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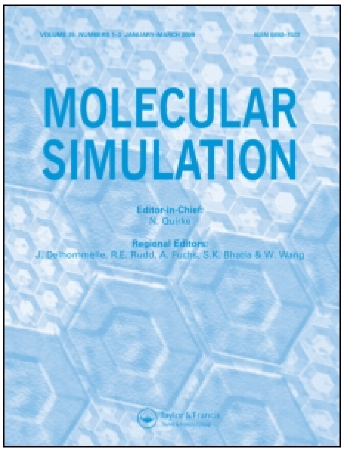

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Recent Advances in the Use of MSA Approach to Electrolyte and Charged Colloid Solutions

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In this paper, a comprehensive review of recent advances in the use of mean spherical approximation (MSA) to the primitive electrolyte model for ionic fluids, the non-primitive electrolyte model for ion–dipole mixtures, the one-Yukawa EOS for neutral fluids, and the two-Yukawa EOS for charged colloid systems is introduced. A reasonable mathematical derivation and theoretical explanation are proposed why the dielectric constant of the vacuum cannot be used in the long-range electrostatic term in some successful EOSs for real electrolyte solutions, although the dipolar solvent is treated as explicit molecule in these theories. All the studies show that the MSA approach is of significance both in theoretical research and practical use.

Keywords: Mean spherical approximation; Electrolyte primitive model; Electrolyte non-primitive model; One Yukawa EOS; Two-Yukawa EOS

INTRODUCTION

In recent years, many authors have paid more attention to the mean spherical approximation (MSA) approach, because the Ornstein–Zernike (OZ) integral equation for some potential functions, such as ion–ion, dipole–dipole, ion–dipole, and Yukawa potentials, can be solved analytically by the MSA method. In this paper, we would like to make a comprehensive review of recent advances in the study of the MSA method to electrolyte solutions and the charged colloid solutions. Firstly, the primitive MSA for aqueous electrolyte system is introduced. Secondly, the non-primitive MSA for ion–dipole mixture is expanded from a low ionic density. Both of their analytical expressions are compared with those from the primitive and non-primitive electrolyte perturbation theories respectively. Thirdly, a new analytic equation of state with one-Yukawa potential for neutral fluids based on MSA is presented and compared with the Lennard–Jones and square-well potential based SAFT EOS. Fourthly, two kinds of the two-Yukawa one-component EOSs based on MSA are established for charged colloid systems. Finally, the potentials of mean electrostatic forces are determined and some attractive electrostatic forces are found between two like-charged colloidal particles in aqueous electrolyte solutions.

PRIMITIVE MSA FOR AQUEOUS ELECTROLYTE SYSTEM

In the electrolyte primitive model, only the electrostatic interaction between ions is included. The solvent molecules are not considered as the interaction particles and treated as a dielectric continuum. So the dielectric constant of solvent is usually adopted in the long-range electrostatic term. The classical Debye–Huckel theory and the Pitzer theory [1] belong to the electrolyte primitive model.

The assumptions of the MSA method are as follows:

$$u^{\mathrm{hs}}(r)=\infty,\ \ g(r)=0,\ \ h(r)=g(r)-1=-1\ \ (r\le\sigma) \quad (1)$$

$$u^{\mathrm{cc}}(r)=\frac{z_i z_j e^2}{Dr},\ \ c(r)=-\frac{u^{\mathrm{cc}}(r)}{kT}\ \ (r>\sigma) \quad (2)$$

Blum [2] has solved the OZ equation by MSA for charged hard spheres. The Helmholtz free energy is

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expressed as follows:

$$\frac{A^{\mathrm{cc}}}{NkT} = -\frac{(2\Gamma)^3(1+3\Gamma\sigma/2)}{12\pi\rho} \tag{3}$$

The thermodynamic properties of the ionic system depend on one single screening parameter Γ, which plays the similar role in the Debye–Huckel inverse length κ. For equal ionic sizes, the relationship between Γ and κ is given by

$$\kappa = 2\Gamma(1+\Gamma\sigma) \tag{4}$$

Here

$$\kappa^2 = \frac{4\pi e^2 \sum_i \rho_i z_i^2}{DkT} \tag{5}$$

Triolo *et al.* [3] and Lu *et al.* [4] used the primitive MSA to correlate the mean ionic activity and osmotic coefficient for the real electrolytes when the diameters of ions must be treated as adjustable parameters with a function of ionic strength. Cai *et al.* [5] used the primitive MSA in consideration with the polyion chain formation and the non-coulombic sticky interaction to polyelectrolyte solutions.

