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Scaling in charged fluids: beyond simple ions

L.Blum

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

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The analytical solution of the Mean Spherical Approximation for a quite general class of interactions is always a function of a reduced set of scaling matrices $\mathbf{\Gamma}_\chi$. We extend this result to systems with multipolar interactions: We show that for the ion-dipole mixture the thermodynamic excess functions are a functional of this matrix. The result for the entropy is $S = -\{kV/3\pi\}(\mathcal{F}[\mathbf{\Gamma}_\alpha])_{\alpha\in\chi}$ where $\mathcal{F}$ is an algebraic functional of the scaling matrices of irreducible representations χ of the closure of the Ornstein-Zernike. The result is also true for arbitrary electrostatic multipolar interactions.

Key words: *Coulomb systems, mean spherical approximation, entropy, ion-dipole mixtures*

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1. Introduction

It is my pleasure to contribute to this issue dedicated to J.-P.Badiali a true scientist and a gentleman.

The remarkable simplicity of the mean spherical approximation (MSA) [1–4] and its extensions using Yukawa closures [5–7] can be summarized by the fact that the entropy for a wide class of systems has a very simple functional form. The MSA [8] is the solution of the linearized Poisson-Boltzmann equation, just as the Debye-Hückel (DH) theory. It shares with the DH theory the remarkable simplicity of a one parameter description (the screening length κ) of all the thermodynamic and structural properties of rather diverse systems. The MSA shares this feature with the DH theory [9]. The major difference is that in the MSA the excluded volume of all the ions is treated exactly.

The MSA is attractive for chemists examining the thermodynamic properties of real electrolyte solutions not only because the model gives simple analytical formulas, but also satisfies exact asymptotic relations, such as the large charge, large density limits of Onsager [10–13] and more recently, the large charge small density limits implied in the Wertheim-Ornstein-Zernike equation. Very recently [5,6] we have been able to extend the MSA closure analytical solutions to any arbitrary closure that can be expanded in damped exponentials (Yukawa functions), and to obtain explicit, analytical forms of the excess thermodynamic functions in terms of a matrix of scaling parameters (the EMSSAP, or Equivalent Mean Spherical Scaling Approach [7]).

For systems with Coulomb and screened Coulomb interactions in a variety of mean spherical approximations (MSA) it is known that the solution of the Ornstein Zernike (OZ) equation is given in terms of a single screening parameter Γ. This includes the 'primitive' model of electrolytes,in which the solvent is a continuum dielectric, but also models in which the solvent is a dipolar hard sphere, and much more recently the YUKAGUA model of water that has the correct tetrahedral structure. The MSA can be deduced from a variational principle in which the energy is obtained from simple electrostatic considerations and the entropy is a universal function. For the primitive model it is

$$\Delta S = -kV \frac{\Gamma^3}{3\pi},$$

where Γ is the MSA screening parameter and in general it will be of the form

$$\Delta S = S(\underline{\underline{\Gamma}}),$$

which is independent of the form of the cavity in this approximation and

$$\underline{\underline{\Gamma}}.$$

is now the scaling matrix. We have shown that in all known cases the scaling matrix $\underline{\underline{\Gamma}}$ is obtained from the variational principle

$$\frac{\partial A}{\partial \underline{\underline{\Gamma}}} = 0 \tag{1}$$

Ionic solutions are mixtures of charged particles, the ions, and the neutral solvent particles, most commonly water, which has an asymmetric charge distribution, a large electric dipole and higher electric moments. Because of the special nature of these forces the charge distribution around a given ion and the thermodynamics does satisfy a series of conditions or sum rules. One remarkable property of mixtures of classical charged particles is that because of the very long range of the electrostatic forces, they must create a neutralizing atmosphere of counterions, which shields *perfectly* any charge or fixed charge distribution. Otherwise the partition function, and therefore all the thermodynamic functions, will be divergent [14]. The size of the region where this charge shielding occurs depends not only on the electrostatics, but also on all the other interactions of the system. For spherical ions this means:

1. The internal energy E of the ions is always the sum of the energies of capacitors. For spherical ions the capacitor is a spherical capacitor, and the *exact*

form of the energy is

$$\Delta E = -\frac{e^2}{\varepsilon}\sum_i \rho_i z_i \frac{z_i^*}{1/\Gamma_i + \sigma_i}, \tag{2}$$

where z_i^* is the effective charge, $\beta = 1/kT$ is the usual Boltzmann thermal factor, ε is the dielectric constant, e is the elementary charge, and ions i have charge, diameter and density ez_i, σ_i, ρ_i, respectively. For the continuum dielectric primitive model $\Gamma_i = \Gamma$ for all i.

