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Exact Analytical Formulas for the Distribution Functions of Charged Hard Spheres in the Mean Spherical Approximation

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Exact analytical expressions are derived for the electrostatic part of the mean spherical approximation (MSA) radial distribution functions (RDFs) for a system of charged hard spheres. These expressions are valid for all distances. In addition, it is shown that these same expressions arise in the MSA description of the charge profile of charged hard spheres near a charged hard wall. We also derive analytical expressions for the non-electrostatic part of the profile in this case, valid for $z \leqslant 5\sigma$, and discuss a numerical method for obtaining results for $z > 5\sigma$. Some simple approximate expressions are also considered.

KEY WORDS: Mean spherical approximation; charged hard spheres; electrolyte solution; electrified interface; electric double layer.

1. INTRODUCTION

Charged hard spheres are a useful and important model both for electrolyte solutions and for molten salts. After the classic work of Debye and Hückel,(1) which is valid only for low concentrations, there was little theoretical progress until the numerical solution of the hypernetted chain approximation by Rasaiah and Friedman(2) and the analytical solution of the mean spherical approximation (MSA) for charged hard spheres of equal diameter by Waisman and Lebowitz(3) and for charged hard spheres of unequal diameter by Blum.(4)

Our interest in this paper is in the Waisman–Lebowitz solution of the

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MSA for charged hard spheres of equal diameter. Although Waisman and Lebowitz obtained an analytical expression for the Laplace transform of the electrostatic part of the radial distribution functions (RDFs) of this system, until recently analytic expressions for the RDFs themselves have not been available. Recently Outhwaite and Hutson(5) and Hirata and Arakawa(6) have obtained explicit expressions for these in the interval for $r \leqslant 6\sigma$, where σ is the hardsphere diameter. In this paper we obtain an analytical expression, valid for any distance, for the electrostatic part of the MSA RDFs for this system. In addition, we examine an approximation to this result due to Blum and Høye(7) for these RDFs, and propose an extension.

Finally, we show that the same function arises in the MSA treatment of charged hard spheres near a charged hard wall. Thus, the results given here also provide a useful description of the charge profile of an electrified interface. We also give analytical expressions for the nonelectrostatic part of the profile in this case, valid in the interval $z \leqslant 5\sigma$.

2. MSA FOR CHARGED HARD SPHERES

For simplicity, consider a model symmetric bulk electrolyte or molten salt consisting of equal numbers of hard spheres of diameter σ with charges $\pm ze$, respectively. It is convenient to introduce the functions

$$h_S(r) = [h_{11}(r) + h_{12}(r)]/2 \tag{1}$$

and

$$h_D(r) = [h_{11}(r) - h_{12}(r)]/2 \tag{2}$$

where $h_{ij}(r) = g_{ij}(r) - 1$ and $g_{ij}(r)$ is the radial distribution function for charged hard spheres of species i and j. For this system the MSA is

$$\begin{aligned} h_S(r) &= -1, & r &< \sigma \\ c_S(r) &= 0 & r &> \sigma \end{aligned} \tag{3}$$

$$\begin{aligned} h_D(r) &= 0, & r &< \sigma \\ c_D(r) &= -q/r, & r &> \sigma \end{aligned} \tag{4}$$

where $q = \beta z^2 e^2/\epsilon$, ϵ is the dielectric constant of the solvent, and $c_S(r) = [c_{11}(r) + c_{12}(r)]/2$ and $c_D(r) = [c_{11}(r) - c_{12}(r)]/2$ are related to $h_S(r)$ and $h_D(r)$ through the Ornstein–Zernike equations

$$h_S(r_{12}) = c_S(r_{12}) + \rho \int h_S(r_{13}) c_S(r_{23})\, d\mathbf{r}_3 \tag{5}$$

$$h_D(r_{12}) = c_D(r_{12}) + \rho \int h_D(r_{13}) c_D(r_{23})\, d\mathbf{r}_3 \tag{6}$$