Based on the primitive electrolyte perturbation theory, Henderson [6] obtained the same expression as follows:

$$\begin{aligned}\frac{A^{\mathrm{cc}}}{NkT} = &-\frac{\kappa^3}{12\pi\rho} - \frac{\kappa^4}{16\pi\rho}\int_0^\infty h^{(0)}(r)\,\mathrm{d}r \\ &+\frac{\kappa^5}{8\pi\rho}\int_0^\infty rh^{(0)}(r)\,\mathrm{d}r - \frac{\kappa^6}{16\pi\rho}\int_0^\infty r^2h^{(0)}(r)\,\mathrm{d}r \\ &+\frac{\kappa^6}{48\pi\rho}\int_0^\infty \mathrm{d}r_{12}\int_0^\infty \mathrm{d}r_{13}\int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} h^{(0)}_{123}(r)\mathrm{d}r_{23}\end{aligned} \tag{6}$$

Larsen *et al.* [7] obtained the analytical expressions for the above integration functions. Stell and Wu [8] established the Pade approximation equation. Chan [9] used the above primitive perturbation equation to correlate the mean ionic activity coefficient for some 1:1 aqueous electrolyte solutions with success.

In Eq. (6), the integration process is completed in the space of $r > 0$. If we take

$$g^{(0)}(r) = 0, \quad h^{(0)}(r) = -1$$

in the range of $0 < r < \sigma$, we can obtain

$$\begin{aligned}\frac{A^{\mathrm{cc}}}{NkT} = &-\frac{\kappa^3}{12\pi\rho}\left(1-\frac{3}{4}\kappa\sigma+\frac{3}{4}\kappa^2\sigma^2-\frac{7}{8}\kappa^3\sigma^3+\cdots\right) \\ &-\frac{\kappa^4}{16\pi\rho}\int_\sigma^\infty h^{(0)}(r)\mathrm{d}r + \cdots\end{aligned} \tag{7}$$

Substituting Eq. (4) into Eq. (7), one obtains

$$\begin{aligned}\frac{A^{\mathrm{cc}}}{NkT} = &-\frac{(2\Gamma)^3(1+3\Gamma\sigma/2)}{12\pi\rho} \\ &-\frac{\kappa^4}{16\pi\rho}\int_\sigma^\infty h^{(0)}(r)\mathrm{d}r + \cdots.\end{aligned} \tag{8}$$

From Eq. (8) it can be seen that the primitive perturbation theory has more terms than primitive MSA (see Eq. (3)). So the perturbation theory is more accurate than the primitive MSA. Compared with the nonprimitive model, the electrolyte primitive model both from MSA and perturbation theory has the advantages of its simplicity, only electrostatic ion–ion interaction is needed. Today the electrolyte primitive MSA is more widely used in industry than the primitive perturbation theory because the former is simpler than the latter. But in the primitive model, the ion–solvent and the solvent–solvent interactions are neglected, and the microscopic structures of the electrolyte solution cannot be exactly described. The primitive model cannot be used for mixed solvent system. In recent years, Liu *et al.* [10] used the primitive MSA to incorporate with the nonprimitive perturbation theory for real electrolyte aqueous systems. Furst and Renon [11], Myers *et al.* [12] used the primitive MSA to incorporate with the cubic EOSs for real electrolyte systems.

NONPRIMITIVE MSA FOR ION–DIPOLE MIXTURES

In the electrolyte nonprimitive model, the solvent molecules are treated as interacting particles. The Chen-NRTL equation [13], the Clegg–Pitzer equation [14], the Lu–Maurer hydration model [15] and the Li–Gmehling electrolyte model [16] are all of nonprimitive models. The nonprimitive model can be used for mixed solvent system. It should be pointed out, in these models the solvent dielectric constant still must be used in their electrostatic term.

