic, while in the dipolar case, it is of a much higher degree. However, in both cases the solution of the inverse problem, i.e., finding the Debye length from a given excess internal energy in the ionic case, is a simple linear equation. This is true also for the point dipole case. What we want to show here is that for the restricted (all equal size) ion–dipole mixture, the solution of this inverse problem is a cubic for the ion–dipole excess internal energy. The MSA for the restricted ion–dipole mixture was first obtained by Blum[4] and Adel-

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man and Deutch,[5] who reduced the MSA integral equation to a set of rather complicated algebraic equations. Further work by Vericat and Blum[6] showed that these algebraic equations could be written in a much simpler form. Our present work is a continuation of Ref. 6, and we will use the notation and symbols of this paper.

Our system consists of a mixture of equal-size hard ions of charge $\pm e$, (where e is the elementary charge), number density ρ_i, and diameter $\sigma_i = 1$, and hard spheres with point dipole μ, density ρ_d, and diameter $\sigma_d = 1$.

We designate the direct pair correlation function $c_{ij}(r)$, and the indirect pair correlation function $h_{ij}(r)$ by the symbol $f_{ij}(r)$. Then the relevant correlation functions are

ion–ion:

$$f_{ii}(r) = \tfrac{1}{2}\left[f_{++}^{000}(r) - f_{+-}^{000}(r)\right] \tag{1}$$

ion–dipole:

$$f_{id}(r) = \tfrac{1}{2}\left[f_{+d}^{011}(r) - f_{-d}^{011}(r)\right](\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\mu}}) \tag{2}$$

dipole–dipole:

$$f_{dd}(r) = -3^{1/2}f^{110}(r)(\hat{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{\mu}}_2) + \left(\tfrac{15}{2}\right)^{1/2}f^{112}(r)\left[3(\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\mu}}_1)(\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\mu}}_2) - (\hat{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{\mu}}_2)\right] \tag{3}$$

where $\hat{\boldsymbol{\mu}}$ the unit vector in the direction of $\boldsymbol{\mu}$.

As was shown in previous work,[4,6] the complete solution of the MSA integral equation is given in terms of three parameters:

$$b_0 = 2\pi\rho_i\int_0^\infty dr\, rh_{ii}(r) \tag{4}$$

$$b_1 = 2\pi(\rho_i\rho_d/3)^{1/2}\int_0^\infty dr\, h_{id}(r) \tag{5}$$

$$b_2 = 3\pi\left(\tfrac{2}{15}\right)^{1/2}\rho_d\int_0^\infty dr\, h_{dd}(r)/r \tag{6}$$

which are a function of the ionic strength (Debye inverse length) parameter d_0 and the dipolar (Clausius–Mossotti) strength parameter d_2:

$$d_0^2 = 8\pi\beta e^2\rho_i \tag{7}$$

$$d_2^2 = (4\pi/3)\beta\mu^2\rho_d \tag{8}$$

where $\beta = (1/\mathrm{k})T$ is the Boltzmann factor.

We have[4,6]

$$a_1^2 + a_2^2 = d_0^2 \tag{9}$$

$$-a_1K_{di} + a_2(1 - K_{dd}) = d_0d_2 \tag{10}$$

$$K_{di}^2 + (1 - K_{dd})^2 = y_1^2 + d_2^2 \tag{11}$$

with

$$a_1 = \left(1/2D_F^2\right)\left(-b_0\beta_6^2 + \tfrac{1}{3}b_1^2\beta_{24}\right) \tag{12}$$

$$a_2 = \left(b_1/2D_F^2\right)\left(\beta_{12} + \tfrac{1}{2}b_0\beta_3 + \tfrac{1}{12}b_1^2\right) \tag{13}$$

$$K_{di} = (b_1/2\Delta)(1 + a_i\Lambda) \tag{14}$$

$$1 - K_{dd} = (1/\Delta)(\beta_3 + \tfrac{1}{2}a_2b_1\Lambda) \tag{15}$$

where

$$\beta_{3\cdot 2^n} = 1 + (-)^n b_2/(3\cdot 2^n) \tag{16}$$

$$\Delta = \beta_6^2 + b_1^2/4 \tag{17}$$

$$D_F = \tfrac{1}{2}\left[\beta_6(1 + b_0) - \tfrac{1}{12}b_1^2\right] \tag{18}$$