2. The Onsagerian limits. When the ionic concentration goes to infinity and at the same time the charge diverges, then the limiting energy is bounded by

$$\Delta E = -\frac{e^2}{\varepsilon}\sum_i \rho_i z_i \frac{z_i^*}{\sigma_i}, \tag{3}$$

obtained by setting $\Gamma_i \to \infty$

3. A further exact limit is the DH limiting law, which simply requires that for all ions in the system

$$2\Gamma_i \to \kappa \qquad \text{with} \qquad \kappa^2 = \frac{4\pi\beta e^2}{\varepsilon}\sum_{j=1}^{m} \rho_j z_j^2. \tag{4}$$

4. Finally in systems that are strongly associating in the limit of *total* association the above equation still holds. This means that if component 1 forms a n-mer the DH limiting law must satisfy

$$\kappa^2 = \frac{4\pi\beta e^2}{\varepsilon}\left[\sum_{j=2}^{m} \rho_j z_j^2 + \rho_1 (n z_1)^2\right]. \tag{5}$$

This limiting law is not satisfied by any closure of the regular Ornstein-Zernike equation, but only for closures of the Wertheim-Ornstein-Zernike equation [15,16].

1.1. Charge-charge interactions

For the primitive model of ionic solutions in the general case [9] the parameter Γ is determined from the equation

$$\frac{4\pi e^2}{\epsilon_W k_\mathrm{B} T}\sum_i \frac{\rho_i z_i^2}{(1+\Gamma)^2} = 4\Gamma^2, \tag{6}$$

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. We have

$$\frac{\kappa^2}{(1+\Gamma)^2} = 4\Gamma^2, \tag{7}$$

where κ is defined by equation (5). The known analytical MSSA solutions for dimers and polymers satisfy a 'universality' principle for the excess entropy

$$\Delta S^{(\mathrm{MSA})} = -kV\frac{\Gamma^3}{3\pi}. \tag{8}$$

Then Γ is determined in every case by the simple variational equation (1)

$$\frac{\partial[\beta\Delta E(\Gamma) + \Gamma^3/(3\pi)]}{\partial\Gamma} = 0. \tag{9}$$

This equation is also obtained by solving the MSA using the standard procedure.

1.2. Dipole-dipole interactions

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

$$d_2^2 = \frac{\lambda^2(\lambda+2)^2}{9}\left(1 - \frac{1}{\epsilon_W}\right), \tag{10}$$

where

$$d_2^2 = \frac{4\pi\rho_s\mu_s^2}{3k_{\mathrm{B}}T} \tag{11}$$

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

$$\epsilon_W = \frac{\lambda^2(\lambda+1)^4}{16}. \tag{12}$$

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. Just as in the case of the ions, there is a physically meaningful way of interpreting the MSA for point dipoles using the variational principle (1). The dipolar system can be represented by a collection of dipolar spheres [12].

A dipolar sphere in a dielectric continuum

$$\begin{aligned} \lambda &= \frac{\epsilon_{\mathrm{in}}}{\epsilon_{\mathrm{out}}}, \\ \frac{b_2}{6} &= g_k^{\mathrm{eff}}, \end{aligned}$$

where b_2 is the dipole-dipole energy parameter defined below equation (23) and g_k^{eff} is the *effective* Kirkwood parameter for this system. From here we calculate the induced dipole

$$\mathcal{X}_d = \frac{3d_2}{\lambda+2} = d_2\beta_6$$

and the excess energy

$$\beta E = d_2\mathcal{X}_d\,.$$

So that the closure equation can be rewritten as

$$\frac{9d_2^2}{(\lambda+2)^2}=\lambda^2-\frac{16}{(\lambda+1)^4}. \tag{13}$$

This corresponds to exactly equation (1) in the form

$$\frac{\partial\beta E}{V\partial\lambda}=-\frac{\pi}{Vk}\frac{\partial S}{\partial\lambda}=\lambda^2-\frac{16}{(\lambda+1)^4}, \tag{14}$$

which can be integrated to yield

$$-\frac{\pi}{kV}S=\frac{1}{3}\left[\lambda^3+2\left(\frac{2}{\lambda+1}\right)^3\right]-1. \tag{15}$$

Now if we define the scaling lengths for the irrep $\chi=0$

$$\Gamma_0=\lambda$$

and for $\chi=\pm1$

$$\Gamma_1=\frac{2}{\lambda+1},$$

then

$$-\frac{\pi}{Vk}S=\frac{1}{3}\left[(\Gamma_0)^3+2\,(\Gamma_1)^3\right]-1. \tag{16}$$