In the nonprimitive MSA, the solvent molecules, such as water, are treated as point dipoles. The ion–dipole and dipole–dipole interaction potentials are considered as follows:

$$u_{ij}^{\mathrm{cd}}(r) = -\frac{z_i e\mu_j}{r^2}(\vec{r_{ij}}\cdot\vec{\mu_j}) \tag{9}$$

$$u_{ij}^{\mathrm{dd}}(r) = -\frac{\mu_i\mu_j}{r^3}\left[3(\vec{\mu_i}\cdot\vec{r_{ij}})(\vec{\mu_j}\cdot\vec{r_{ij}}) - (\vec{\mu_i}\cdot\vec{\mu_j})\right] \tag{10}$$

The ion–ion interaction potential should be:

$$u_{ij}^{\mathrm{cc}}(r) = \frac{z_i z_j e^2}{r} \tag{11}$$

Blum [17] solved the OZ equation by MSA in the restricted case (all the diameters are the same).

Hoye and Stell [18] used the statistical mechanics to yield the explicit form for the ion–ion, ion–dipole and dipole–dipole pair distribution functions and also the potentials of mean forces in the limit of vanishing ion charge or ion concentration. Blum and Wei [19] gave the solutions of three nonlinear equations in the case of arbitrary diameters. In a semi-restricted case (with equal size hard sphere ions and different size hard sphere dipoles), the coupled nonlinear equations are as follows:

$$\begin{aligned} &a_1^2 + a_2^2 = d_0^2 \\ &a_1 K_{10} - a_2[1 - K_{11}] = d_0 d_2 \\ &K_{10}^2 + [1 - K_{11}]^2 - y_1^2 = d_2^2 \end{aligned} \tag{12}$$

Here

$$d_0^2 = \frac{4\pi \sum_i z_i^2 e^2 \rho_i \sigma_i^2}{kT} = (\kappa_0 \sigma_i)^2 \tag{13}$$

$$d_2^2 = 3y = \frac{4\pi \rho_d \mu^2}{3kT} \tag{14}$$

The excess internal energy of the ion–dipole system is given by

$$\frac{U^{\mathrm{MSA}}}{NkT} = \frac{1}{4\pi\rho\sigma_d^3}\left[p^3 d_0^2 b_0 - 2p^2 d_0 d_2 b_1 - 2d_2^2 b_2\right] \tag{15}$$

Here

$$p = \frac{\sigma_d}{\sigma_i} \tag{16}$$

The definitions of three energy parameters b_0 (ion–ion), b_1(ion–dipole) and b_2 (dipole–dipole) are given by

$$\begin{aligned} b_0 &= 2\pi\rho_i \int_0^\infty h_{ii}(r) r \sigma_i \,\mathrm{d}r \\ b_1 &= 2\pi(\rho_i \rho_d/3)^{1/2} \int_0^\infty h_{id}(r) \sigma_i \sigma_d \,\mathrm{d}r \\ b_2 &= 3\pi\rho_d (2/15)^{1/2} \int_0^\infty \frac{h_{112}(r)\sigma_d^3}{r} \,\mathrm{d}r \end{aligned} \tag{17}$$

Blum and Wei [19] expanded MSA in the low ionic density region to obtain an explicit solution, which is verified accurate up to 0.1 M. But the expansion was only to the second order and there were no more discussions based on the expansion. We used the similar technique and expanded MSA to the third order [20]. A set of equation (12) can be written as

$$\begin{aligned} F_0(d_0, d_2) &= d_0^2 \\ F_1(d_0, d_2) &= d_0 d_2 \\ F_2(d_0, d_2) &= d_2^2 \end{aligned} \tag{18}$$

The Taylor series of F_k $(k = 0, 1, 2)$ at $d_0 = 0$ are

$$\begin{aligned} F_k(d_0, d_2) = F_k(0, d_2) &+ d_0 \left.\frac{\partial F_k}{\partial d_0}\right|_{d_0=0} \\ &+ \frac{d_0^2}{2}\left.\frac{\partial^2 F_k}{\partial d_0^2}\right|_{d_0=0} + \frac{d_0^3}{6}\left.\frac{\partial^3 F_k}{\partial d_0^3}\right|_{d_0=0} + \cdots. \end{aligned} \tag{19}$$

