

Solution of the Ornstein–Zernike Equation for a Soft-Core Yukawa Fluid. III. A Restricted Model for Electrolytes and Fused Salts

P. T. Cummings¹ and C. C. Wright^{1,2}

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A model for dense electrolytes and fused salts is proposed which incorporates both the known long-range asymptotic form for the direct correlation function and a parametric form for the total correlation function appropriate to a soft-core interaction potential. A special case extending the MSA for the restricted primitive model for electrolytes is discussed in some detail.

KEY WORDS: Ornstein–Zernike equation; soft-core fluid; Yukawa closure; electrolyte; fused salts.

1. INTRODUCTION

The restricted primitive model (RPM) for electrolyte solutions and molten salts consists of equal numbers of oppositely charged hard spheres of diameter R immersed in a homogeneous medium of dielectric constant ϵ , the two species being present at number density $\rho/2$. The interaction between two particles is given by

$$\phi_{ij}(r)/kT = \begin{cases} \infty, & x < 1 \\ (-1)^{i+j}B/x, & x > 1 \end{cases} \quad (1)$$

where $x = r/R$ (r is the interparticle separation) and $B = q^2/\epsilon RkT$, where $\pm q$ is the charge, k is Boltzmann's constant, and T is the absolute temperature.

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¹ Department of Mathematics, University of Melbourne, Parkville, Victoria, Australia.

² Present Address: Department of Physics, University of Guelph, Guelph, Ontario, Canada.

If we introduce the reduced density η , given by

$$\eta = \pi\rho R^3/6 \quad (2)$$

then typical values of B and η for a 2 M 1-1 electrolyte are $B \approx 2$ and $\eta \approx 0.1$. In the case of fused salts, for which $\epsilon = 1$, typically $B \approx 50$ and $\eta \approx 0.4$ (i.e., the high- B , high- η domain) (see, for example, Ref. 1).

Studies of the RPM via machine simulation,⁽¹⁻⁴⁾ numerical solution of the hypernetted chain (HNC) and Percus-Yevick (PY) approximations,⁽⁵⁻⁷⁾ and analytic solution of the mean spherical approximation (MSA)⁽⁸⁻¹⁰⁾ have indicated that the HNC is the most accurate integral equation approximation for the RPM. However, more recent developments, such as the exponential (EXP) approximation⁽¹¹⁾ and the generalized mean spherical approximation (GMSA),⁽¹²⁻¹⁴⁾ have been used successfully in improving the MSA results.

Further, the GMSA provides a fully analytic theory for both structural and thermodynamic properties whose accuracy is comparable to that of the HNC.⁽¹⁴⁾

Hence we see that the RPM is now able to be described with satisfactory accuracy via an integral equation approach, particularly in the electrolyte regime. However, the RPM itself can only be regarded as a qualitatively correct model for fused salts.⁽³⁾ The major deficiency in the model is the presence of the hard core, which requires that the total correlation functions $h_{ij}(x)$ satisfy the exact hard-core condition

$$h_{ij}(x) = -1, \quad x < 1 \quad (3)$$

A more careful treatment of the soft-core part of the interaction potential can have significant consequences even in the electrolyte regime.⁽¹⁵⁾ Hence it would be of interest to consider a nonprimitive model for electrolytes for which the hard-core condition [Eq. (3)] is relaxed.

One method by which the hard-core condition may be relaxed is through the use of a perturbation theory, such as the Weeks-Chandler-Andersen optimized cluster theory.⁽¹⁶⁾ However, this approach appears to be unsatisfactory in the fused salt regime (see Ref. 16, Sec. IV.H).

In this paper we adopt a more direct approach first introduced in Ref. 17 [hereafter referred to as I; equations from I are referred to as (I.1), etc.]. We relax the hard-core condition [Eq. (3)] by assuming that $h_{ij}(x)$, on the domain $0 < x < 1$, takes the form

$$h_{ij}(x) = -1 + \sum_{k=1}^M \frac{\alpha_{ij}^k \lambda_k}{\cosh \lambda_k} \left[\frac{\sinh(\lambda_k x) - 1}{\lambda_k x} \right], \quad 0 < x < 1 \quad (4)$$

where α_{ij}^k and λ_k are parameters yet to be determined. To specify the direct correlation functions $[c_{ij}(r)]$ we adopt an approach suggested by the success

of the GMSA⁽¹²⁻¹⁴⁾ by writing

$$c_{ij}(x) = \sum_{l=1}^{N+1} \frac{K_{ij}^l e^{-z_l(x-1)}}{x}, \quad x > 1 \tag{5}$$

where $K_{ij}^{N+1} = (-1)^{i+j+1}B$, and the parameters K_{ij}^l, z_l ($l = 1, \dots, N$) are as yet undetermined. We ensure that $c_{ij}(x)$ has the correct asymptotic behavior at large x by taking the limit $z_{N+1} \rightarrow 0$. Equations (4) and (5) may be regarded as the closures to the Ornstein-Zernike (OZ) equation⁽¹⁸⁾ for mixtures, viz.

