JOURNAL OF COMPUTATIONAL PHYSICS **124,** 230–241 (1996)
ARTICLE NO. 0055

Analysis of the Bulk and Surface-Induced Structure of Electrolyte Solutions Using Integral Equation Theories

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Received May 4, 1995; revised August 14, 1995

We have developed robust and efficient numerical methods for solving integral equation theories for electrolyte solutions. These methods are hybrids of Newton–Raphson and Picard iterations and have been obtained as extended versions of the previous methods for pure solvents by solving nontrivial problems posed by the inclusion of ions. Bulk electrolytes and electrolytes near both inert and metallic surfaces are considered. The basic equations previously derived for a one-component fluid near a planar wall are extended to a multicomponent fluid. Analytical expressions for elements of the Jacobian matrices are arranged in compact form. A striking feature of the method for surface problems is that the Jacobian is determined only from bulk properties. A discussion of some special treatments that need to be considered for asymmetric anions and cations is included. These methods have been demonstrated using the full reference hypernetted-chain theory for various sizes of ions in a wide range of ionic concentrations. © 1996 Academic Press, Inc.

I. INTRODUCTION

There has been considerable interest in analyzing the structure of electrolyte solutions near both uncharged and charged surfaces. A goal is to develop a completely molecular description of the electrical double layer which plays an important role in various fields of physics and chemistry. In these studies, it is doubtless that the integral equation theories are very attractive. Among currently available theories, we are particularly interested in the reference hypernetted-chain (RHNC) theory. There are several subjects to be investigated such as the development of a molecular model for water, the mathematical reduction of the Ornstein–Zernike (OZ) equation to a tractable form, the construction of reliable bridge functions, and the development of robust and efficient numerical methods for solving the basic equations. The present article is concerned with the last subject.

Robust and efficient algorithms were already developed by Kinoshita and Harada for pure solvents. They first treated dipolar spheres in the bulk [1] and near surfaces [2], and then extended their algorithms to more sophisticated models of spheres with embedded dipoles and quadrupoles [3]. The algorithm described in Ref. [2] has recently been applied to dipolar hard spheres near a metallic wall [4]. These studies, however, have never included ions (anions and cations) in the system. It is generally recognized that a numerical method often becomes quite unstable once highly charged ions are included in the solvents [1, 2]. The objective of the present article is to extend earlier methods to electrolyte solutions, mixtures of solvent molecules and ions, without deterioration in the convergence properties of the numerical methods. Although the basic equations are described for mixtures of dipolar hard spheres (solvent molecules) and charged hard spheres (ions), they can readily be adapted to other related models.

Since the pair interactions are angle-dependent and the system of interest comprises multiple components, the basic equations derived are very complicated. In the present article, reliable numerical methods are obtained by judicious application of the Newton–Raphson method. The Newton–Raphson method is applied only to the variables which govern convergence properties. Techniques to reduce the number of variables are employed, and care is taken so that the Jacobian matrix can be calculated analytically. The analytical expressions are manipulated so that the matrix can be calculated quite efficiently using the fast Fourier transform (FFT) method.

In the present article, we consider 1:1 electrolyte solution near uncharged inert and metallic surfaces. When the surface is inert and the ions are "symmetrical" (i.e., the ion diameters are equal), the density profile near the surface is identical for both anions and cations. However, at a metallic surface or when the ion diameters differ, the wall–anion and wall–cation density profiles differ. In the latter cases, special numerical considerations are required. The present article describes some details of the numerical methods used in a previous publication [5] in which theoretical results for the structure of metal-electrolyte solution interfaces are reported. The readers should refer to Ref. [5] for numerical results obtained using the present method.

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0021-9991/96 $18.00

II. BULK ELECTROLYTE SOLUTIONS

Integral equation theories for multicomponent systems are defined by two relationships connecting the pair and direct correlation functions, h and c, respectively. These are the Ornstein–Zernike (OZ) equation

$$h_{\alpha\beta}(12) - c_{\alpha\beta}(12) = \sum_{\gamma} \frac{\rho_\gamma}{8\pi^2} \int h_{\alpha\gamma}(13) c_{\gamma\beta}(32)\, d(3), \quad \text{(1a)}$$

and an appropriate closure approximation which can be written in general as

$$\begin{aligned} h_{\alpha\beta}(12) &- c_{\alpha\beta}(12) \\ &= \ln[h_{\alpha\beta}(12) + 1] + u_{\alpha\beta}(12)/k_{\mathrm{B}}T - b^{R}_{\alpha\beta}(12), \end{aligned} \quad \text{(1b)}$$

where the numbers 1, 2, and 3 in parenthesis denote the coordinates of particles of species α, β, and γ, respectively, and the sum is over all particle species. u is the pair interaction, $k_{\mathrm{B}}T$ is the Boltzmann constant times the temperature and b^{R} is an approximation for the bridge diagrams [6]. A general theoretical formalism for solving these equations for molecular systems has been developed by Fries, Kusalik, and Patey [7, 8] and implemented using a Picard iteration strategy. However, the Picard method is characterized by a slow rate of convergence. Hence, using the same general formalism Kinoshita and Harada [1, 2] have developed a more efficient numerical algorithm for a pure solvent system which is a hybrid of the Picard and Newton–Raphson iteration strategies.

The numerical algorithm is to some extent system dependent and the extension of the method to the case of a multicomponent mixture of solvent molecules and ions requires special consideration. In this paper, we consider a mixture in which the solvent molecules are represented as hard spheres with embedded point dipoles and the ions are represented as hard spheres with embedded point charges—the so-called "civilized" model of an electrolyte solution. Furthermore, our results are restricted to 1:1 electrolytes. However, the discussion can readily be extended to mixed valence electrolytes, "soft" spheres or more sophisticated solvent models such as spheres with embedded dipoles and quadrupoles [3, 9] and we will consider such system in the future. For a detailed discussion of the numerical method, the reader is referred to Refs. [1, 3]. Here, we should point out that in solving the integral equation theories for molecular species, the pair functions (for example, h) are expanded using rotational invariants [7]. For a pair of linear molecules as an example, the expansion is

$$h_{\alpha\beta}(12) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{l=|m-n|}^{m+n} h^{mnl}_{\alpha\beta}(r)\Phi^{mnl}(12), \quad \text{(2)}$$

where the rotational invariants Φ depend only on the angular coordinates and $m + n + l$ must be even for projections $h^{mnl}_{\alpha\beta}$ to be nonzero.

A. *Numerical Method*

In solving the integral equations numerically, we iterate on the functions $c_{\alpha\beta}(12)$ and $\eta_{\alpha\beta}(12) = h_{\alpha\beta}(12) - c_{\alpha\beta}(12)$ which have the projections

$$x^{mnl}_{ss}(r), x^{0nn}_{+s}(r), x^{0nn}_{-s}(r), x^{000}_{++}(r), x^{000}_{+-}(r), x^{000}_{--}(r),$$

where x denotes c or η, the subscripts s, $+$, and $-$ denote the "solvent," "cation," and "anion" species, respectively, and the superscripts m, n, and l are defined in Eq. (2). In numerical solution, the expansion in Eq. (2) is truncated for maximum values of m and n. The convergence properties of the integral equations are governed primarily by the nonzero projections with m and $n \leq 1$ (i.e., those occurring in the mean spherical approximation (MSA)) and include

$$\begin{aligned} &x^{000}_{ss}(r), x^{011}_{ss}(r), x^{110}_{ss}(r), x^{112}_{ss}(r), x^{000}_{+s}(r), x^{011}_{+s}(r), \\ &x^{000}_{-s}(r), x^{011}_{-s}(r), x^{000}_{++}(r), x^{000}_{+-}(r), \text{and } x^{000}_{--}(r). \end{aligned} \quad \text{(3)}$$

However, we note that $c^{011}_{ss}(r)$ and $\eta^{011}_{ss}(r)$ make only minor contributions to the rate of convergence unless the anion and cation diameters are very different and the concentration is high. The importance of the remaining projections with m and $n \leq 1$ is related to the pair potential which has projections

$$\begin{aligned} &u^{000}_{ss}(r), u^{112}_{ss}(r), u^{000}_{+s}(r), u^{011}_{+s}(r), u^{000}_{-s}(r), \\ &u^{011}_{-s}(r), u^{000}_{++}(r), u^{000}_{+-}(r), \text{and } u^{000}_{--}(r). \end{aligned}$$