Thus, b_j $(j = 0, 1, 2)$ can be written as the polynomials of κ as follows

$$\begin{aligned} b_j &= b_j\big|_{d_0=0} + d_0 \left.\frac{\partial b_j}{\partial d_0}\right|_{d_0=0} + \frac{d_0^2}{2}\left.\frac{\partial^2 b_j}{\partial d_0^2}\right|_{d_0=0} + \frac{d_0^3}{6}\left.\frac{\partial^3 b_j}{\partial d_0^3}\right|_{d_0=0} + \cdots \\ &= b_{j0} + \kappa\sigma_i b_{j1} + \frac{(\kappa\sigma_i)^2}{2} b_{j2} + \frac{(\kappa\sigma_i)^3}{6} b_{j3} + \cdots. \end{aligned} \tag{20}$$

Here

$$\kappa\sigma_i = \frac{d_0}{D^{1/2}} = \frac{\kappa_0 \sigma_i}{D^{1/2}},$$

D is the Wertheim's dielectric constant,

$$D = \frac{\lambda^2 (1+\lambda)^4}{16} \qquad \lambda = \frac{1 + b_2/3}{1 + b_2/6}$$

From Eqs.(15) and (20), the excess internal energy is derived

$$\begin{aligned} \frac{U^{\mathrm{MSA}}}{NkT} = \frac{1}{4\pi\rho\sigma_d^3}\Bigg[-2d_2^2 b_{20} + \sum_{i=0}^{\infty} \frac{(\kappa\sigma)^{i+2}}{i!}\Bigg(p^3 D b_{0i} \\ - \frac{2p^2 d_2 D^{1/2} b_{1,i+1}}{i+1} - \frac{2d_2^2 b_{2,i+2}}{(i+1)(i+2)}\Bigg)\Bigg] \end{aligned} \tag{21}$$

The excess Helmholtz free energy is obtained by the integration of internal energy

$$\begin{aligned} \frac{A^{\mathrm{MSA}}}{NkT} &= \frac{A - A^{\mathrm{hs}}}{NkT} = \int_0^\beta \left(\frac{U}{N}\right) \mathrm{d}\beta \\ &= \frac{1}{4\pi\rho\sigma_d^3}\left[-2C_{20} + \sum_{i=0}^{\infty} \frac{f_{i+2}}{i!}\left(\frac{d_0}{d_2}\right)^{i+2}\right] \\ &= \frac{A_0}{NkT} + \frac{A_2}{NkT} + \frac{A_3}{NkT} + \cdots. \end{aligned} \tag{22}$$

Here

$$\beta = \frac{1}{kT}$$

Thus, the first three terms for the Helmholtz free energy can be expanded as

$$\frac{A_0}{NkT} = -\frac{1}{3\pi\rho\sigma_d^3}\left[(\lambda^2-1)^2 + 2 + \frac{32}{(\lambda+1)^4} - \frac{16}{(\lambda+1)^2}\right] \tag{23}$$

$$\frac{A_2}{NkT} = \frac{1}{4\pi\rho\sigma_d^3} f_2\left(\frac{d_0}{d_2}\right)^2 = -\frac{\kappa^2}{4\pi\rho\sigma_i}\frac{(D-1)}{(1+p/\lambda)} \tag{24}$$

$$\frac{A_3}{NkT} = \frac{1}{4\pi\rho\sigma_d^3} f_3\left(\frac{d_0}{d_2}\right)^3 = -\frac{\kappa^3}{12\pi\rho} \tag{25}$$

A_0 represents the dipole–dipole interaction term, A_2 is the ion–dipole interaction term and is so called the Born term in classical electrolyte theory at $p \to 0$. A_3 is the ion–ion electrostatic interaction term. Although the input of the electrostatic ion–ion term from nonprimitive MSA is the κ_0 with vacuum dielectric constant (see Eqs.(12) and (13)), the final output in Eq. (25) is the κ with solvent dielectric constant.