where $\rho = N/V$ is the density of N atoms in a volume V. Equations (3) and (5) constitute the Percus–Yevick approximation$^{(8)}$ for uncharged hard spheres, which has been solved by Wertheim$^{(9)}$ and Thiele,$^{(10)}$ who obtained analytical expressions for $c_S(r)$ and the Laplace transform of $g_S(r) = h_S(r) + 1$. Smith and Henderson$^{(11)}$ have inverted this Laplace transform analytically to obtain expressions for $g_S(r)$ for $r \leqslant 5\sigma$.

Waisman and Lebowitz$^{(3)}$ have solved Eqs. (4) and (6) and have shown that

$$h_D(\xi) = -[q/(1 + \Gamma\sigma)^2]f(\xi - 1)/\xi \tag{7}$$

where $\xi = r/\sigma$, and Γ is related to the Debye screening length $\kappa = (4\pi\rho z^2 e^2 \beta/\epsilon)^{1/2}$ by

$$2\Gamma\sigma = (1 + 2\kappa\sigma)^{1/2} - 1 \tag{8}$$

Waisman and Lebowitz did not obtain $f(x)$. However, they did show that the Laplace transform of $f(x)$ is given by

$$\mathscr{L}[f](s) = \int_0^\infty e^{-sx} f(x)\, dx = \frac{s}{s^2 + 2(\Gamma\sigma)s + 2(\Gamma\sigma)^2(1 - e^{-s})} \tag{9}$$

Hirata and Arakawa$^{(6)}$ have inverted Eq. (9) to obtain explicit expressions for $f(x)$ for $0 \leqslant x \leqslant 3\sigma$. They used a zonal expansion, similar to that used by Wertheim$^{(9)}$ and Smith and Henderson$^{(11)}$ for $g_S(r)$, and expanded

$$\frac{s}{s^2 + 2(\Gamma\sigma)s + 2(\Gamma\sigma)^2(1 - e^{-s})} = \sum_{n=1}^{\infty} [2(\Gamma\sigma)^2]^{n-1} \frac{se^{-(n-1)s}}{[(s + \Gamma\sigma)^2 + (\Gamma\sigma)^2]^n} \tag{10}$$

Thus

$$f(x) = \sum_{n=1}^{\infty} g_n(x - n + 1)u(x - n + 1) \tag{11}$$

where $u(y)$ is the Heaviside step function, and

$$\begin{aligned} g_n(y) &= [2(\Gamma\sigma)^2]^{n-1}\left\{\mathscr{L}^{-1}\left[\frac{s}{[(s + \Gamma\sigma)^2 + (\Gamma\sigma)^2]^n}\right]\right\}(y) \\ &= [2(\Gamma\sigma)^2]^{n-1} e^{-(\Gamma\sigma)y}\left\{\mathscr{L}^{-1}\left[\frac{s - \Gamma\sigma}{[s^2 + (\Gamma\sigma)^2]^n}\right]\right\}(y) \end{aligned} \tag{12}$$

For n small, the inverse transform may be found in almost any table of Laplace transforms or may easily be calculated directly. Hirata and Arakawa$^{(6)}$ obtained $g_n(y)$ for $n \leqslant 3$.

The expressions of Hirata and Arakawa, which give $h_D(r)$ for $\sigma \leqslant r \leqslant 3\sigma$, are most useful for high concentrations where electrical screening is high and

$h_D(r)$ tends to zero rapidly. At lower concentrations where $h_D(r)$ tends to zero slowly some extension of the Hirata–Arakawa expressions to larger r must be obtained.