In addition, the convergence properties are influenced mainly by the short-range contributions to the projections in Eq. (3). Hence, we apply the Newton–Raphson method to selected projections only for $r \leq D_{\alpha\beta}$ ($D_{\alpha\beta} < d_{\alpha\beta}$, $d_{\alpha\beta} = (d_\alpha + d_\beta)/2$; $\alpha, \beta = s, +$ and $-$, and d_α is the hard-sphere diameter of component α). In the regime where the hard-sphere cores overlap, the potential is

$$u^{000}_{\alpha\beta}(r) = \infty, \quad r < d_{\alpha\beta}, \quad \text{(4)}$$

and the closure equation is simply $c_{\alpha\beta}(12) = -1 - \eta_{\alpha\beta}(12)$ [1]. It is found that only the 10 projections

$$\begin{aligned} &\eta^{000}_{ss}(r), \eta^{110}_{ss}(r), \eta^{112}_{ss}(r), \eta^{000}_{+s}(r), \eta^{011}_{+s}(r), \\ &\eta^{000}_{-s}(r), \eta^{011}_{-s}(r), \eta^{000}_{++}(r), \eta^{000}_{+-}(r), \quad \text{and } \eta^{000}_{\eta--}(r), \end{aligned} \quad \text{(5)}$$

for $r \leq D_{\alpha\beta}$ need to be treated specially by decomposing them into "coarse" (a_{tz}) and "fine" ($\Delta\eta_{ti}$) variables [10] using the projective representation

$$\eta_{ti} = \sum_{z=1}^{\kappa_t} a_{tz} P_{tzi} + \Delta\eta_{ti}. \tag{6}$$

For notational simplicity, the 10 discretized projections in Eq. (5) are denoted by η_{ti} for "projection t" ($t = 1, ..., 10$) at $r = i\ \delta r$ ($i = 0, 1, ..., N - 1$) for a grid spacing of δr, P_{tzi} is the discretized zth basis function for projection t at $r = i\ \delta r$ and κ_t is the number of roof basis functions for projection t. The 10 projections for $r > D_{\alpha\beta}$, $\Delta\eta_{ti}$ and all the other projections of c and η constitute the fine variables. For a given approximation of the fine variables, the coarse variables a_{tz} are solved using the Newton–Raphson iteration strategy. The fine variables are then updated using the Picard method and the cycle is repeated until the variables are converged. One cycle of the Newton–Raphson calculation can be summarized as follows:

1. Starting with initial "input" values of the coarse variables a_{tz}, construct η_{ti} from Eq. (6).
2. Calculate the projections of $c_{\alpha\beta}(12)$ using a closure approximation to the OZ equation. The RHNC closure is used in the present article.
3. Calculate $\tilde{c}^{mnl}_{\alpha\beta}(12)$, the Hankel transforms [7] of $c^{mnl}_{\alpha\beta}(12)$.
4. Using the OZ equation, calculate $\tilde{\eta}^{mnl}_{\alpha\beta}(12)$, the Hankel transform of $\eta^{mnl}_{\alpha\beta}(12)$.
5. Calculate $\eta^{mnl}_{\alpha\beta}(12)$, the back Hankel transforms [7] of $\tilde{\eta}^{mnl}_{\alpha\beta}(12)$. The newly calculated values of η_{ti} are denoted by η'_{ti}.
6. Evaluate new "output" values of the coarse variables a'_{tz} by decomposing η'_{ti} from

$$a'_{tz} = \sum_{i=0}^{\kappa_t i_{bt}-1} \eta'_{ti} Q_{tzi}, \tag{7}$$

where Q_{tzi} are the discretized conjugate basis functions determined from P_{tzi} and the prime denotes output values from the present cycle. We use the roof basis functions for P_{tzi} [1] with unit height and width $2i_{bt}\delta r$. It should be emphasized that κ_t and i_{bt} may differ for different projection pairs t and this is an additional complication for multicomponent systems.

The Newton–Raphson iteration solves for the roots of

$$f_{tz} = a_{tz} - a'_{tz} \quad (t = 1, ..., 10;\ z = 1, ..., \kappa_t). \tag{8}$$

A major concern in this method is the derivation of analytical expressions for the Jacobian matrix having elements

$$\frac{\partial f_{tz}}{\partial a_{sy}} = \delta_{ts}\delta_{zy} - \frac{\partial a'_{tz}}{\partial a_{sy}} \tag{9}$$

$$(t, s, = 1, ..., 10;\ z = 1, ..., \kappa_t, y = 1, ..., \kappa_s)$$

$$\frac{\partial a'_{tz}}{\partial a_{sy}} = \sum_{j=1}^{\kappa_s i_{bs}-1} P_{syj} \sum_{i=0}^{\kappa_t i_{bt}-1} Q_{tzi} \frac{\partial \eta'_{ti}}{\partial \eta_{sj}}, \tag{10}$$

where δ_{ij} is the Kronecker delta function and the partial derivative $\partial\eta'_{ti}/\partial\eta_{sj}$ is given by

$$\frac{\partial \eta'_{ti}}{\partial \eta_{sj}} = \sum_{p=1}^{N-1} \frac{\partial \eta'_{ti}}{\partial \tilde{\eta}_{tp}} \frac{\partial \tilde{\eta}_{tp}}{\partial \tilde{c}_{sp}} \frac{\partial \tilde{c}_{sp}}{\partial c_{sj}} \frac{\partial c_{sj}}{\partial \eta_{sj}}, \tag{11a}$$

$$\frac{\partial c_{sj}}{\partial \eta_{sj}} = -1. \tag{11b}$$

Here, $\tilde{\eta}_{1p}$ denotes, for example, $\tilde{\eta}^{000}_{ss}(p\delta k)$ and $\tilde{\eta}^{000}_{ss}(k)$ is the Hankel transform of $\eta^{000}_{ss}(r)$. Equation (11b) is based on the fact that the closure equation for $r < d_{\alpha\beta}$ has the very simple form mentioned above. Because of Eq. (11b), the expression for $\partial\eta'_{ti}/\partial\eta_{sj}$ is reduced to Eq. (11a). As a result, the analytical expressions for the elements of the Jacobian matrix can be derived with no difficulty.

The partial derivative $\partial\tilde{\eta}_{tp}/\partial\tilde{c}_{sp}$ can be derived by applying "matrix calculus" to the OZ equation as explained in Appendix A. By examining the OZ equation arranged in matrix form, we note that some of the elements of the Jacobian matrix are zero and it can be shown that $\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(k)/\partial\tilde{c}^{mnl}_{\alpha\beta}(k)$ is zero when one of the pairs (β', n') or (β, n) is (s, 0) and the other is (s, 1). For instance,

$$\frac{\partial\tilde{\eta}^{000}_{ss}(k)}{\partial\tilde{c}^{011}_{+s}(k)} = \frac{\partial\tilde{\eta}^{000}_{+s}(k)}{\partial\tilde{c}^{110}_{ss}(k)} = \frac{\partial\tilde{\eta}^{000}_{ss}(k)}{\partial\tilde{c}^{110}_{ss}(k)} = \frac{\partial\tilde{\eta}^{000}_{ss}(k)}{\partial\tilde{c}^{011}_{+s}(k)} = \cdots = 0.$$

Thus, many elements of the Jacobian matrix are zero. This results in a considerable saving in computation time needed to construct the matrix. The derivative $\partial\tilde{c}_{sp}/\partial c_{sj}$ can be derived by expressing the forward hat and Fourier transforms [7] in discrete form. It should be noted that only for $s = 3$ do we have $\hat{c}^{112}_{ss}(i\ \delta r) \neq c^{112}_{ss}(i\ \delta r)$ [1, 7], where "$\hat{\ }$" denotes the hat transform. For $s = 5$ and 7, the Fourier transform has a more complicated form [7]. Thus, for $s =$ 3, 5, and 7, special considerations are needed in deriving $\partial\tilde{c}_{sp}/\partial c_{sj}$. The derivative $\partial\eta'_{ti}/\partial\tilde{\eta}_{tp}$ can be derived from the discretized back Fourier and hat transforms. Similar considerations are needed for $t = 3, 5,$ and 7. Analytical expressions for $\partial\eta'_{ti}/\partial\eta_{sj}$ (obtained from Eq. (11)) are arranged so that the FFT technique can be applied directly to the calculations. The final expressions thus obtained are given in Appendix B for a few representative projection pairs t and s.