We compare the results from the electrolyte nonprimitive MSA with the electrolyte nonprimitive perturbation theory. Henderson *et al.* [21] deduced the following expressions for ion–ion (cc), ion–dipole (cd) and dipole–dipole (dd) interaction terms, respectively.

$$\begin{aligned}\frac{A^{\mathrm{cc}}}{NkT} &= -\frac{\kappa_0^4}{16\pi\rho}\int_0^\infty \mathrm{d}r + \frac{\kappa_0^6}{6(4\pi)^3\rho}\iint_0^\infty \frac{\mathrm{d}r_2\,\mathrm{d}r_3}{r_{12}r_{23}r_{31}} \\ &\quad - \frac{\kappa_0^4\sigma}{16\pi\rho}I_1^{\mathrm{cc}} + \frac{\kappa_0^5\sigma^2}{8\pi\rho}I_2^{\mathrm{cc}} - \frac{\kappa_0^6\sigma^3}{16\pi\rho}I_3^{\mathrm{cc}} \\ &\quad + \frac{\kappa_0^6\sigma^3}{48\pi\rho}I^{\mathrm{ccc}}\end{aligned} \tag{26}$$

$$\begin{aligned}\frac{A^{\mathrm{cd}}}{NkT} &= -\frac{3\kappa_0^2 y}{8\pi\rho\sigma}I^{\mathrm{cd}} + \frac{3\kappa_0^4 y\sigma}{16\pi\rho}I^{\mathrm{ccd}} + \frac{3\kappa_0^4 y\sigma}{4\pi\rho}I_1^{\mathrm{cc}} \\ &\quad + \frac{3\kappa_0^4 y}{2(4\pi)^3\rho}\iint_0^\infty \frac{\cos\theta_3\,\mathrm{d}r_2\,\mathrm{d}r_3}{r_{12}r_{13}^2r_{23}^2} \\ &\quad + \frac{9\kappa_0^2y^2}{16\pi\rho\sigma}I^{\mathrm{cdd}}\end{aligned} \tag{27}$$

$$\frac{A^{\mathrm{dd}}}{NkT} = -\frac{27y^2}{8\pi\rho\sigma^3}I^{\mathrm{dd}} + \frac{27y^3}{16\pi\rho\sigma^3}I^{\mathrm{ddd}} \tag{28}$$

Henderson *et al.* [21] summed the three divergent terms in Eqs.(26) and (27) and obtained the extra term as

$$\frac{A^I}{NkT} = -\frac{\kappa_0^3}{12\pi\rho}\left(1 - \frac{9}{2}y\right) \tag{29}$$

We re-summed six divergent terms and obtained the extra term as follows:

$$\begin{aligned}\frac{A^I}{NkT} &= -\frac{\kappa_0^4}{16\pi\rho}\int_0^\infty \mathrm{d}r + \frac{\kappa_0^6}{6(4\pi)^3\rho}\iint_0^\infty \frac{\mathrm{d}r_2\,\mathrm{d}r_3}{r_{12}r_{23}r_{31}} \\ &\quad + \frac{3\kappa_0^4 y}{2(4\pi)^3\rho}\iint_0^\infty \frac{\cos\theta_3\,\mathrm{d}r_2\,\mathrm{d}r_3}{r_{12}r_{13}^2r_{23}^2} \\ &\quad - \frac{3\kappa_0^6 y}{2(4\pi)^4\rho}\iiint \frac{\cos\theta_4\,\mathrm{d}r_2\,\mathrm{d}r_3\,\mathrm{d}r_4}{r_{12}r_{23}r_{34}^2r_{14}^2} \\ &\quad + \frac{117\kappa_0^6y^2}{40(4\pi)^5\rho}\iiiint \frac{\cos\theta_4\cos\theta_5\,\mathrm{d}r_2\,\mathrm{d}r_3\,\mathrm{d}r_4\,\mathrm{d}r_5}{r_{12}r_{14}^2r_{34}^2r_{25}^2r_{35}^2} \\ &\quad - \frac{27\kappa_0^6y^3}{16(4\pi)^6\rho}\int\!\!\int\!\!\int\!\!\int\!\!\int \\ &\qquad \times \frac{\cos\theta_4\cos\theta_5\cos\theta_6\,\mathrm{d}r_2\,\mathrm{d}r_3\,\mathrm{d}r_4\,\mathrm{d}r_5\,\mathrm{d}r_6}{r_{14}^2r_{24}^2r_{25}^2r_{35}^2r_{16}^2r_{36}^2} \\ &= -\frac{\kappa_0^3}{12\pi\rho}\left(1 - \frac{9}{2}y - \frac{81}{14}y^2 + \cdots\right) \\ &= -\frac{\kappa_0^3}{12\pi\rho D^{3/2}} = -\frac{\kappa^3}{12\pi\rho}\end{aligned} \tag{30}$$