Fortunately, it is possible to invert Eq. (12) and obtain general expressions for $g_n(y)$ for *any n*. The keys to these general expressions are the relations

$$\mathscr{L}[y^\nu J_\nu(\mu)](s) = \frac{2^\nu}{\sqrt{\pi}}\Gamma\left(\nu + \frac{1}{2}\right)\frac{(\Gamma\sigma)^\nu}{[s^2 + (\Gamma\sigma)^2]^{(2\nu+1)/2}} \tag{13}$$

$$\mathscr{L}[y^{\nu+1} J_\nu(\mu)](s) = \frac{2^{\nu+1}}{\sqrt{\pi}}\Gamma\left(\nu + \frac{3}{2}\right)\frac{(\Gamma\sigma)^\nu}{[s^2 + (\Gamma\sigma)^2]^{(2\nu+1)/2}} \tag{14}$$

where $\mu = (\Gamma\sigma)y$, and $\Gamma(a)$ is the gamma function (which is not to be confused with the parameter Γ). Setting $\nu = n - \frac{1}{2}$ and introducing the spherical Bessel functions

$$j_n(x) = (\pi/2x)^{1/2} J_{n+1/2}(x) \tag{15}$$

we have

$$[2(\Gamma\sigma)^2]^{n-1}\frac{s - \Gamma\sigma}{[s^2 + (\Gamma\sigma)^2]^n} = \mathscr{L}\left\{\frac{\mu^n}{(n-1)!}[j_{n-2}(\mu) - j_{n-1}(\mu)]\right\}(s) \tag{16}$$

Hence

$$g_n(y) = e^{-\mu}\frac{\mu^n}{(n-1)!}[j_{n-2}(\mu) - j_{n-1}(\mu)] \tag{17}$$

Equation (17) is valid for all n. However, if one desires, $j_{-1}(\mu)$ can be avoided by treating $n = 1$ as a separate case. Thus

$$g_1(y) = e^{-\mu}(\cos\mu - \sin\mu) \tag{18}$$

Equation (17) is convenient for numerical calculations. We have obtained $g_n(y)$ for $n \leqslant 100$ without difficulty.

Equation (17) reduces to the results of Hirata and Arakawa for $n \leqslant 3$ but is much more simple and elegant. Hirata and Arakawa give their results in terms of trigonometric functions, and as a result the simplicity of Eq. (17) is lost. Outhwaite and Hutson[(5)] have also obtained a general result for $g_n(y)$. However, like that of Hirata and Arakawa, their result is given in terms of trigonometric functions so that the simplicity and elegance of (17) is lost. Their result is not explicit, as is (17), but involves a complex set of recursion formulas among the coefficients of the sines and cosines. As a result, explicit results are obtained only for $n \leq 5$.

Blum and Høye[(7)] have suggested that at low concentrations, a useful approximation to $f(x)$ may be obtained by neglecting $2\Gamma^2(1 - e^{-s\sigma})$ in Eq. (9), so that

$$\mathscr{L}[f](s) = 1/(s + 2\Gamma\sigma) \tag{19}$$

and

$$f(x) = e^{-2(\Gamma\sigma)x} \tag{20}$$

An approximation which is closer to the exact MSA result can be obtained by expanding the exponential in Eq. (9) to give

$$\mathscr{L}[f](s) = \frac{s}{s^2 + s2\Gamma\sigma(1 + \Gamma\sigma)} = \frac{1}{s + \kappa\sigma} \tag{21}$$

Thus,

$$f(x) = e^{-(\kappa\sigma)x} \tag{22}$$

Equations (20) and (22) have the correct contact value. Both reduce to the Debye–Hückel result when $\Gamma\sigma \to 0$. However, Eq. (22) is valid to order $(\Gamma\sigma)^2$ and so has a wider range of usefulness than Eq. (20), which is valid only to order $\Gamma\sigma$. Equation (22) gives the correct MSA thermodynamics if the energy equation is used. Although Eq. (22) satisfies charge neutrality only to order $(\Gamma\sigma)^2$, the degree to which it fails to satisfy charge neutrality is bounded as $\Gamma\sigma \to \infty$, whereas the failure of Eq. (20) to satisfy charge neutrality is unbounded.