The basic iteration strategies for the inner Newton–

TABLE I

Systems considered in the present work. In the macroparticle and wall cases the surface is in contact with a solution of total reduced density $\rho^* = 0.7$. The reduced solvent dipole moment and ionic charge are $\mu^{*2} = 3$ and $q_+^* = -q_-^* = 8$, respectively. The solvent diameter d_s was taken to be 2.8 Å. The label "Eq" represents an ion with a diameter equal to the solvent diameter.

Salt	d_+/d_s	d_-/d_s	ρ_s^*	$\rho_\pm^*$	Molarity
none			0.7	0	0
LiI	0.68	1.44	0.675	0.0125	0.945
NaCl	0.84	1.16	0.675	0.0125	0.945
			0.6	0.05	3.78
			0.5	0.1	7.56
EqEq	1.0	1.0	0.675	0.0125	0.945
RbF	1.16	0.84	0.675	0.0125	0.945
			0.6	0.05	3.78
			0.5	0.1	7.56
CsF	1.28	0.84	0.675	0.0125	0.945
CsI	1.28	1.44	0.675	0.0125	0.945

Raphson and outer Picard loops are similar to those described in Ref. [1]. The Picard iteration is considered converged once

$$E_{\text{out}} = \frac{1}{N_{\text{fine}}} \sum_{i=1}^{N_{\text{fine}}} \left| \frac{V_i^{\text{new}} - V_i^{\text{old}}}{V_i^{\text{new}}} \right| < 10^{-4}, \tag{12}$$

where V_i^{old} and V_i^{new} represent the N_{fine} fine variables before and after a single Picard iteration.

Even for mixtures of spheres with embedded dipoles, quadrupoles, and higher multipole moments and charged spheres [8], the same 10 projections (Eq. (5)) need to be decomposed into coarse and fine variables in the manner defined above. Analytical expressions for the Jacobian matrix can also be derived in virtually the same manner.

B. *Numerical Examples*

We tested the numerical method for the several example systems listed in Table I. In all cases, the reduced dipole moment squared of the solvent, $\mu^{*2} = \mu^2/k_BTd_s^3 = 3.0$, the reduced charge of the ions, $q_+^* = -q_-^* = q/k_BTd_s)^{1/2} = 8.0$, and the total reduced number density, $\rho^* = \rho d_s^3 = \rho_s^* + \rho_+^* + \rho_-^* = 0.7$ (where ρ_α is the number density of component α) were held constant and the ion diameters and relative concentrations were varied [11].

Using this method, we observed the following convergence properties. When a converged result is used as the initial guess for a similar condition, convergence is achieved in only a few tens of the total Newton–Raphson iterations using the same Jacobian matrix (calculated once for the initial condition). In other words, only one calculation of the Jacobian matrix is needed and, for example, using a Jacobian matrix of dimension 120 and starting from the results for $d_+ = 0.84d_s$, $d_- = 1.16d_s$, and $\rho_+^* = \rho_-^* = 0.0125$ (a simple model for 0.945M NaCl), the result for a new ionic concentration of $\rho_+^* = \rho_-^* = 0.0250$ was obtained in 29 Picard iterations and a total of 35 Newton–Raphson iterations. The numerical method exhibits similar convergence properties when the solvent is modeled as a hard sphere with embedded dipole and quadrupole moments and the ions are modeled as above but with a full ionic charge at 298K ($q_+^* = -q_-^* = 14.1527$).

When the anion and cation diameters differ, the odd l projections of the dipole–dipole correlation functions are not zero. Table II shows the contact values for several representative projections of the total correlation function and gives us an idea of the degree of the contribution from the odd l projections. The table shows for the ionic charge tested that the contribution from the odd l projections is small, except when the ion diameters differ greatly and the ionic concentration is very high.

III. ELECTROLYTE SOLUTIONS NEAR A MACROPARTICLE

A. *Numerical Method*

In this section, we consider the three component ion–dipole mixture near a macroparticle m at infinite dilution. Since, $\rho_m = 0$, the OZ equation decouples into two sets of equations describing the bulk particle–particle correlation functions (as discussed in Section II) and the macroparticle–particle correlation functions.

Following the usual reduction of the bulk OZ equation [7, 12], the macroparticle OZ equation can be reduced to expressions of the form

$$\tilde{N}_{ms}^{0n}(k) = \rho_s \sum_{n_1} \tilde{H}_{ss}^{n_1 n}(k)\tilde{C}_{ms}^{0n_1}(k), + \sum_{\alpha=+,-} \rho_\alpha \tilde{H}_{\alpha s}^{0n}(k)\tilde{C}_{m\alpha}^{00}(k), \tag{13a}$$

$$\tilde{N}_{m\beta}^{00}(k) = \rho_s \sum_{n_1} (-)^{n_1} \tilde{H}_{\beta s}^{0n_1}(k)\tilde{C}_{ms}^{0n_1}(k) + \sum_{\alpha=+,-} \rho_\alpha \tilde{H}_{\alpha\beta}^{00}(k)\tilde{C}_{m\alpha}^{00}(k),$$

$$\beta = +, -, \tag{13b}$$

where $\tilde{N}_{m\beta}^{0n}(k)$, $\tilde{C}_{m\beta}^{0n}(k)$, and $\tilde{H}_{\alpha\beta}^{n_1 n}(k)$ ($\alpha, \beta = s, +,$ and $-$) are the χ transforms (evaluated at $\chi = 0$) of $\tilde{\eta}_{m\beta}^{0nn}(k)$, $\tilde{c}_{m\beta}^{0nn}(k)$, and $\tilde{h}_{\alpha\beta}^{n_1 nl}(k)$ which in turn are the Hankel transforms of $\eta_{m\beta}^{0nn}(r)$, $c_{m\beta}^{0nn}(r)$, and $h_{\alpha\beta}^{n_1 nl}(r)$, respectively [7, 12]. Also, we have used the definition $f^{mnl} = \sqrt{(2m+1)(2n+1)}$. Much of the numerical method is similar to the bulk case and will not be repeated here.

TABLE II

Contribution of two major odd projections for the dipole-dipole pair. In this table, contact values for several projections of the total correlation function are compared. Projections with $m, n \leq 4$ are included. The RHNC theory is used with Lee-Levesque [18] bridge functions ($\delta r = 0.01d_s$, $N = 4096$, $f^{mnl} = l!/\begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix}$, where f^{mnl} is a nonzero constant in the rotational invariant expansion [12]).

System	h_{ss}^{011}	h_{ss}^{121}	h_{ss}^{022}	h_{ss}^{044}	h_{ss}^{330}
0.945M EqEq	0.000	0.000	1.850	0.015	0.401
0.945M NaCl	0.029	0.054	1.858	0.015	0.409
3.78M NaCl	0.094	0.162	1.504	0.008	0.317
7.56M NaCl	0.144	0.256	1.234	0.004	0.266
0.945M LiI	0.079	0.138	1.870	0.016	0.438

In the numerical solution, care must be taken when the cation and anion diameters are different. For the dipole–dipole pair, the projections with ($n_1 + n =$ odd) are not zero and must be included. For the macroparticle–solvent and macroparticle–ion pair correlation functions, the odd n projections are also not zero. In addition, we should point out that in this case $c_{m+}^{000}(0)$ and $c_{m-}^{000}(0)$, even in the limit $d_m \to \infty$, are functions of $h_{ms}^{011}(r)$ and $[h_{m+}^{000}(r) - h_{m-}^{000}(r)]$ as shown in Appendix C and cannot be calculated until the equations are solved. Because a unique algorithm is used in the planar limit $d_m \to \infty$, this feature requires special treatment for the wall case as discussed in Sections IV.A and IV.B. When the cation and anion diameters are equal, the projections with ($n_1 + n =$ odd) for the dipole–dipole pair are zero. However, with an electric field near the surface the odd-n projections of the macroparticle–solvent and macroparticle–ion pair are not zero and the special treatment mentioned above is again required.