$$\Lambda = \tfrac{1}{2}b_0 + \tfrac{2}{3}\beta_{24} \tag{19}$$

$$y_1 = \beta_6/\beta_{12}^2 \tag{20}$$

It is easy to see that, using (14) and (15), we can write Eqs. (10)–(11) as

$$-a_1b_1/2 + a_2\beta_3 = -d_0\Delta A \tag{21}$$

$$b_1^2/4 + \beta_3^2 = y_1^2\Delta^2 + \Delta^2A^2 \tag{22}$$

with

$$A = d_2 - d_0(b_1/2\Delta)\left[\tfrac{1}{2}(1 + b_0) + \tfrac{1}{6}\beta_6\right] \tag{23}$$

But from (9), (21), and (22) we can see that

$$a_1\beta_3 + a_2b_1/2 = d_0y_1\Delta \tag{24}$$

and from (12) and (13)

$$-\left(b_0\beta_3 + b_1^2/6\right) = y_1d_02D_F^2 \tag{25}$$

which is our crucial relation. We can eliminate d_0 from here by squaring and again using (9), (12), and (13). We get

$$\left(b_0\beta_3+\tfrac{1}{6}b_1^2\right)^2 = y_1^2\left\{\left[-\beta_6^2b_0+\tfrac{1}{3}b_1^2\beta_{24}\right]^2+b_1^2\left[\beta_{12}+\tfrac{1}{2}\left(\beta_3b_0+\tfrac{1}{6}b_1^2\right)\right]^2\right\} \tag{26}$$

which is a cubic equation in b_1^2 (see Fig. 1):

$$c_6b_1^6 + c_4b_1^4 + c_2b_1^2 + c_0 = 0 \tag{27}$$

with

$$c_0 = b_0^2\left(\beta_6^4y_1^2 - \beta_3^2\right) = b_0^2\beta_3^2(1/\epsilon_0 - 1) \tag{28}$$

$$c_2 = \left(\beta_{12}^2 + b_0^2\beta_3^2/4\right)y_1^2 + b_0\left[\left(\tfrac{4}{3}\beta_{12}^3 - \beta_6^2\right)y_1^2 - \beta_3/3\right] \tag{29}$$

$$c_4 = \tfrac{1}{36}\left[y_1^2(9 + \beta_{12}^2 + 3b_0\beta_3) - 1\right] \tag{30}$$

$$c_6 = y_1^2/144 \tag{31}$$

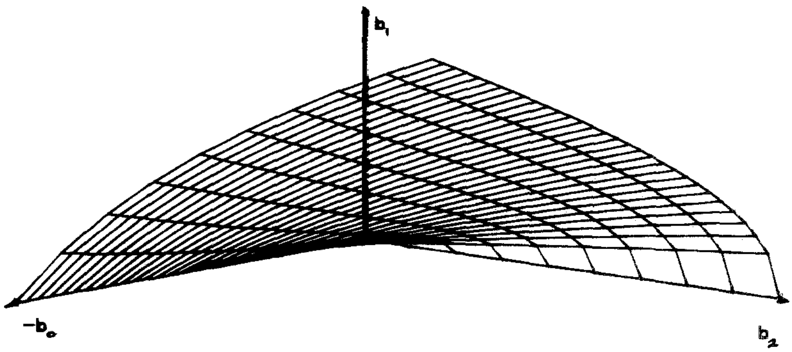

Fig. 1. Solution of Eq. (27). b_1 as a function of b_0 and b_2.

The numerical solution consists, then, in—for a given value of b_0 and b_2—finding b_1^2 by solving (26). From b_0, b_1, and b_2 we compute the values of d_0 and d_2 using Eqs. (9) and (11). From this all the relevant thermodynamic and structure functions can be computed. We refer the reader to Ref. 6 for explicit expressions.

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