If Eqs. (11), (20), and (22) are compared, it is found that for $r \sim \sigma$, Eq. (20) is a better approximation than Eq. (22). However, for larger r, Eq. (22) becomes the more accurate approximation. Even for Γ small, κ rather than Γ is the better measure of the decay of $f(x)$. Equation (22) is overall more accurate than Eq. (20). At very large r, neither Eq. (20) nor (22) shows the oscillations about zero that are shown by the exact MSA result. However, Eq. (22) gives the more accurate magnitudes.

Blum(12) has used the results of this paper to obtain the RDFs of charged hard spheres of unequal diameter. Thus Eq. (11) is of value in treatments of asymmetric electrolytes also.

As we shall see below, Eq. (11) also arises in the theory of charged hard spheres near a charged electrode.

3. MSA FOR AN ELECTRIFIED INTERFACE

Recently, Henderson, Abraham, and Barker(13) (HAB) have modified the Ornstein–Zernike equation to describe density and charge profiles near smooth, solid walls. Subsequently, Blum(14) has solved the HAB equation, using the MSA, for the case of charged hard spheres near a charged wall. For the especially simple case of a model symmetric electrolyte (hard spheres of equal diameter and charge), Blum obtains the profile

$$g_{Wi}(z) = g_{WS}(z) + (\beta e z_i E/\kappa) f(z) \tag{23}$$

where $g_{Wi}(z)$ has been normalized so that $g_{wi}(z) \to 1$ as $z \to \infty$; $z_i e$ is the charge of species i; $E/4\pi$ is the charge density on the wall; $f(z)$ is given by Eq. (11); z is the normal distance for the ion species i from the wall; and $g_{WS}(z)$ is the profile for hard spheres near a hard wall, which has been calculated by HAB.

Equations (22) and (23) satisfy the charge neutrality condition

$$\rho |z_i| e \int_0^\infty h_{WD}(z)\, dz = E/4\pi \tag{24}$$

where $h_{WD}(z) = [g_{W1}(z) - g_{W2}(z)]/2$, exactly, whereas Eq. (20) fails to satisfy Eq. (24).

3.1. Exact MSA Results for g_{WS} for $z \leqslant 5\sigma$

HAB have expressed $g_{WS}(z) = [g_{W1}(z) + g_{W2}(z)]/2$ as an integral over $g_S(r)$. If the analytical results of Smith and Henderson$^{(11)}$ are substituted into the HAB result, analytical expressions for $g_{WS}(z)$ can be obtained. These same expressions can also be obtained directly from the Laplace transform of g_{WS}. Lebowitz$^{(15)}$ has shown that the Laplace transform of $g_{WS}(z)$ is

$$\mathscr{L}[g(z)](s) = \frac{(1+2\eta)s^2 e^s}{12\eta L(s) + e^s S(s)} \tag{25}$$

where

$$L(s) = (1 + \tfrac{1}{2}\eta)s + 1 + 2\eta \tag{26}$$

$$S(s) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta s - 12\eta(1+2\eta) \tag{27}$$

and $\eta = \pi\rho\sigma^3/6$. Following our earlier treatment$^{(11)}$ of the analogous Percus–Yevick (PY) hard-sphere result, (25) may be expanded to give

$$\mathscr{L}[g(z)](s) = (1+2\eta)s^2 \sum_{n=1}^{\infty} (-12\eta)^{n-1} L^{n-1}(s) S^{-n}(s) \exp[-(n-1)s] \tag{28}$$

yielding the zonal expansion

$$g(z) = \sum_{n=1}^{\infty} g_n^*(z-n+1)u(z-n+1) \tag{29}$$

where

$$g_n^*(y) = \frac{(1 + 2\eta)(-12\eta)^{n-1}}{(n - 1)!} \sum_{i=0}^{2} \lim_{t \to t_i} \frac{d^{n-1}}{dt^{n-1}} [(t - t_i)^n t^2 L^{n-1}(t) S^{-n}(t) e^{ty}] \tag{30}$$