If we consider the general case when the macroparticle generates an electrostatic field, then the nonzero projections of the macroparticle–particle interactions are $u_{ms}^{000}(r)$, $u_{ms}^{011}(r)$, $u_{m+}^{000}(r)$, and $u_{m-}^{000}(r)$, and it is expected that the convergence properties of the macroparticle–particle equations are governed mainly by the projections

$$\eta_{ms}^{000}(r), \eta_{ms}^{011}(r), \eta_{m+}^{000}(r), \text{and } \eta_{m-}^{000}(r) \tag{14}$$

for $r \leq D_{m\alpha}$. We note that since the Newton–Raphson method is applied only to the projections for $r \leq D_{m\alpha}$ and the closure equation in this range has the very simple form discussed previously the projections of the direct correlation functions at all separations are not included in the independent variables. Hence, the above four projections for $r \leq D_{m\alpha}$ are treated specially by decomposing them into coarse and fine variables as in Section II. Analytical expressions for the Jacobian matrix needed in the Newton–Raphson iteration can be derived in a manner similar to that used in the bulk case. However, since the bulk and macroparticle OZ equations are decoupled, we find that the Jacobian matrix is a constant (defined by the bulk correlation functions). As a result, the set of equations to be solved in the Newton–Raphson loop is linear for the independent variables chosen and is solved *exactly* from the Jacobian matrix (i.e., it is independent of the initial guess and no iteration is required).

B. *Numerical Examples*

We have found that the convergence properties for the macroparticle–particle and wall–particle system are similar, except that an additional iterative loop must be considered in the wall case (see Sections IV.A and IV.B). Hence, a more detailed discussion of the convergence properties will be given in Section IV.B. Here, we briefly summarize the convergence properties for the macroparticle systems.

The numerical method was tested for macroparticles of diameter $d_m = 10d_s$ and $d_m = 30d_s$ in several of the bulk electrolyte solutions listed in Table I. Although the number of grid points for $r \leq D_{m\alpha}$ that are decomposed into coarse and fine parts is large, the dimensionality of the Jacobian matrix can be greatly reduced by an appropriate choice of basis functions. In the case of the roof basis functions, choosing larger values of i_{bt} will drastically reduce the dimensionality of the Jacobian matrix [3]. In all cases, the ideal gas condition is sufficient as an initial guess of the macroparticle–particle correlation functions.

In the case of an inert macroparticle, we obtained convergence in about 10 Picard iterations (each consisting of a single Newton–Raphson step). By incorporating a positive electric field (generated by a neutral metallic wall [4, 5]) emanating from the macroparticle, we also tested several cases where the macroparticle was not inert but metallic. In this case, the direct macroparticle–particle pair interaction for an uncharged macroparticle is relatively short-ranged and is attractive for anions and repulsive for cations with $u_{m+}^{000}(r) = -u_{m-}^{000}(r)$. Even for strong electric fields [4, 5] outside of contact, convergence was achieved in 20 to 25 Picard iterations.

The two values $c_{m+}^{000}(0)$ and $c_{m-}^{000}(0)$ are obtained from the self-consistent solution. As shown in Appendix C, in the limit $d_m \to \infty$, these values can also be calculated by integrating $h_{ms}^{000}(r)$ and $r[h_{m+}^{000}(r) - h_{m-}^{000}(r)]$. A good check of the algorithm is to see if the results from the two methods agree with each other for large d_m. We have verified for $d_m = 30d_s$ that the two results are almost identical (the discrepancy is about 0.1%).

IV. ELECTROLYTE SOLUTIONS NEAR A PLANAR WALL

A. *Basic Equations*

The mathematical reduction of the wall-particle OZ equation and the numerical solution are significantly different from the bulk and macroparticle cases as a result of the one-dimensional nature of the wall. The basic reduction of the OZ equations for a one-component fluid near a wall has already been described [13, 2, 3] and the reader is referred to this earlier work for details. The extension of these equations to a multicomponent fluid is not difficult.

As in earlier work, using the hybrid algorithms near a planar surface [2–4], we choose the origin such that the surface is at z_w and apply the approximation $c_{w\beta}^{0nn}(z < 0) = c_{w\beta}^{0nn}(-\infty)$ ($\beta = s, +, -$) for the wall–particle direct correlation functions. When the origin ($z = 0$) is set sufficiently deep inside the wall, this approximation is essentially exact and we have verified that results for $z_w = 5d_s/2$ and $z_w = 3d_s/2$ are almost indistinguishable. Before proceeding, we define $c_{w\beta}^{0nn(+)}(z)$ and $c_{w\beta}^{0nn(-)}(z)$ as

$$c_{w\beta}^{0nn(+)}(z) = \begin{cases} c_{w\beta}^{0nn}(z), & z \geq 0, \\ 0, & z < 0, \end{cases} \tag{15a}$$

$$c_{w\beta}^{0nn(-)}(z) = \begin{cases} 0, & z \geq 0, \\ c_{w\beta}^{0nn}(-\infty), & z < 0, \end{cases} \tag{15b}$$

where

$$c_{w\beta}^{0nn}(z) = c_{w\beta}^{0nn(+)}(z) + c_{w\beta}^{0nn(-)}(z), \tag{15c}$$

and note that $c_{ws}^{0nn}(-\infty) = 0$ for $n \neq 0$. It follows that [2, 3, 13]

$$\eta_{w\beta}^{0nn}(z) = \eta_{w\beta}^{0nn(+)}(z) + \eta_{w\beta}^{0nn(-)}(z), \tag{16}$$

where $\eta_{w\beta}^{0nn}(z)$ are the projections of $\eta_{w\beta}(1) = h_{w\beta}(1) - c_{w\beta}(1)$.

Arranging the OZ equation [2, 13] yields expressions of the form

$$\tilde{N}_{ws}^{0n(+)}(k) = \rho_s \sum_{n_1} \tilde{H}_{ss}^{n_1 n}(k)\, \tilde{C}_{ws}^{0n_1(+)}(k) + \sum_{\alpha=+,-} \rho_\alpha \tilde{H}_{\alpha s}^{0n}(k)\, \tilde{C}_{w\alpha}^{00(+)}(k), \tag{17a}$$

$$\tilde{N}_{w\beta}^{00(+)}(k) = \rho_s \sum_{n_1} (-)^{n_1} \tilde{H}_{\beta s}^{0n_1}(k)\, \tilde{C}_{ws}^{0n_1(+)}(k) + \sum_{\alpha=+,-} \rho_\alpha \tilde{H}_{\alpha\beta}^{00}(k)\, \tilde{C}_{w\alpha}^{00(+)}(k), \tag{17b}$$

$$\beta = +, -,$$

and

$$\eta_{w\gamma}^{0nn(-)}(z > 0) = -2\pi \sum_{\alpha=s,+,-} \rho_\alpha c_{w\alpha}^{000}(-\infty) \times \int_{|z|}^{r} r^2 S_n(z, r) h_{\alpha\gamma}^{0nn}(r)\, dr, \tag{18}$$

where

$$\tilde{N}_{w\gamma}^{0n(+)}(k) = \frac{(-)^n}{\sqrt{2n+1}}\, \tilde{\eta}_{w\gamma}^{0nn(+)}(k), \tag{19a}$$

$$\tilde{C}_{w\gamma}^{0n(+)}(k) = \frac{(-)^n}{\sqrt{2n+1}}\, \tilde{c}_{w\gamma}^{0nn(+)}(k), \quad \gamma = s, +, -, \tag{19b}$$

$\tilde{\eta}_{w\gamma}^{0nn(+)}(k)$ and $\tilde{c}_{w\gamma}^{0nn(+)}(k)$ are the one-dimensional Fourier transforms of $\eta_{w\gamma}^{0nn(+)}(z)$ and $c_{w\gamma}^{0nn(+)}(z)$, respectively, and the bulk functions $\tilde{H}_{\alpha\beta}^{mn}(k)$ are defined in Section III.A. The function S_n is defined in Ref. [13].