Notice that they satisfy the Wertheim ‘density’ of the irreps since they are obtained by setting

$$\rho_1=-(1/2)\rho_0\,.$$

Furthermore, observe that because of the structure of the equations the natural assignment is

$$X_d=\frac{3}{\lambda+2}d_2=\beta_6 d_2\,. \tag{17}$$

1.3. Charge-dipole interactions

We summarize the results of the previous work [18–24]. We use the invariant expansion formalism [25], in which the total pair correlation $h(12)$ is expanded in terms of rotational invariants

$$h(12)=\hat{h}^{000}(r_{12})+\hat{h}^{011}(r_{12})\hat{\Phi}^{011}+\hat{h}^{101}(r_{12})\hat{\Phi}^{101}+\hat{h}^{110}(r_{12})\hat{\Phi}^{110}+\hat{h}^{112}(r_{12})\hat{\Phi}^{112}, \tag{18}$$

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:

$$h_{ii}(r)=(1/2)\left[\hat{h}^{000}_{++}(r)-\hat{h}^{000}_{+-}(r)\right]; \tag{19}$$

- ion-dipole:
$$h_{in}(r) = (1/2)\left[\hat{h}^{011}_{+n}(r) - \hat{h}^{011}_{-n}(r)\right](\hat{\mathbf{r}}\cdot\hat{\mu}); \tag{20}$$

- dipole-dipole:
$$\begin{aligned} h_{nn}(r) &= -\sqrt{3}\hat{h}^{110}_{nn}(r)\hat{\mu}_1\cdot\hat{\mu}_2 \\ &+ \sqrt{\frac{15}{2}}\hat{h}^{112}_{nn}(r)\left[3(\hat{\mathbf{r}}\cdot\hat{\mu}_1)(\hat{\mathbf{r}}\cdot\hat{\mu}_2) - \hat{\mu}_1\cdot\hat{\mu}_2\right], \end{aligned} \tag{21}$$

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:
$$b_0 = 2\pi\rho_i\int_0^\infty \mathrm{d}r h_{ii}(r)r; \tag{22}$$

- ion-dipole:
$$b_1 = 2\pi\sqrt{\frac{\rho_i\rho_s}{3}}\int_0^\infty \mathrm{d}r h_{in}(r); \tag{23}$$

- dipole-dipole:
$$b_2 = 3\pi\rho_s\sqrt{\frac{2}{15}}\int_0^\infty \mathrm{d}r\frac{\hat{h}^{112}(r)}{r}, \tag{24}$$

which, as will be shown below are proportional to the ion-ion, ion-dipole and dipole-dipole excess internal energy [21]. In the MSA they are functions of the ion charge and the solvent dipole moment, through the parameters

$$d_0^2 = \frac{4\pi e^2}{k_\mathrm{B}T}\sum_j \rho_j z_j^2 \tag{25}$$

and d_2^2 is defined by equation (11) These parameters are required to satisfy the following equations [18]

$$\begin{aligned} a_1^2 + a_2^2 &= d_0^2\,, && (26)\\ a_1K_{10} - a_2[1-K_{11}] &= d_0d_2, && (27)\\ K_{10}^2 + [(1-K_{11})]^2 &= y_1^2 + d_2^2\,. && (28) \end{aligned}$$

where

$$\mathcal{D} = 1 + \mathcal{B}_1 \tag{29}$$

with

$$\mathcal{B}_1 = \frac{b_1^2}{4\beta_6^2} = \frac{b_1^2(\lambda+2)^2}{36}, \tag{30}$$

$$\beta_6 = 1 - \frac{b_2}{6}\,.$$

A simple set of equations is obtained when we use the proper scaling lengths [22,23]. In terms of the excess energy parameters b_0, b_1 and b_2 of equations (22–24):

$$\begin{aligned} b_0 &= \frac{-\Gamma}{1+\Gamma} + \mathcal{B}_1\mathcal{D}_\Lambda\,, && (31)\\ b_1 &= \sqrt{\mathcal{B}_1}\frac{6}{2+\lambda} && (32) \end{aligned}$$

and

$$b_2 = 6\frac{\lambda-1}{2+\lambda}. \qquad (33)$$

The entropy can be computed using [21,26]

$$\frac{S}{kV} = \frac{\beta}{V}[E-A], \qquad (34)$$

which leads to

$$\frac{S}{kV} = \frac{1}{12\pi}\left(b_0{d_0}^2 - 4\;b_1d_0d_2 - 6b_2d_2^2 + 2\,{q'}^2 + {Q'_{dd}}^2 + 2\,{Q'_{id}}^2 + [Q'_{ii}]^2\right). \qquad (35)$$

The contact pair correlations are [21–23]

- ion-ion

$$Q'_{ii} = \frac{2}{\mathcal{D}}\{[\Gamma]^2 + \mathcal{B}_1\}; \qquad (36)$$

- ion-dipole

$$Q'_{id} = \frac{2\sqrt{\mathcal{B}_1}}{\mathcal{D}}\{[1+\Gamma]\mathcal{D}_{\lambda g} - 1]\}; \qquad (37)$$