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k h_{ik} * c_{kj}(r) \tag{6}$$

where $*$ indicates a convolution integral over all space.

In Section 2 we solve Eq. (6) for the closures given in Eqs. (4) and (5), which we call the soft-core restricted model (SCRM) for electrolytes and fused salts. In Section 3 we discuss a special case of our analysis.

2. METHOD OF SOLUTION

From symmetry considerations, we note that in Eq. (6) we have two distinct equations:

$$h_{11}(x) = c_{11}(x) + (3/\pi)\eta(h_{11} * c_{11} + h_{12} * c_{12})(x) \tag{7a}$$

$$h_{12}(x) = c_{12}(x) + (3/\pi)\eta(h_{11} * c_{12} + h_{12} * c_{11})(x) \tag{7b}$$

for the four distinct functions h_{11} ($= h_{22}$), h_{12} ($= h_{21}$), c_{11} ($= c_{22}$), and c_{12} ($= c_{21}$). Note that symmetry conditions also require that $\alpha_{12}^k = \alpha_{21}^k, \alpha_{11}^k = \alpha_{22}^k$ in Eq. (4) and that $K_{12}^l = K_{21}^l, K_{11}^l = K_{22}^l$ in Eq. (5). It is more convenient to redefine our problem in terms of the sum ($h_s(x), c_s(x)$) and difference ($h_d(x), c_d(x)$) correlation functions given by

$$h_s(x) = \frac{1}{2} [h_{11}(x) + h_{12}(x)], \quad c_s(x) = \frac{1}{2} [c_{11}(x) + c_{12}(x)] \tag{8}$$

$$h_d(x) = \frac{1}{2} [h_{11}(x) - h_{12}(x)], \quad c_d(x) = \frac{1}{2} [c_{11}(x) - c_{12}(x)] \tag{9}$$

Using Eqs. (4), (5), and (7)–(9), solution of the SCRM reduces to the solution of two separate problems. For the sum correlation functions, we require the solution of an OZ equation

$$h_s(x) = c_s(x) + (6/\pi)\eta h_s * c_s(x) \tag{10a}$$

subject to the closures

$$h_s(x) = -1 + \sum_{k=1}^M \frac{\alpha_s^k \lambda_k^2}{\cosh \lambda_k} \left[\frac{\sinh(\lambda_k x) - 1}{\lambda_k x} \right], \quad 0 < x < 1 \tag{10b}$$

$$c_s(x) = \sum_{l=1}^N \frac{K_s^l e^{-z_l(x-1)}}{x}, \quad x > 1 \tag{10c}$$

where

$$\alpha_s^k = \frac{1}{2}(\alpha_{11}^k + \alpha_{12}^k), \quad K_s^l = \frac{1}{2}(K_{11}^l + K_{12}^l)$$

This problem has already been treated in detail in I, and numerical calculations for this system have been performed.⁽¹⁹⁾

For the difference correlation functions, we must solve the OZ equation

$$h_d(x) = c_d(x) + (6/\pi)\eta h_d * c_d(x) \tag{11a}$$

subject to the closures

$$h_d(x) = \sum_{k=1}^M \frac{\alpha_d^k \lambda_k^2}{\cosh \lambda_k} \left(\frac{\sinh(\lambda_k x) - 1}{\lambda_k x} \right), \quad 0 < x < 1 \tag{11b}$$

$$c_d(x) = \sum_{l=1}^{N+1} \frac{K_d^l e^{-z_l(x-1)}}{x}, \quad x > 1 \tag{11c}$$

where

$$\alpha_d^k = \frac{1}{2}(\alpha_{11}^k - \alpha_{12}^k), \quad K_d^l = \frac{1}{2}(K_{11}^l - K_{12}^l)$$

We solve this latter problem using the Baxter Wiener–Hopf factorization technique⁽²⁰⁾ which was utilized in I. In the present case, however, we note that some care must be exercised in taking the limit $z_{N+1} \rightarrow 0$.⁽²⁴⁾