In our formulation, $c_{w+}^{000}(-\infty)$ and $c_{w-}^{000}(-\infty)$ are treated as input and, as in the case of very large macroparticles, they can be written as (see Appendix C)

$$c_{w+}^{000}(-\infty) = -1 + \rho_s \tilde{c}_{+s}^{000}(0) + \rho_+ \tilde{c}_{++}^{000;\mathrm{SR}}(0) + \rho_- \tilde{c}_{+-}^{000;\mathrm{SR}}(0) - \Lambda, \tag{20a}$$

$$c_{w-}^{000}(-\infty) = -1 + \rho_s \tilde{c}_{-s}^{000}(0) + \rho_+ \tilde{c}_{-+}^{000;\mathrm{SR}}(0) + \rho_- \tilde{c}_{--}^{000;\mathrm{SR}}(0) + \Lambda, \tag{20b}$$

where it is assumed that the anions and cations are equally charged and $c^{000;\mathrm{SR}}$ is defined in Eq. (C5). Since Λ depends on the wall–particle correlations, $c_{w+}^{000}(-\infty)$ and $c_{w-}^{000}(-\infty)$ are unknown until the wall calculation is finished ($\Lambda = 0$ only when the anion and cation diameters are equal and there is no electric field). However, this minor problem can be solved readily by incorporating an additional iterative loop in the numerical method as discussed in the following section.

B. *Numerical Method*

The numerical method for the wall problem is obtained after judiciously extending the previous version for pure solvents [2, 3] to electrolyte solutions. Again, it is based on the hybrid Newton–Raphson and Picard iteration strategy.

We derive more convenient forms of the back Fourier transforms of Eq. (17) so that analytical expressions for the Jacobian matrix can readily be derived. Noting that $\tilde{H}_{ss}^{n_1 n}(k)$ ($n_1 + n$ = odd) and $\tilde{H}_{\alpha s}^{0n}(k)$ ($\alpha = \pm$; n = odd) are purely imaginary [8, 7], we get

$$N_{ws}^{0n(+)}(z) = \rho_s \sum_{n_1=\text{even}} O_1[\tilde{H}_{ss}^{n_1 n}(k), C_{ws}^{0n_1(+)}(z)] + \rho_s \sum_{n_1=\text{odd}} O_2[-I\tilde{H}_{ss}^{n_1 n}(k), C_{ws}^{0n_1(+)}(z)] + \sum_{\alpha=+,-} \rho_\alpha O_1[\tilde{H}_{\alpha s}^{0n}(k), C_{w\alpha}^{00(+)}(z)], \quad \text{for even } n, \tag{21a}$$

$$N_{ws}^{0n(+)}(z) = \rho_s \sum_{n_1=\text{even}} O_2[-\tilde{H}_{ss}^{n_1 n}(k), C_{ws}^{0n_1(+)}(z)] + \rho_s \sum_{n_1=\text{odd}} O_1[\tilde{H}_{ss}^{n_1 n}(k), C_{ws}^{0n_1(+)}(z)] + \sum_{\alpha=+,-} \rho_\alpha O_2[-I\tilde{H}_{\alpha s}^{0n}(k), C_{w\alpha}^{00(+)}(z)], \quad \text{for odd } n, \tag{21b}$$

$$N_{w\beta}^{00(+)}(z) = \rho_s \sum_{n_1=\text{even}} (-)^{n_1} O_1[\tilde{H}_{\beta s}^{0n_1}(k), C_{ws}^{0n_1(+)}(z)] + \rho_s \sum_{n_1=\text{odd}} (-)^{n_1} O_2[-I\tilde{H}_{\beta s}^{0n_1}(k), C_{ws}^{0n_1(+)}(z)] + \sum_{\alpha=+,-} \rho_\alpha O_1[\tilde{H}_{\alpha\beta}^{00}(k), C_{w\alpha}^{00(+)}(z)], \quad \beta = +, -, \tag{21c}$$

where $I = \sqrt{-1}$, O_1 and O_2 are defined as

$$O_1[\tilde{F}(k), G(z)] = \frac{1}{\pi}\left(\int_0^\infty \tilde{F}(k)\tilde{Y}_c(k)\cos(kz)\,dk + \int_0^\infty \tilde{F}(k)\tilde{Y}_s(k)\sin(kz)\,dk\right), \tag{22a}$$

$$O_2[\tilde{F}(k), G(z)] = \frac{1}{\pi}\left(\int_0^\infty \tilde{F}(k)\tilde{Y}_c(k)\sin(kz)\,dk - \int_0^\infty \tilde{F}(k)\tilde{Y}_s(k)\cos(kz)\,dk\right), \tag{22b}$$

$$\tilde{Y}_c(k) = \int_0^\infty G(z)\cos(kz)\,dz, \tag{23a}$$

$$\tilde{Y}_s(k) = \int_0^\infty G(z)\sin(kz)\,dz, \tag{23b}$$

and $\tilde{F}(k)$ is real.

As in the macroparticle case, the four projections

$$\eta_{ws}^{000}(i\,\delta z),\ \eta_{ws}^{011}(i\,\delta z),\ \eta_{w+}^{000}(i\,\delta z), \text{ and } \eta_{w-}^{000}(i\,\delta z) \tag{24}$$

are treated specially by decomposing them into coarse and fine variables for $0 \le z \le z_w + D_\alpha/2 < z_w + d_\alpha/2$ ($z_w = 5d_s/2$), using the projective representation (6). These four projections are denoted by η_{ti} ($t = 1, ..., 4$), respectively. Denoting the coarse variables for η_{ti} by a_{tz} ($z = 1, ..., \kappa_t$), we summarize one cycle of the Newton–Raphson iteration (where the fine variables are held constant) as follows:

1. Starting from the input values of the coarse variables a_{tz}, construct η_{ti} from Eq. (6).
2. Calculate the projections $c_{w\beta}^{0nn(+)}(z)$, for example, from the RHNC closure.
3. Calculate the sine and cosine transforms of $c_{w\beta}^{0nn(+)}(z)$.
4. Calculate $\eta_{w\beta}^{0nn(+)}(z)$ from Eqs. (21)–(23).
5. Calculate $\eta'^{0nn}_{w\beta}(z)$ from Eq. (16).
6. Evaluate the new output values of the coarse variables a'_{tz} by decomposing η'_{ti} from Eq. (7).

The Newton–Raphson method solves for the roots of

$$f_{tz} = a_{tz} - a'_{tz} \quad (t = 1, ..., 4; z = 1, ..., \kappa_t). \tag{25}$$

The elements of the Jacobian matrix are expressed as in Eqs. (9) and (10), except that t, s = 1, ..., 4. Equations (21)–(23) are then expressed in discrete form and analytical expressions for the partial derivatives, $\partial\eta'_{ti}/\partial\eta_{sj}$ are derived by extending the procedure described in Ref. [2] to electrolyte solutions. It turns out that the expressions fall into only two different forms as explained in Appendix D. We note that the Jacobian matrix is determined from the bulk functions alone and is just part of the input data. Hence, Eq. (25) is linear for the independent variables chosen, and it is exactly solved by the Newton–Raphson method in a single step. Thus, the great advantages of the numerical method reported for pure solvents [2, 3] are totally preserved, even in the present case. In addition, in the Picard iteration, we have never come across a case where a mixing parameter smaller than one is needed.

The numerical method for the wall calculation already includes a Picard iteration and a single Newton–Raphson step. However, since Λ in Eq. (20) is not known a priori, an additional iteration must be included to evaluate the equations for a self-consistent value of Λ. A reliable method is to find Λ satisfying the charge neutrality condition

$$C_N = \int_0^\infty [h_{w+}^{000}(z) - h_{w-}^{000}(z)]\,dz, \tag{26}$$

where we assume that $q_+^* = -q_-^*$. The root of this equation

($C_N(\Lambda) = 0$) is solved using Newton's method with the derivative $dC_N/d\Lambda$ evaluated numerically. The algorithm is organized such that Λ is iterated as the most outer iteration step (i.e., Λ is held constant during the Picard iteration of the fine variables.) Charge neutrality is considered satisfied once $|C_N|$ is smaller than 10^{-7}. We note that $\Lambda = 0$ only when the wall is inert and the anion and cation diameters are equal.

C. *Numerical Examples*

In the present section, we consider the numerical method and convergence properties of both inert and metallic walls in contact with the bulk electrolyte solutions listed in Table I. A detailed discussion of the results for these systems is presented in Ref. [5].

After the calculation is complete and a converged value of Λ is obtained, $c_{w+}^{000}(-\infty)$ and $c_{w-}^{000}(-\infty)$ are calculated from Eq. (20). These values must approach $c_{m+}^{000}(-\infty)$ and $c_{m-}^{000}(-\infty)$, respectively, in the limit $d_m \rightarrow \infty$. We have verified that this requirement is satisfied for $d_m = 30d_s$. Hence, we are confident in our computing procedures for both the macroparticle and wall problems.