- dipole-dipole

$$\begin{aligned} Q'_{dd} &= \frac{2}{\mathcal{D}}\{[\lambda^2 - 1 + \mathcal{B}_1[\mathcal{D}_{\lambda g}^2 - 1]\} \quad (\chi = 0),\\ q' &= \frac{(\lambda-1)(\lambda+3)}{(\lambda+1)^2} \quad (\chi = 1). && (38) \end{aligned}$$

We also get

$$\begin{aligned} a_1 &= \frac{2}{\mathcal{D}}\Gamma(1+\Gamma), && (39)\\ a_2 &= -\frac{2\sqrt{\mathcal{B}_1}}{\mathcal{D}}(1+\Gamma)\mathcal{D}_{\lambda g} && (40) \end{aligned}$$

with

$$\begin{aligned} \mathcal{D}_{\lambda g} &= 1 + [\Gamma + \lambda], && (41)\\ \mathcal{D}_{dd} &= 1 + \frac{3\Gamma}{2+\lambda}, && (42) \end{aligned}$$

$$\begin{aligned}
\mathcal{D}_\Lambda &= \frac{1}{1+\Gamma} + \left\{\frac{1}{2+\lambda}\right\}, && (43)\\
D_f &= \frac{\beta_6}{2(1+\Gamma)}\left[1+\left(\frac{b_1(2+\lambda)}{6}\right)^2\right], && (44)\\
\mathcal{B}_1 &= \left(\frac{b_1(2+\lambda)}{6}\right)^2. && (45)
\end{aligned}$$

We have

$$1-K_{11} = \frac{2+\lambda}{3\mathcal{D}}\left\{\lambda + [1+\Gamma]\mathcal{B}_1\mathcal{D}_{\lambda g}\mathcal{D}_\Lambda\right\} \tag{46}$$

and

$$K_{10} = \frac{(2+\lambda)\sqrt{\mathcal{B}_1}}{3\mathcal{D}}(1+\Gamma)\left[(1+\Gamma)\mathcal{D}_\Lambda - \left\{\frac{1}{2+\lambda}\right\}\right]. \tag{47}$$

Our main result is the new expression for the MSA excess entropy

$$S = -\left(\frac{kV}{3\pi}\right)\{s_0 + s_1\} \tag{48}$$

with

$$\begin{aligned}
s_0 &= \left[\Gamma_T^3\sqrt{\left\{1-\frac{16\mathcal{D}}{\Gamma_T^2(1+\lambda)^4}\right\}\left\{1+\frac{16[(\mathcal{D}(1-2\Gamma_T^2)+\lambda^2-1]}{\Gamma_T^4(1+\lambda)^4}\right\}}\,\right], && (49)\\
s_1 &= \left[\frac{32}{(1+\lambda)^3}\left(1-\frac{\mathcal{D}}{2(1+\lambda)}\right)-3\right] && (50)
\end{aligned}$$

and

$$\Gamma_T = \sqrt{\Gamma^2 + \lambda^2 + \frac{2\,\mathcal{B}_1\,(1+\Gamma)\,(1+\lambda)}{\mathcal{D}}}. \tag{51}$$

The excess pressure can also be computed [26]. The expression is [22]

$$P/k_\mathrm{B}T = S/Vk_\mathrm{B}\,. \tag{52}$$

Then,

$$G = E \tag{53}$$

still holds.

It is easy to see that this expression yields the correct asymptotic results when either the ions or the dipoles are turned off. Another interesting limit is that of very large dielectric constant. Then we get

$$S = \left(\frac{kV}{3\pi}\right)\{\Gamma_T^3\}. \tag{54}$$

A full discussion of these results will be done in a future publication.

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Скейлінг у заряджених флюїдах: поза простими іонами

Л.Блюм

Фізичний факультет, університет Пуерто Ріко,
Ріо П'єдрас, PR 00931–3343

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Аналітичний розв'язок середньосферичного наближення для достатньо загального класу взаємодій є завжди функцією редукованого набору скейлінгових матриць. Ми розширюємо цей результат на випадок систем з мультипольними взаємодіями. Ми показуємо, що для іонно-дипольної суміші термодинамічні надлишкові функції є функціями цієї матриці. Результат для ентропії є $S = -\{kV/3\pi\}(\mathcal{F}[\mathbf{\Gamma}_\alpha])_{\alpha\in\chi}$, де F – алгебраїчний функціонал скейлінгових матриць незвідних представлень замикання Орнштейна-Церніке. Результат дійсний також і для довільних електростатичних мультипольних взаємодій.

Ключові слова: *кулонівські системи, середньосферичне наближення, ентропія, іонно-дипольні суміші*

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