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Dielectric behavior for saline solutions from renormalized diagrammatically proper interaction site model theory

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Abstract

We consider the dielectric response of angularly dependent site–site theories for models of aqueous saline solutions. We find that we can use relatively low order approximations of the angularly dependent correlation functions with correct long ranged behavior to obtain good estimates of the dielectric constant for three site water models and simple 1–1 salts. We find that the solution thermodynamics results for this level of theory, as measured by the Kirkwood G integrals and the excess chemical potentials, are in good quantitative agreement with simulation even when the details of the short ranged structure is not as accurately determined. We find that the dielectric constant predictions of both the pure fluid and the salt-water mixtures are similarly predictive, in comparison to both simulation and experiment.

Keywords

integral equations; liquid state; polar fluids

1. Introduction

The theoretical works of Stell on the dielectric response of polar liquids forms the basis for many approaches to analyze the thermodynamics of saline solutions [1, 2]. In this work we explore the dielectric response of angularly dependent site–site theories for models of aqueous saline solutions. We find that we can use relatively low order approximations of the angularly dependent correlation functions with correct long ranged behavior to obtain good estimates of the dielectric constant for three site water models and simple 1–1 salts. In works with Stell it has previously been noted that short ranged correlations are only weakly coupled to the long ranged behavior of a fluid [3]. Here, we explore the inverse as a predictive theory, that is whether a low order angular dependence in an interaction site model (ISM) theory is capable of yielding reasonable dielectric behavior.

The dielectric constant dominates at long range the effect a liquid has on the interaction between two immersed charges [4]. Predicting the dielectric constant of a particular liquid from first principles has been central to the theory of liquids [5], and remains a fundamental hurdle for any predictive theory of liquid state structure. A liquid state theory that otherwise successfully predicts the structure and thermodynamics of a solution should, in principle, also lead to a nontrivial prediction of the dielectric constant. Typically, this has been one of

the most demanding of the fundamental measures of quality a liquid state theory should meet.

The problem is an essential theme of the development of the modern understanding of the liquid state, especially at the intersection between the two categories of models of the interaction potential between molecules in a liquid, the multipole models [6, 7] and the interaction site models [8, 9]. The equivalence between the two different model routes to the dielectric constant and related functions can be formalized [1, 2, 10] and applied to improve [3] the predictive capabilities of both the standard [11] reference interaction site model theory (RISM) [12–14] and multipole theories [15, 16].

The dielectric behavior of polar fluids underlies the development of an explicit formal connection between the ISM and multipole models via the diagrammatically proper interaction site model theory. Formally, if we examine in detail the form of an ISM liquid theory [17, 18], we find a diagrammatic series constructed via the reference Ornstein–Zernike equations [9] has topologically distinct classes [19] that can be separated algebraically [20]. This has important formal consequences for both the predicted structure [21] and the predicted dielectric constant [22]. The practical realization of the diagrammatically proper ISM theory for either the structure or the dielectric properties of polar liquids as complicated as water has remained elusive [23–25].

In prior work, we used diagrammatic analysis [18, 21, 26] as a guide to diatomic model liquids [27], finding both that the diagrammatically proper equations can be extended beyond the first closures [20] to the complete ISM hypernetted-chain (HNC) approximation equivalent to the multipole case [28], and that the results for diatomic, polar liquids [29], the related electrolytes [30], and the isomorphic problem of *n*-butane in a simple fluid [31], could all be reliably obtained by the resulting theory, including the structure, solution thermodynamics, and the dielectric constant.

This prior work was limited to linear molecules and single-site ions. In this work, we extend the diagrammatically proper ISM theory to account for mixtures of molecules, nonlinear in general and with an arbitrary number of sites. We apply the resulting theory to the three standard 3-site models of water, SPC, SPC/E, and TIP3P, and to aqueous solutions of NaCl with each of the three water models. We find that the solution thermodynamics results for this level of theory, as measured by the Kirkwood *G* integrals [32] and the excess chemical potentials [33], are in good quantitative agreement. Further, we find that the dielectric constant predictions of both the pure fluid and the salt-water mixtures are of similar quality, in comparison to both simulation and experiment.