When the anion and cation diameter are equal and the wall is inert, the iteration over Λ is not necessary. In these cases, the ideal gas distribution as an initial guess of the wall–particle correlation functions always led to convergence in about 10 Picard iterations. In all other cases, the iteration over Λ must be included. Although, for the systems studied, only three to six iterations over Λ were needed to reach convergence. Since C_N is a monotonic function of Λ, the initial value of Λ is not important. The first iteration usually gave a solution $C_N(\Lambda) \approx 0$. Two to four Picard-loop iterations were required to evaluate the derivative $dC_N/d\Lambda$.

As an example, the wall–particle correlation functions were solved for 0.945*M* NaCl in the ground state self-consistent field of a simple quantum mechanical metallic wall [4, 5, 14]. The average bulk electron density $\bar{n}$, represented by the Wigner–Seitz radius $r_s = (4\pi\bar{n}/3)^{1/3}$, was $2.65a_o$, where a_o is the Bohr radius, and we assumed a temperature of 298°K. Starting from the ideal gas condition for the wall–particle correlation functions and using a Jacobian matrix of dimension 119, five iterations over Λ were needed to obtain convergence. In the first iteration over Λ, 25 Picard loop iterations were needed. In the second, third, fourth, and fifth iterations, the number of Picard iterations needed was 6, 4, 4, and 4, respectively. In all, 59 Picard (and Newton–Raphson) iterations were needed. (Again, only one Newton–Raphson step is needed for each Picard iteration.) This number decreased to 35 when there was no external field. When the result obtained for similar characteristics was used as the initial guess (such a result is usually available), only about 30 Picard iterations were needed even in the presence of the metal field. The reliability of the algorithm did not deteriorate for all systems and concentrations studied. This observation is in marked contrast with the situation reported for conventional numerical methods where hundreds of iterations are required with a careful setting of the starting point [15, 16] and often fail to give converged solutions for significantly asymmetric anions and cations [17].

TABLE III

Converged values of Λ. The metallic wall is uncharged and the values of r_s for the jellium wall [5, 14] is $2.65a_0$. The RHNC theory is used and the bridge functions are estimated by a modified version of the Henderson-Plischke parameterization [5, 19] ($\delta z = 0.01d_s$, $N = 4096$).

System	Inert wall	Metallic wall
0.453M EqEq	0.000	8.767
0.945M EqEq	0.000	8.724
3.78M EqEq	0.000	8.555
0.945M NaCl	−0.195	8.645
3.78M NaCl	−1.020	7.581
7.56M NaCl	−2.151	6.316
0.453M RbF	0.072	8.821
0.945M RbF	0.195	8.911
3.78M RbF	1.020	9.736
7.56M RbF	2.151	11.03
0.945M LiI	−0.518	8.449
0.945M CsF	0.303	9.011
0.945M CsI	−0.171	8.672

Table III shows the converged values of Λ for the systems studied. An understanding of the degree of asymmetry can be obtained from these values. In the inert wall case, Λ is negative for $d_+ < d_-$ and positive for $d_+ > d_-$. In the metallic wall case where a positive electrostatic field is present, Λ is positive for all systems tested.

V. CONCLUSION

The algorithms previously developed for pure solvents have been extended to mixtures of solvent molecules and ions by solving significant problems posed by the inclusion of ions. The extended versions are hybrids of the Newton–Raphson and Picard iteration methods. The analytical expressions derived for the Jacobian matrix are compact despite the complexity of the basic equations. The dimensionality of the matrix is sufficiently small for numerical calculations. It is demonstrated that the robustness and efficiency of the previous algorithms does not deteriorate with the inclusion of ions. Two types of numerical methods have thus been obtained for bulk fluids and fluids near surfaces.

The numerical method for the surface problem is particularly powerful, making the integral equation theories a very attractive means of analyzing the surface-induced structure of electrolyte solutions. The Jacobian matrix is determined only by the bulk parameters and remains constant in the calculation of the macroparticle—fluid and wall–fluid correlation functions. That is, any change in the surface and surface-particle parameters (including the interaction potential) has no influence on the Jacobian matrix. The ideal gas condition was successful as the initial guess of the wall–particle correlation functions in all cases studied. The Newton–Raphson step is solved exactly in a single step, independently of the initial guess. There is no need to use a mixing parameter smaller than one in the outer Picard loop (direct iteration is adequate). When anions and cations are not symmetrical or an electric field is present in a planar surface, an additional iteration step is required. This treatment assures satisfaction of the charge neutrality condition which proved to be essential in the self-consistent calculation for the whole metal–solution system [5].

The numerical methods are expected to prove very useful in further studies of the electrical double layer. In fact, they are currently being used successfully in studies of metal–solution interfaces [4, 5].

APPENDIX A: ANALYTICAL EXPRESSIONS FOR $\partial\tilde{\eta}_{tp}/\partial\tilde{c}_{sp}$

In general, $\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(k)/\partial\tilde{c}^{mnl}_{\alpha\beta}(k)$ is given by

$$\frac{\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(k)}{\partial\tilde{c}^{mnl}_{\alpha\beta}(k)} = \sum_{\chi=-\min(m,n)}^{\min(m,n)} \frac{\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(k)}{\partial\tilde{N}^{m'n'}_{\alpha'\beta',\chi}(k)} \frac{\partial\tilde{N}^{m'n'}_{\alpha'\beta',\chi}(k)}{\partial\tilde{C}^{mn}_{\alpha\beta,\chi}(k)} \frac{\partial\tilde{C}^{mn}_{\alpha\beta,\chi}(k)}{\partial\tilde{c}^{mnl}_{\alpha\beta}(k)}\,,$$

$$k = p\,\delta k, \quad p = 1, ..., N-1, \tag{A1}$$

where $\tilde{N}^{mn}_{\alpha\beta,\chi}$ and $\tilde{C}^{mn}_{\alpha\beta,\chi}$ are the χ transforms [7, 12] of $\tilde{\eta}^{mnl}_{\alpha\beta}$ and $\tilde{c}^{mnl}_{\alpha\beta}$, respectively, and

$$\frac{\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(k)}{\partial\tilde{N}^{m'n'}_{\alpha'\beta',\chi}(k)} = (2l+1)\begin{pmatrix} m' & n' & l' \\ \chi & -\chi & 0 \end{pmatrix}, \tag{A2a}$$

$$\frac{\partial\tilde{C}^{mn}_{\alpha\beta,\chi}(k)}{\partial\tilde{c}^{mnl}_{\alpha\beta}(k)} = \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix}. \tag{A2b}$$

The partial derivatives $\partial\tilde{N}^{m'n'}_{\alpha'\beta',\chi}(k)/\partial\tilde{C}^{mn}_{\alpha\beta,\chi}(k)$ can be evaluated as follows. The OZ equation for a multicomponent system is expressed as the set of matrix equations

$$\boldsymbol{\kappa} = (-)^{\chi}\boldsymbol{\rho}, \tag{A3a}$$

$$\tilde{\mathbf{N}}_{\chi} = \tilde{\mathbf{C}}_{\chi}\boldsymbol{\kappa}\tilde{\mathbf{C}}_{\chi}\tilde{\mathbf{E}}_{\chi}, \tag{A3b}$$

$$\tilde{\mathbf{E}}_{\chi} = [\mathbf{U} - \boldsymbol{\kappa}\tilde{\mathbf{C}}_{\chi}]^{-1}, \tag{A3c}$$

where $\mathbf{U}$ is the unit matrix and $\boldsymbol{\rho}$, $\tilde{\mathbf{C}}_{\chi}$, and $\tilde{\mathbf{N}}_{\chi}$ are defined by Kusalik and Patey [8]. Applying matrix calculus to Eq. (A3), we obtain

$$(d\tilde{\mathbf{N}}_{\chi})_{(i-j)} = \sum_{v=1}^{J}\sum_{w=1}^{J} [(d\tilde{\mathbf{C}}_{\chi})_{(i-v)}(\boldsymbol{\kappa})_{(v-v)}(\tilde{\mathbf{C}}_{\chi})_{(v-w)}(\tilde{\mathbf{E}}_{\chi})_{(w-j)}$$
$$+ (\tilde{\mathbf{D}}_{\chi})_{(i-v)}(\boldsymbol{\kappa})_{(v-v)}(d\tilde{\mathbf{C}}_{\chi})_{(v-w)}(\tilde{\mathbf{E}}_{\chi})_{(w-j)}], \tag{A4a}$$

$$\tilde{\mathbf{D}}_{\chi} = \tilde{\mathbf{C}}_{\chi} + \tilde{\mathbf{N}}_{\chi}, \tag{A4b}$$

where J in the dimensionality of the matrices and $(\tilde{\mathbf{C}}_{\chi})_{(i-j)}$ is the (i, j) element of $\tilde{\mathbf{C}}_{\chi}$. Then it can be shown that

$$\frac{\partial(\tilde{\mathbf{N}}_{\chi})_{(i-j)}}{\partial(\tilde{\mathbf{C}}_{\chi})_{(v-w)}} = \left[\sum_{n=1}^{J} \delta_{iv}(\boldsymbol{\kappa})_{(w-w)}(\tilde{\mathbf{C}}_{\chi})_{(w-n)}(\tilde{\mathbf{E}}_{\chi})_{(n-j)} + (\tilde{\mathbf{D}}_{\chi})_{(i-v)}(\boldsymbol{\kappa})_{(v-v)}(\tilde{\mathbf{E}}_{\chi})_{(w-j)}\right]. \tag{A5}$$