The summation in (30) is over the zeros t_i ($i = 0, 1, 2$) of $S(t)$, given in our earlier paper.$^{(11)}$

Equation (30) becomes, after some manipulation,

$$g_n^*(y) = \frac{(1 + 2\eta)(-12\eta)^{n-1}}{n - 1} \sum_{i=0}^{2} \exp(t_i y) \sum_{r=0}^{n-1} y^{n-r-1} \beta_{nr}^i \tag{31}$$

where

$$\beta_{nr}^i = \binom{n-1}{r} \sum_{s=0}^{r} \binom{r}{s} A_{n,r-s}(t_i) B_{ns}(t_i) \tag{32}$$

$$A_{nk}(t) = [t^2 L^{n-1}(t)]^{(k)} \tag{33}$$

$$B_{nk}(t) = \left[\left(\frac{t - t_i}{S(t)}\right)^n\right]^{(k)} \tag{34}$$

and the superscript (k) denotes the kth derivative.

The results for $n \leqslant 5$ are as follows:

$$A_{j0}(t) = t^2 L^{j-1}(t), \qquad B_{j0}(t) = [S_1(t)]^{-j} \tag{35}$$

$$A_{21}(t) = t(2L + tL_1), \qquad B_{21}(t) = -S_2/S_1^3 \tag{36}$$

$$A_{31}(t) = 2tL(L + tL_1), \qquad B_{31}(t) = -3S_2/2S_1^4$$

$$A_{32}(t) = 2(L + tL_1)^2 + 2tLL_1, \qquad B_{32}(t) = (3S_2^2 - S_1S_3)/S_1^5 \tag{37}$$

$$A_{41}(t) = tL^2(2L + 3tL_1), \qquad B_{41}(t) = -2S_2/S_1^5$$

$$A_{42}(t) = L(2L + 3tL_1)(L + 2tL_1) + 5tL^2L_1$$

$$B_{42}(t) = (15S_2^2 - 4S_1S_3)/3S_1^6 \tag{38}$$

$$A_{43}(t) = 6L_1(3L^2 + 6tL_1L + t^2L_1^2)$$

$$B_{43}(t) = 5S_2(2S_1S_3 - 3S_2^2)/S_1^7$$

$$A_{51}(t) = 2tL^3(L + 2tL_1), \qquad B_{51}(t) = -5S_2/2S_1^6$$

$$A_{52}(t) = 2L^2(L^2 + 8tLL_1 + 6t^2L_1^2)$$

$$B_{52}(t) = 5(9S_2^2 - 2S_1S_3)/6S_1^7$$

$$A_{53}(t) = 24L_1L(L^2 + 3tLL_1 + t^2L_1^2) \tag{39}$$

$$B_{53}(t) = 15S_2(-7S_2^2 + 4S_1S_3)/4S_1^8$$

$$A_{54}(t) = 24L_1^2(6L^2 + 8tLL_1 + t^2L_1^2)$$

$$B_{54}(t) = 5(2S_1^2S_3^2 - 21S_1S_2^2S_3 + 21S_2^4)/S_1^9$$

Also

$$L = L(t), \qquad L_1 = L'(t), \qquad S_1 = S'(t), \qquad S_2 = S''(t), \qquad S_3 = S'''(t) \tag{40}$$