2. Theory

We consider a liquid mixture of *n* molecular species with total number density $\rho_T = \sum_i^n \rho_i$ and the potential between any given pair of molecules, labeled by species as *i, j*, of the general site–site form [11],

$$U(\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \sum_{\gamma}^m \sum_{\nu}^l u(\mathbf{r}_{\gamma\nu}), \quad (1)$$

with $\mathbf{R}_{ij}$ the displacement vector between arbitrary molecular centers of molecules i, j , Ω_i the orientation of molecule i with respect to an external lab frame of reference, γ labels the m sites of molecule i , ν labels the l sites of molecule j , and $\mathbf{r}_{\gamma\nu}$ is the displacement vector between site γ on molecule i and site ν on molecule j .

In this notation, i, j may be the same species, but always refer to different individual molecules. One may substitute 1, 2 for i, j where the topological and functional distinction between different molecules is necessary [18].

In general [7, 17, 34, 35], the molecular pair distribution function, $g(\mathbf{R}_{ij}, \Omega_i, \Omega_j)$, between molecules i, j is given by the equation

$$g(\mathbf{R}_{ij}, \Omega_i, \Omega_j) = \exp(-\beta U_{ij} + t_{ij} + b_{ij}), \quad (2)$$

where we suppress the $(\mathbf{R}_{ij}, \Omega_i, \Omega_j)$ dependence on the right side of the equation for notational convenience, and $\beta^{-1} = k_B T$ with k_B Boltzmann's constant, T the temperature in Kelvin. Equation (2) is usually understood as the closure equation, though in the general case equation (2) is a single, nonlinear equation in which t_{ij} , the indirect correlation function, and b_{ij} , the bridge function, are, by construction, functional integral equations [17] of g_{ij} . For this work, we use the hypernetted-chain approximation [17, 35] to equation (2), i.e. set $b_{ij} = 0$.

If we follow the diagrammatic analysis of Ladanyi, Chandler, and Richardson [18, 19, 21], then we find [27] that, if we choose the molecular displacement vector, $\mathbf{R}_{ij} = \mathbf{r}_{ij}$, so that it coincides with one of the site-site displacement vectors, then the potential naturally decomposes into the *none, left, right, both* terms of the diagrammatically proper theory [19]. In that case, the full molecular potential is of the general form

$$U_{ij} = u_{ij}^o + u_{ij}^l + u_{ij}^r + u_{ij}^b, \quad (3)$$

where, if i labels an arbitrary site on molecule 1, j an arbitrary site on molecule 2,

$$u_{ij}^o = u_{ij}(r)$$

$$u_{ij}^l = \sum_{\gamma \neq i} u(|\mathbf{r}_{ij} - \mathbf{d}_{\gamma}|)$$

$$u_{ij}^r = \sum_{\nu \neq j} u(|\mathbf{r}_{ij} + \mathbf{d}_\nu|)$$

$$u_{ij}^b = \sum_{\gamma \neq i} \sum_{\nu \neq j} u(|\mathbf{r}_{ij} - \mathbf{d}_\gamma + \mathbf{d}_\nu|), \quad (4)$$

and we have assumed that the potential between sites displaced by $\mathbf{r}_{ij}$ is radially symmetric, $\mathbf{d}_\gamma$ is the displacement of site γ from the molecular center now made with reference to $\mathbf{r}_{ij}$, and the o, l, r, b are the conventional labels for the *none, left, right, both* decomposition referring to the absence or presence of intervening intramolecular bonds or correlations.