$\tilde{N}^{mn}_{\alpha\beta,\chi}(p\,\delta k)$ and $\tilde{C}^{mn}_{\alpha\beta,\chi}(p\,\delta k)$ are real for $m + n =$ even and purely imaginary for $m + n =$ odd. However, there is no need to use complex numbers in computer programming. The arithmetic operations are performed as if the numbers were all real with the exception that when a product of two pure imaginary numbers occur the result is simply multiplied by (-1). Taking care in handling pure imaginary numbers, Eqs. (A1), (A2), (A3c), (A4b), and (A5) allow us to calculate analytically the partial derivatives $\partial\tilde{\eta}^{m'n'l'}_{\alpha'\beta'}(p\,\delta k)/\partial\tilde{c}^{mnl}_{\alpha\beta}(p\,\delta k)$ or $\partial\tilde{\eta}_{tp}/\partial\tilde{c}_{sp}$.

APPENDIX B: ANALYTICAL EXPRESSIONS FOR $\partial\eta'_{1i}/\partial\eta_{5j}$, $\partial\eta'_{2i}/\partial\eta_{5j}$ AND $\partial\eta'_{5i}/\partial\eta_{5j}$

We define $\partial\eta'^{000}_{ss}(i\,\delta r)/\partial\eta^{011}_{+s}(j\,\delta r)$ as $\partial\eta'_{1i}/\partial\eta_{5j}$. However, as explained in the text, $\partial\tilde{\eta}^{000}_{ss}(p\,\delta k)/\partial\tilde{c}^{011}_{+s}(p\,\delta k)$ is zero and it follows from Eq. (11a) that

$$\frac{\partial\eta'_{1i}}{\partial c_{5j}} = 0. \tag{B1}$$

The other two partial derivatives are given by

$$\frac{\partial\eta'_{2i}}{\partial\eta_{5j}} = \frac{j}{iN}[\Omega(i+j) + \Omega(i-j)]$$
$$+ \frac{1}{i\pi}[\Pi(i+j) - \Pi(i-j)], \tag{B2a}$$

$$\frac{\partial\eta'_{20}}{\partial\eta_{5j}} = \frac{2\pi j}{N^2}\varepsilon(j) - \frac{2}{N}\Omega(j), \tag{B2b}$$

where

$$\Omega(L)=\sum_{p=1}^{N-1}\left(\frac{\partial\tilde{\eta}_{2p}}{\partial(-I\tilde{c}_{5p})}\right)\sin(pL\pi/N), \tag{B2c}$$

$$\Pi(L)=\sum_{p=1}^{N-1}\frac{1}{p}\left(\frac{\partial\tilde{\eta}_{2p}}{\partial(-I\tilde{c}_{5p})}\right)\sin(pL\pi/N), \tag{B2d}$$

$$\varepsilon(L)=\sum_{p=1}^{N-1}p\left(\frac{\partial\tilde{\eta}_{2p}}{\partial(-I\tilde{c}_{5p})}\right)\cos(pL\pi/N), \tag{B2e}$$

and

$$\begin{aligned}\frac{\partial\eta'_{5i}}{\partial\eta_{5j}}&=-\frac{j}{iN}[\Xi(i+j)+\Xi(i-j)]\\&\quad+\frac{N}{i^2\pi^2}[\Theta(i+j)-\Theta(i-j)]\\&\quad+\frac{1}{i^2\pi}[(i+j)\Psi(i+j)-(i-j)\Psi(i-j)],\end{aligned} \tag{B3a}$$

$$\frac{\partial\eta'_{50}}{\partial\eta_{5j}}=0, \tag{B3b}$$

where

$$\Xi(L)=\sum_{p=1}^{N-1}\left(\frac{\partial\tilde{\eta}_{5p}}{\partial\tilde{c}_{5p}}\right)\cos(pL\pi/N), \tag{B3c}$$

$$\Theta(L)=\sum_{p=1}^{N-1}\frac{1}{p^2}\left(\frac{\partial\tilde{\eta}_{5p}}{\partial\tilde{c}_{5p}}\right)\cos(pL\pi/N), \tag{B3d}$$

$$\Psi(L)=\sum_{p=1}^{N-1}\frac{1}{p}\left(\frac{\partial\tilde{\eta}_{5p}}{\partial\tilde{c}_{5p}}\right)\sin(pL\pi/N), \tag{B3e}$$

$I=\sqrt{-1}$ and both $(-I\tilde{c}_{5p})$ and $(-I\tilde{\eta}_{5p})$ are real. For simplicity, $\partial(-I\tilde{\eta}_{5p})/\partial(-I\tilde{c}_{5p})$ is written as $\partial\tilde{\eta}_{5p}/\partial\tilde{c}_{5p}$. For example, the analytical expressions for $\partial\tilde{\eta}_{2i}/\partial\tilde{c}_{7j}$ and $\partial\tilde{\eta}_{8i}/\partial\tilde{c}_{7j}$ have the same forms as that for $\partial\tilde{\eta}_{2i}/\partial\tilde{c}_{5j}$.

We note that these final forms are amenable to direct application of the FFT technique.

APPENDIX C: $c^{000}_{m+}(0)$ AND $c^{000}_{m-}(0)$ IN THE LIMIT $d_m \to \infty$

Consider a mixture of dipolar and charged hard spheres near a large macroparticle. When $c^{0nn}_{\alpha\beta}(r)$ is short-ranged and $h^{0nn}_{m\beta}(r)=0$ for $r<(d_\alpha+d_\beta)/2$, then $c^{0nn}_{\alpha\beta}(r)h^{0nn}_{m\beta}(r)\sim 0$ in the limit $d_m\to\infty$. Hence from the OZ equation we write

$$\begin{aligned}\eta^{000}_{m+}(0)&=-1-c^{000}_{m+}(0)\\&\sim 4\pi\rho_s\int_0^\infty r^2\,c^{000}_{+s}(r)h^{000}_{ms}(r)\,dr\\&\quad+\frac{4\pi\rho_s}{3}\int_0^\infty r^2\,c^{011}_{+s}(r)h^{011}_{ms}(r)\,dr\\&\quad+4\pi\rho_+\int_0^\infty r^2\,c^{000}_{++}(r)h^{000}_{m+}(r)\,dr\\&\quad+4\pi\rho_-\int_0^\infty r^2\,c^{000}_{+-}(r)h^{000}_{m-}(r)\,dr.\end{aligned} \tag{C1}$$

It should be noted that

$$h^{000}_{ms}(r)=-1,\, h^{011}_{ms}(r)=0,\quad \text{for } r<(d_m+d_s)/2, \tag{C2a}$$

$$h^{000}_{m+}(r)=-1,\quad \text{for } r<(d_m+d_+)/2, \tag{C2b}$$

$$h^{000}_{m-}(r)=-1,\quad \text{for } r<(d_m+d_-)/2, \tag{C2c}$$

and $c^{011}_{+s}(r)$, $c^{000}_{++}(r)$ and $c^{000}_{+-}(r)$ are long-ranged. Since $c^{000}_{+s}(r)$ is short-ranged, in the limit $d_m\to\infty$ $h^{000}_{ms}(r)$ can be replaced by (-1). Thus,

$$4\pi\rho_s\int_0^\infty r^2 c^{000}_{+s}(r)\,h^{000}_{ms}(r)\,dr\sim-\,\rho_s\tilde{c}^{000}_{+s}(0). \tag{C3}$$