Equations (31)–(40) are easily programmed on a computer, similarly to our previous PY hard-sphere results. For completeness, we remark here that these previous results can be extended to the shell $5\sigma \leqslant r \leqslant 6\sigma$ using the above expressions. Thus, we have

$$xg_5^{\mathrm{HS}}(x) = \varphi \sum_{i=0}^{2} \exp[t_i(x - n)] \sum_{r=0}^{4} (x - n)^{4-r} e_r(t_i) \tag{41}$$

where, using the same notation as in Eqs. (35)–(40), $\varphi = 864\eta^4$,

$$e_r(t) = \binom{4}{r} \sum_{s=0}^{r} C_{5,r-s}(t_i) B_{5s}(t_i)$$

$$C_{50}(t) = tL^5, \qquad C_{51}(t) = L^4(L + 5tL_1), \qquad C_{52}(t) = 10L^3L_1(L + 2tL_1)$$

$$C_{53}(t) = 60L^2L_1^{\,2}(L + tL_1), \qquad C_{54}(t) = 120LL_1^{\,3}(2L + tL_1) \tag{42}$$

3.2. Numerical Extrapolation Past 5σ for $g_{WS}(z)$

Values of $g_{WS}(z)$ for $z \geqslant 5\sigma$ may be determined numerically from the relation,(13) valid for $z \geqslant 1$,

$$h(z) = 2\pi\rho \int_0^1 tc(t)\,dt \int_{z-t}^{z+t} h(s)\,ds \tag{43}$$

where $h(z) = g_{WS}(z) - 1$ and $c(t)$ is the bulk fluid direct correlation function, given by(9,10)

$$c(t) = \alpha + \beta t + \gamma t^3 \tag{44}$$

where

$$\begin{aligned} \alpha &= -(1 + 2\eta)^2/(1 - \eta)^2 \\ \beta &= 6\eta(1 + \eta/2)^2/(1 - \eta)^4 \\ \gamma &= -\tfrac{1}{2}\eta(1 + 2\eta)^2/(1 - \eta)^4 \end{aligned} \tag{45}$$

Interchanging the order of integration in (43) and performing the inner integral yields

$$h(z) = 2\pi\rho \int_{z-1}^{z+1} h(s) f(z, s)\,ds \tag{46}$$

where

$$f(z, s) = \tfrac{1}{2}\alpha[1 - (z - s)^2] + \tfrac{1}{3}\beta[1 - |z - s|^3] + \tfrac{1}{4}\gamma[1 - (z - s)^4] \tag{47}$$

The integral in (46) is then approximated by a quadrature rule. Using equally spaced abscissas with weights $\{W_j\}$ and setting $z_k = kh$, $s_k = kh$, $f_{ki} = f(z_k, s_i)$, $h = 1/N$, we find that Eq. (46) becomes

$$h_k = 2\pi\rho \sum_{i=k-N}^{k+N} h_i f_{ki} \tag{48}$$

We see that h_{k+N} is determined from the values $(h_{k+N-1}, h_{k+N-2}, \ldots, h_{k-2N})$. Changing variables and solving for this unknown quantity yields

$$h_k = \left(\frac{h_{k-N}}{2\pi\rho} - \sum_{i=k-2N}^{k-1} W_i f_{k-N,i}\right) \Big/ W_k f_{kk} \tag{49}$$

The above procedure may also be used to determine the bulk PY hard-sphere values. Perram(16) has recently devised a numerical scheme related to the above to determine these hard-sphere values. His technique is based on use of Baxter's(17) modified form of the Ornstein–Zernike equation. We emphasize the fact that our technique may be applied directly to the usual unmodified form of the Ornstein–Zernike equation in this case, using the same procedure as we describe above.

4. SUMMARY

Exact MSA analytic expressions, valid for all distances, have been obtained for the electrostatic part of the radial distribution functions of a system of charged hard spheres. To the best of the authors' knowledge, this is the first time that an explicit exact analytical expression for an RDF, valid for all distances, has been obtained for any nontrivial approximation. These same expressions also describe the MSA charge profile of a system of charged hard spheres near a charged wall. In addition, two simple approximations to these expressions have been examined.

We have also obtained analytical expressions for the nonelectrostatic part of the profile of the latter system valid for $r \leqslant 5\sigma$, and have discussed a numerical means of obtaining such results past $r = 5\sigma$.

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