As in I, we find that the OZ equation may be decoupled into two equations for $h_d(x)$ and $c_d(x)$ given by [cf. Eqs. (I.12)–(I.15)]

$$H(x) = q(x) + 12\eta \int_0^\infty dt q(t)H(|x - t|) \tag{12}$$

$$S(x) = q(x) + 12\eta \int_x^\infty dt q(t)q(t - x) \tag{13}$$

with

$$H(x) = \int_x^\infty h_d(t)t dt \tag{14}$$

$$S(x) = \int_x^\infty c_d(t)t dt \tag{15}$$

and the function $q(x)$ is given by

$$q(x) = q_0(x) + \sum_{l=1}^{N+1} \beta_l e^{-z_l(x-1)} \tag{16}$$

where

$$q_0(x) = 0, \quad x < 0, \quad x \geq 1 \tag{17}$$

and

$$B_l = K_d^l / z_l \hat{Q}(iz_l) \tag{18}$$

The function $\hat{Q}(k)$ is given by

$$\hat{Q}(k) = 1 - 12\eta \int_0^\infty e^{ikx} q(x) dx \tag{19}$$

From Eqs. (16) and (19), we find that $z_{N+1} \hat{Q}(z_{N+1})$ is nonzero in the limit $z_{N+1} \rightarrow 0$ and is equal to $6\eta\beta_{N+1}$. Hence,

$$6\eta\beta_{N+1}^2 = K_d^{N+1} = B \tag{20}$$

This corresponds to the result obtained in the MSA for the RPM.

To find the form of $q_0(x)$ we substitute Eqs. (11b), (14), and (16) into Eq. (12), yielding on the domain $0 < x < 1$

$$\begin{aligned} H(x) = & q_0(x) + \sum_{l=1}^N \beta_l e^{-z_l(x-1)} + \beta_{N+1} \\ & + 12\eta \int_0^1 q_0(t) H(|x-t|) dt \\ & + 12\eta \sum_{l=1}^N \beta_l \int_0^\infty e^{-z_l(t-1)} H(|x-t|) dt \\ & + 12\eta\beta_{N+1} \int_0^\infty H(|x-t|) dt \end{aligned} \tag{21}$$

In general, we are not assured that the last integral in Eq. (21) is convergent. However, we invoke the Stillinger–Lovett electroneutrality condition,⁽²¹⁾ which for an \mathfrak{N} -component system of charges states that

$$4\pi \sum_{n=1}^{\mathfrak{N}} q_n \rho_n \int_0^\infty r^2 g_{nj}(r) dr = -q_j \tag{22}$$

For the present case this simplifies to

$$\int_0^\infty H(x) dx = -1/24\eta \tag{23}$$

On the domain $0 < x < 1$, we find that $H(x)$ is given by [cf. Eq. (I.19)]

$$H(x) = H_0 + \frac{1}{2} \gamma x^2 - \sum_{k=1}^M \Delta_k [\cosh \lambda_k x - 1], \quad 0 < x < 1 \tag{24}$$

where

$$H_0 = \int_0^\infty th(t) dt \tag{25}$$

$$\gamma = \sum_{k=1}^M \alpha_{kd} \lambda_k^2 / \cosh \lambda_k \tag{26}$$

$$\Delta_k = \alpha_{kd} / \cosh \lambda_k \tag{27}$$

Substitution of Eqs. (23) and (24) into Eq. (21) then yields the following form for $q_0(x)$ [cf. Eqs. (I.23)–(I.29)]:

$$\begin{aligned}
 q_0(x) = & -2\beta\eta\gamma(x^3 - 1) + \frac{1}{2}q_2(x^2 - 1) + q_1(x - 1) \\
 & + \sum_{k=1}^M [Q_{k1}(\cosh \lambda_k x - \cosh \lambda_k) + Q_{k2}(\sinh \lambda_k x - \sinh \lambda_k)] \\
 & + \sum_{l=1}^N \beta_l d_l [1 - e^{-z_l(x-1)}] \tag{28}
 \end{aligned}$$

where

$$q_1 = 12\eta\gamma \left[\int_0^1 dt t q_0(t) + \sum_{l=1}^N \frac{\beta_l e^{z_l}}{z_l^2} \right] - 12\eta\beta_{N+1} \left(H_0 + \sum_{k=1}^M \Delta_k \right) \tag{29}$$

$$q_2 = \gamma \left[1 - 12\eta \int_0^1 q_0(t) dt - \sum_{l=1}^N \frac{\beta_l e^{z_l}}{z} \right] \tag{30}$$

$$Q_{k1} = \Delta_k \left[-1 + 12\eta \int_0^1 q_0(t) \cosh \lambda_k t dt + 12\eta \sum_{l=1}^N \frac{\beta_l z_l e^{z_l}}{z_l^2 - \lambda_k^2} \right] \tag{31}$$