Since $h^{011}_{ms}(r)$ is zero except for very large r, $c^{011}_{+s}(r)\to -\mu q_+/(k_BTr^2)$ and we obtain

$$\frac{4\pi\rho_s}{3}\int_0^\infty r^2 c^{011}_{+s}(r)h^{011}_{ms}(r)\,dr\to-\frac{4\pi\,\mu q_+\,\rho_s}{3k_BT}\int_0^\infty h^{011}_{ms}(r)\,dr. \tag{C4}$$

Here, we define the two short-ranged functions by

$$c^{000;\mathrm{SR}}_{++}(r)=c^{000}_{++}(r)+\frac{q_+^2}{rk_BT}(1-\exp(-r)), \tag{C5a}$$

$$c^{000;\mathrm{SR}}_{+-}(r)=c^{000}_{+-}(r)+\frac{q_+q_-}{rk_BT}(1-\exp(-r)). \tag{C5b}$$

It should be noted that $\exp(-r)/r$ is also a short-ranged function. Then, it can be shown that

$$\begin{aligned}&4\pi\rho_+\int_0^\infty r^2\,c^{000}_{++}(r)h^{000}_{m+}(r)\,dr\\&\quad+4\pi\rho_-\int_0^\infty r^2\,c^{000}_{+-}(r)h^{000}_{m-}(r)\,dr\\&\sim-\rho_+\,\tilde{c}^{000;\mathrm{SR}}_{++}(0)-\rho_-\,\tilde{c}^{000;\mathrm{SR}}_{+-}(0)\\&\quad-\frac{4\pi q_+}{k_BT}\int_0^\infty r[\rho_+q_+h^{000}_{m+}(r)+\rho_-q_-h^{000}_{m-}(r)]\,dr,\end{aligned} \tag{C6}$$

where $\rho_+q_++\rho_-q_-=0$. Substituting Eqs. (C3), (C4) and

(C6) into Eq. (C1) yields a desired result. The limiting behavior of $c^{000}_{m-}(0)$ can also be analyzed in a similar manner.

Here, for simplicity, we assume that the anions and cations are equally charged ($q_+ = -q_-$ and $\rho_+ = \rho_-$) and get

$$c^{000}_{m+}(0) \sim -1 + \rho_s \tilde{c}^{000}_{+s}(0) + \rho_+ \tilde{c}^{000;\mathrm{SR}}_{++}(0) + \rho_- \tilde{c}^{000;\mathrm{SR}}_{+-}(0) - \Lambda, \tag{C7a}$$

$$c^{000}_{m-}(0) \sim -1 + \rho_s \tilde{c}^{000}_{-s}(0) + \rho_+ \tilde{c}^{000;\mathrm{SR}}_{+-}(0) + \rho_- \tilde{c}^{000;\mathrm{SR}}_{--}(0) + \Lambda, \tag{C7b}$$

where

$$\Lambda = -\frac{4\pi \mu q_+ \rho_s}{3k_B T}\int_0^\infty h^{011}_{ms}(r)\,dr - \frac{4\pi \rho_+ q_+^2}{k_B T}\int_0^\infty r\left(h^{000}_{m+}(r) - h^{000}_{m-}(r)\right)dr. \tag{C8}$$

We note for an inert macroparticle and for anions and cations of equal diameter that $h^{011}_{ms}(r) = 0$, $h^{000}_{m+}(r) = h^{000}_{m-}(r)$ and $\Lambda = 0$.

APPENDIX D: ANALYTICAL EXPRESSIONS FOR $\partial\eta'_{ti}/\partial\eta_{sj}$

It should be emphasized that $\partial c^{(+)}_{sj}/\partial\eta_{sj} = -1$ leads to significant reduction of the analytical expressions. For $s = 2$ and/or $t = 2$, special considerations are needed because odd n projections of the wall-solvent correlation functions occur. When neither or both of the two subscripts t and s are equal to 2, the partial derivative is expressed in the form of the cosine transforms. For example, $\partial\eta'_{3i}/\partial\eta_{4j}$ is given by

$$\frac{\partial\eta'_{3i}}{\partial\eta_{4j}} = -\frac{\rho_-}{N}\left[\sum_{m=0}^{N-1}\tilde{H}^{00}_{+-}(m\,\delta k)\cos\left(|i-j|\frac{m\pi}{N}\right) - \tilde{H}^{00}_{+-}(0)/2\right],$$
$$(j=1,\ldots,N-1;\, i=0,\ldots,N-1) \tag{D1a}$$

$$\frac{\partial\eta'_{3i}}{\partial\eta_{40}} = -\frac{\rho_-}{4N}\left[\sum_{m=0}^{N-1}\tilde{H}^{00}_{+-}(m\,\delta k)\cos\left(\frac{im\pi}{N}\right) - \tilde{H}^{00}_{+-}(0)/2\right],$$
$$(j=0;\, i=0,\ldots,N-1). \tag{D1b}$$

Equation (D1b) differs from the previously reported expression [2] by a factor of 1/2. This is because $c^{0nn(+)}_{w\beta}(0)$ (discontinuous at $z = 0$) denotes $c^{0nn(+)}_{w\beta}(0+)$ in the present article.

On the other hand, when only one of the two subscripts t and s is equal to 2, the partial derivatives are expressed in the form of sine transforms. For example, $\partial\eta'_{2i}/\partial\eta_{1j}$ is given by

$$\frac{\partial\eta'_{2i}}{\partial\eta_{1j}} = -\frac{\sqrt{3}\rho_s}{N}\left[\sum_{m=1}^{N-1}(-I)\tilde{H}^{01}_{ss}(m\,\delta k)\sin\left[(i-j)\frac{m\pi}{N}\right]\right],$$
$$(j = 1, \ldots, N-1;\, i = 0, \ldots, N-1) \tag{D2a}$$

$$\frac{\partial\eta'_{2i}}{\partial\eta_{10}} = -\frac{\sqrt{3}\rho_s}{4N}\left[\sum_{m=1}^{N-1}(-I)\tilde{H}^{01}_{ss}(m\,\delta k)\sin\left(\frac{im\pi}{N}\right)\right],$$
$$(j = 0;\, i = 0, \ldots, N-1), \tag{D2b}$$

where $(-I)\tilde{H}^{01}_{ss}(m\,\delta k)$ is real and we have used $\partial\eta^{011(+)}_{ws}(j\,\delta k)/\partial N^{01(+)}_{ws}(j\,\delta k) = -\sqrt{3}$. As another example,

$$\frac{\partial\eta'_{3i}}{\partial\eta_{2j}} = \frac{\rho_s}{\sqrt{3}N}\left[\sum_{m=1}^{N-1}(-I)\tilde{H}^{01}_{+s}(m\,\delta k)\sin\left[(i-j)\frac{m\pi}{N}\right]\right],$$
$$(j = 1, \ldots, N-1;\, i = 0, \ldots, N-1) \tag{D3a}$$

$$\frac{\partial\eta'_{3i}}{\partial\eta_{20}} = \frac{\rho_s}{4\sqrt{3}N}\left[\sum_{m=1}^{N-1}(-I)\tilde{H}^{01}_{+s}(m\,\delta k)\sin\left(\frac{im\pi}{N}\right)\right],$$
$$(j = 0;\, i = 0, \ldots, N-1), \tag{D3b}$$

where $(-I)\tilde{H}^{01}_{+s}(m\,\delta k)$ is real and $\partial C^{01(+)}_{ws}(j\,\delta k)/\partial c^{011(+)}_{ws}(j\,\delta k) = -1/\sqrt{3}$.

We note that these expressions are compact in spite of the complexity of the basic equations and can be calculated quite efficiently using the FFT technique.

ACKNOWLEDGMENTS

We wish to express our sincere thanks to G. N. Patey for valuable comments and suggestions. Partial financial support of the Natural Sciences and Engineering Research Council of Canada is greatfully acknowledged. The present study was performed while M. Kinoshita was benefiting from the hospitality of the Department of Chemistry at UBC as a research fellow sponsored by the ministry of Education, Science and Culture of Japan.

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