Here

$$D = 1 + 3y + \frac{27}{7}y^2 + \cdots \tag{31}$$

We can also derive Eq. (31) approximately from the Taylor expansion of y in the third equation of Eq. (18) at $d_0 = 0$ and $d_2 = 0$.

The last three terms in Eq. (30) are all the ion–dipole interactions in higher perturbation orders. It can be seen from electrolyte nonprimitive perturbation theory that the κ with solvent dielectric constant appeared again although the input is κ_0 with vacuum dielectric constant (see Eq. (26)). It is also found that the κ with solvent dielectric constant comes from the ion–dipole interactions in higher perturbation terms although we have put the solvent molecules as interacting particles (as point dipoles) as in lower perturbation terms (see Eq. (27)).

Lo *et al.* [22], Eggebrecht and Ozler [23] and Li *et al.* [24] studied the ion–dipole mixtures using Monte Carlo simulation. Either the primitive MSA or nonprimitive MSA both with vacuum dielectric constant and total number density including dipoles can provide good agreements for ion–ion electrostatic term (U^{cc}/NkT) with MC simulation data [25]. So the molecular simulation study cannot directly explain why the solvent dielectric constant must be used for the real electrolyte aqueous systems. But the perturbation theory and MSA both cannot obtain good agreements for ion–dipole term (U^{cd}/NkT)

and dipole–dipole term (U^{dd}/NkT)[25]. Now the reason is clear because we neglected the high order terms in our theoretical calculation for nonprimitive model both from perturbation theory or MSA. The higher order terms both in nonprimitive perturbation theory and MSA are very tedious. The only convenient method is to use the solvent dielectric constant to compensate the neglect of the higher order terms.

Jin and Donohue [26] used the HBT nonprimitive perturbation theory with PACT to establish EOS to real electrolyte aqueous solutions with solvent dielectric constant. Wu *et al.* [27] proposed a mixture of charged hard spheres and neutral hard spheres as a new reference system into electrolyte nonprimitive theory. Chan [28] and Wu *et al.* [29] used the semiprimitive perturbation theory and MC simulation to study the new reference system. Liu *et al.* [10] used this new reference system and SAFT into the nonprimitive perturbation theory to establish a new EOS to real electrolyte aqueous solution also with solvent dielectric constant. For each electrolyte, only one cation diameter parameter is needed with less interaction terms and reasonable accuracy is obtained. Li *et al.* [30] and Liu *et al.* [31] used Blum–Wei nonprimitive MSA to establish EOS for real electrolyte solutions with vacuum dielectric constant. The accuracy from MSA is less than that from perturbation theory.

ONE YUKAWA EOS FOR NEUTRAL FLUIDS

The Yukawa dispersion potential can be expressed as follows:

$$u^{\mathrm{hs}}(r) = \infty \quad (r \le \sigma) \tag{32}$$

$$u^{\mathrm{dis}}(r) = -\frac{\varepsilon \exp[-\lambda(r/\sigma - 1)]}{r/\sigma} \quad (r > \sigma) \tag{33}$$

Here λ is the range parameter. We choose the value $\lambda = 1.8$, which yields the results comparable with those obtained from the Lennard–Jones potential. From a theoretical point of view the most important feature of the hard-core Yukawa fluid is that an analytic solution of OZ integral equation is available within the MSA approach. Waisman [32] obtained an analytical MSA solution in the Baxter formalism of the correlation functions and thermodynamic functions for a fluid with Yukawa potential. Although analytical, Waisman's solution involves six nonlinear algebraic equations with six unknowns. Using Waisman's formulas, Henderson *et al.* [33] obtained the lowest order coefficients analytically in the density expansion of these six unknown parameters. Tang and Lu [34] solved the OZ equation and derived an analytical expression of the first order Yukawa radial distribution function based on MSA. They [35,36] found a new two-Yukawa potential can mimic very closely the LJ potential and derived the analytical expression of the second-order Yukawa radial distribution function based on MSA. Henderson *et al.* [37] showed an analytical solution of the MSA for a dipolar Yukawa fluid. Szalai *et al.* [38] reported the computer simulations and structure of a dipolar Yukawa fluid.