$$Q_{k2} = -12\eta\Delta_k \left[\int_0^1 q_0(t) \sinh \lambda_k t dt - \frac{\beta_{N+1}}{\lambda_k} + \lambda_k \sum_{l=1}^N \frac{\beta_l e^{z_l}}{z_l^2 - \lambda_k^2} \right] \tag{32}$$

$$d_l = 1 - \frac{12\eta}{z_l} \left[\tilde{h}(z_l) + \frac{\lambda}{z_l^2} - \sum_{k=1}^M \frac{\Delta_k \lambda_k^2}{\lambda_k^2 - z_l^2} \right] \tag{33}$$

and $\tilde{h}(s)$ is the Laplace transform of $xh_d(x) = xg_d(x)$ [cf. Eq. (I.29)]. These equations are analogous to those obtained in I, except for the appearance of the term $H_0 + \sum_{k=1}^M \Delta_k$ in Eq. (29). A quadratic equation for the parameter H_0 in the terms of the other parameters ($q_1, q_2, Q_{k1}, Q_{k2}, d_l$) may be found easily by equating the constant terms in Eq. (21).

The remaining parameters may now be determined using methods similar to those outlined in I, using the relationship between $\tilde{h}(s)$ and the Laplace transform of $xq(x)$ [cf. Eqs. (I.30)–(I.35)]. The quantities q_1, q_2, Q_{k1}, Q_{k2} may be found as functions of β_l, d_l ($l = 1, \dots, N$), H_0 , and β_{N+1} (known), since Eqs. (29)–(32) are linear in these variables. Then H_0 may be determined using the quadratic equation mentioned above. This introduces nonlinearities not present in the problem of I. Thus for N Yukawa terms we are reduced to the problem of solving $2N$ nonlinear algebraic equations for the parameters β_l, d_l ($l = 1, \dots, N$). This is to be contrasted with I, where only N nonlinear equations need be considered.

3. THE CASE $M = 1, N = 0$

For the case $M = 1, N = 0$, the SCRM represents the simplest extension of the MSA for the RPM that incorporates a soft core. The sum direct correlation function now satisfies

$$c_s(x) = 0, \quad x > 1 \tag{34}$$

This problem has already been considered in detail by Wright and Peram.⁽²²⁾ We note here that the solution to this problem reduces to the relatively simple problem of solving four linear equations for the parameters of $q(x)$.

The difference correlation functions satisfy the equations

$$h_d(x) = \frac{\alpha\lambda^2}{\cosh\lambda} \left(\frac{\sinh\lambda x}{\lambda x} - 1 \right), \quad 0 < x < 1 \tag{35a}$$

$$c_d(x) = \frac{B}{x}, \quad x > 1 \tag{35b}$$

The parameter β is given explicitly as

$$\beta = (B/6\eta)^{1/2} \tag{36}$$

where the negative root is chosen to ensure agreement with known hard-core MSA results in the limit $\alpha \rightarrow 0$. It is then straightforward to verify that the parameters q_1, q_2, Q_{11}, Q_{12} are the solutions of a set of linear equations of the form (cf. Ref. 19)

$$\mathfrak{R} \begin{bmatrix} q_1 \\ q_2 \\ Q_{11} \\ Q_{22} \end{bmatrix} = \mathbf{L}_0 + H_0 \mathbf{L}_1 \tag{37}$$

where the elements of the matrix \mathfrak{R} and the array \mathbf{L}_0 do not explicitly depend on H_0 and

$$\mathbf{L}_1 = \begin{bmatrix} -12\eta\beta \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{38}$$

The elements in the matrix \mathfrak{R} and vector \mathbf{L}_0 are easily found and thus not given here. Multiplying Eq. (37) by \mathfrak{R}^{-1} , we obtain expansions for the quantities q_1, q_2, Q_{11} , and Q_{12} of the form

$$\begin{bmatrix} q_1 \\ q_2 \\ Q_{11} \\ Q_{12} \end{bmatrix} = \mathbf{A}_0 + H_0 \mathbf{A}_1 \tag{39}$$

Using these expansions in Eq. (21) evaluated at $x = 0$ yields a quadratic equation for the parameter H_0 . This is similar in form to that obtained for the corresponding H_0 in the MSA for the RPM.⁽²³⁾

Hence, the solution for the parameters in the SCRM may be found explicitly in the case $N = 0$ for a given set of soft-core parameters α_{11} , α_{12} , λ_{11} , λ_{12} .

Methods for choosing the soft-core parameters have been discussed both in I and Ref. 19. At present we are performing numerical calculations when λ_{11} and λ_{12} are kept fixed and α_{11} and α_{12} are chosen so that $h_{11}(x)$ and $h_{12}(x)$ are continuous at $x = 1$.

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