In the one-Yukawa case, Ginoza [39] found that the solution can be reduced to a single nonlinear equation and the thermodynamic functions can be expressed in terms of a rational function of Γ, which is determined by the following equation:

$$\Gamma(\Gamma + \lambda)(1 + \psi\Gamma)^2 + \beta\varepsilon w = 0 \tag{34}$$

Henderson *et al.* [40] obtained the fifth-order inverse temperature expansion of the internal energy, free energy and the pressure based on the solution of Ginoza.

$$\frac{U}{NkT} = -\frac{1}{2}\sum_{n=1}^{5} v_n(\beta\varepsilon)^n \tag{35}$$

$$\frac{A - A^{\mathrm{hs}}}{NkT} = -\frac{1}{2}\sum_{n=1}^{5} \frac{v_n}{n}(\beta\varepsilon)^n \tag{36}$$

$$Z - Z^{\mathrm{hs}} = -\frac{1}{2}\sum_{n=1}^{5}\left(\eta\frac{\partial v_n}{\partial \eta}\right)\frac{(\beta\varepsilon)^n}{n} \tag{37}$$

Duh and Mier-Y-Teran [41] extended Henderson's free energy expansion to infinite order and presented an explicit and analytical EOS for the hard-core Yukawa fluid. They found that the EOS agrees very well with the molecular simulation data. The expressions of Mier-Y-Teran's EOS are as follows:

$$\frac{A - A^{\mathrm{hs}}}{NkT} = -\frac{\alpha_0}{\Phi_0}\beta\varepsilon - \frac{\lambda^3}{6\eta}\left[F(x) - F(y) - (x - y)\frac{\mathrm{d}F(y)}{\mathrm{d}y}\right] \tag{38}$$

$$F(x) = -\frac{1}{4}\ln(1 - 2x) - 2\ln(1 - x) - \frac{3}{2}x - \frac{1}{1 - x} + 1 \tag{39}$$

$$x = \frac{(1 + \lambda\psi)w}{\lambda^2}\beta\varepsilon \quad \text{and} \quad y = \frac{w\psi}{\lambda}\beta\varepsilon$$

$$\beta = \frac{1}{kT}, \quad \eta = \frac{\pi\rho\sigma^3}{6}$$

We used Eq. (38) to 42 pure real neutral fluids (including spherical, nonpolar, polar, chain-like and associating fluids) with good results [42]. The dipolar Yukawa EOS was proved to be better than that with the Stockmayer potential. The Yukawa SAFT EOS is also better than the original SAFT EOS with square well potential as perturbation term. But it is not as good as the Lennard–Jones reference based SAFT EOS [43].

TWO-YUKAWA ONE-COMPONENT EOS FOR CHARGED COLLOID SYSTEMS

The double-layer repulsive charge–charge electrostatic interaction between like-charged colloid particles can be also expressed by the Yukawa potential as

$$u^{\mathrm{cc}}(r) = \frac{z_p^2 e^2 \exp[-\kappa(r-\sigma)]}{Dr(1+\kappa\sigma/2)^2} \quad (r > \sigma) \tag{40}$$

$$z_p = \nu_+ - \nu_- \tag{41}$$

Here z_p is the colloid charge number (valence), ν is the number of cations and anions bound in one colloid particle, and D is the dielectric constant of water. κ is the Debye screening parameter related to the density number, the valence of microion and the absolute temperature (the same as in Eq. (5)). Equation (40) comes from the classical DLVO theory [44], which was derived using the linear approximation of the Poisson–Boltzmann equation. Based on the McMillan–Mayer theory and the DLVO theory, the charged colloid aqueous electrolyte solution with ternary system is treated as a pseudo one-component system with electrolyte primitive model. The osmotic compressibility factor Z in colloid solution can be expressed as follows:

$$Z = \frac{\pi}{\rho_p kT} = Z^{\mathrm{donnan}} + Z^{\mathrm{hs}} + Z^{\mathrm{dis}} + Z^{\mathrm{cc}} \tag{42}$$

Here π is the osmotic pressure. The superscripts donnan, hs, dis and cc represent the contributions of the Donnan effect, hard sphere repulsion, attractive dispersion and double-layer repulsive charge–charge interactions, respectively. By use of the summation of the infinite order expansion of the Duh and Mier-Y-Teran EOS twice, we used two-Yukawa potentials to calculate Z^{dis} and Z^{cc}, respectively, [45,46] instead of the classical DLVO theory.

Another method to establish one-component two-Yukawa EOS is based on the Baxter–Wertheim factorization of the OZ equation for the one-component and w-Yukawa case made by Blum and Herrera [47]. We obtained an implicit solution to the MSA closure with non-dimensional variables as follows [48]:

$$c(r) = \frac{-u(r)}{kT} = \sum_{n=1}^{w} K_n \frac{\exp(-\lambda_n r/\sigma)}{r/\sigma} \tag{43}$$

$$K_n\delta_n^2 = \frac{\varepsilon}{kT}, \quad \delta_n = \exp\left(\frac{-\lambda_n}{2}\right) \quad (n = 1,2,\ldots,w) \tag{44}$$

$$2\pi K_n\rho^*[X_n]^2 + \lambda_n\beta_n\left(1+\sum_{m=1}^{w}\frac{1}{\lambda_n+\lambda_m}\beta_m\right) = 0 \quad (n = 1,2,\ldots w) \tag{45}$$

$$\rho* = \rho\sigma^3 \quad X_n = \frac{\delta_n}{I_n + \Gamma_n J_n} \tag{46}$$

Equation (45) is still a rather formidable equation to solve because both β_n and X_n are complex functions of the parameters of the problem. There is an important relation with a linear matrix equation between β_n and Γ_n as follows:

$$\Gamma = M\beta \tag{47}$$

By solving Eqs. (45), (46) and (47), one may obtain β_n, X_n and Γ_n, from which the thermodynamic properties can be calculated.

Following the work of Blum and Ubriaco [49], the incremental pressure can be calculated from the following equation:

$$\frac{p - p^{\mathrm{hs}}}{\rho kT} = \frac{S - S^{\mathrm{hs}}}{Nk} + \frac{1}{2}\left(\frac{1}{\chi} - \frac{1}{\chi^{\mathrm{hs}}}\right) \tag{48}$$

Here χ is the isothermal compressibility for the Yukawa fluid. We derived a new expression of the excess entropy as follows [48]:

$$\frac{S - S^{\mathrm{hs}}}{Nk} = -\frac{1}{144\eta}\Bigg[\beta_1^3 + 3\beta_1^2(\lambda_1+\beta_2) + \beta_2^3 + 3\beta_2^2(\lambda_2+\beta_1) + 3\beta_1\beta_2(\lambda_1+\lambda_2) - \frac{3(\lambda_1-\lambda_2)^2\beta_1\beta_2}{(\lambda_1+\lambda_2+\beta_1+\beta_2-1)}\Bigg] \tag{49}$$

Equation (49) has been tested to be reliable compared with our MC simulation data [50].

By using the experimental osmotic pressure data for aqueous BSA (bovine serum albumin)-NaCl solutions, the two methods to establish the one-component two-Yukawa EOSs can both give reasonable correlation results [45,46,48]. The former is simpler in mathematics and the latter seems much strict in theory. Our calculations show that the two-Yukawa EOS has better correlation and prediction results for BSA-NaCl solution than other published models. Recently the electrostatic potentials of mean force were determined by MC (Monte Carlo simulation) and HNC (hypernetted-chain) methods and the electrostatic attractive forces in short ranges were found between the same charged BSA molecules at low BSA valences and high NaCl concentrations [51,52]. So the two-Yukawa potential should be improved further for charged colloid systems.

All the above studies show that the MSA approach is of significance both in theoretical research and practical use.

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