As with the potential, the indirect pair distribution function, t_{ij} , may be decomposed into its o, l, r, b set. If we make use of the techniques of diagrammatic or functional re-summation [17, 36], so that $t_{ij} - \phi_{ij} + \phi_{ij} = \tau_{ij} + \phi_{ij}$, the argument of the closure is given by

$$U_{ij} - t_{ij} = u_{ij}^o + u_{ij}^l + u_{ij}^r + u_{ij}^b - \tau_{ij} + \phi_{ij} = \bar{u}_{ij}^o + \bar{u}_{ij}^l + \bar{u}_{ij}^r + \bar{u}_{ij}^b - \tau_{ij}^o - \tau_{ij}^l - \tau_{ij}^r - \tau_{ij}^b \quad (5)$$

where

$$\bar{u}_{ij}^o = u_{ij}^o - \phi_{ij}^o \quad (6)$$

etc. for l, r, b

and the $\phi_{ij} = \phi_{ij}^o + \phi_{ij}^l + \phi_{ij}^r + \phi_{ij}^b$ renormalization functions are to be determined via the diagrammatically proper molecular Ornstein–Zernike equation.

In the standard molecular fluids approach [6], for molecular pair potentials based on the multipole expansion [7] it is convenient to expand the molecular pair functions of rigid molecules in terms of rotational invariants, so that the pair distribution function is determined from

$$g(\mathbf{R}, \Omega_1, \Omega_2) = \sum_{mnl\mu\nu} g_{\mu\nu}^{mnl}(r) \Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \hat{\mathbf{R}}), \quad (7)$$

where $\hat{\mathbf{R}}$ denotes the angles of the vector $\mathbf{R}$, and we follow Fries and Patey [28] for the rotational invariants, $\Phi_{\mu\nu}^{mnl}$, in the convention of Messiah [37]. The coefficients of the expansion, $g_{\mu\nu}^{mnl}$, are defined in the usual way for polynomial expansions [38],

$$g_{\mu\nu}^{mnl}(r) = n_{\mu\nu}^{mnl} \iint d\hat{\mathbf{R}} d\mathbf{\Omega}_1 d\mathbf{\Omega}_2 g(\mathbf{R}, \mathbf{\Omega}_1 \mathbf{\Omega}_2) \Phi_{\mu\nu}^{mnl}(\mathbf{\Omega}_1, \mathbf{\Omega}_2, \hat{\mathbf{R}}), \quad (8)$$

where the coefficients $n_{\mu\nu}^{mnl}$ are generalized normalization constants chosen for convenience [6, 7, 28].

Here we truncate the expansion of the re-summed indirect correlation function at first order, $\tau \sim \tau_{00}^{000}(r)$, and the closure equations take [27] the relatively simple form

$$c_{ij}^o(r) = g_{ij}^o(r) - t_{ij}^o(r) - 1$$

$$c_{ij}^l(r) = g_{ij}^o(r) (g_{ij}^l(r) [\exp(t_{ij}^l(r))] - 1) - t_{ij}^l(r)$$

$$c_{ij}^r(r) = g_{ij}^o(r) (g_{ij}^r(r) [\exp(t_{ij}^r(r))] - 1) - t_{ij}^r(r)$$

$$c_{ij}^b(r) = g_{ij}^o(r) \{ g_{ij}^b(r) [\exp(t_{ij}^b(r) + t_{ij}^l(r) + t_{ij}^r(r))] - g_{ij}^l(r) [\exp(t_{ij}^l(r))] g_{ij}^r(r) [\exp(t_{ij}^r(r))] + 1 \} - t_{ij}^b(r),$$

(9)

where the spherical coefficients are defined as

$$g_{ij}^l(r) = \omega^{-1} \int d\mathbf{\Omega}_1 \exp(-\beta \bar{u}_{ij}^l(r, \mathbf{\Omega}_1))$$

$$g_{ij}^r(r) = \omega^{-1} \int d\mathbf{\Omega}_2 \exp(-\beta \bar{u}_{ij}^r(r, \mathbf{\Omega}_2))$$

$$g_{ij}^b(r) = \omega^{-2} \iint d\mathbf{\Omega}_1 d\mathbf{\Omega}_2 \times \exp(-\beta \bar{u}_{ij}^b(r, \mathbf{\Omega}_1, \mathbf{\Omega}_2) - \beta \bar{u}_{ij}^l(r, \mathbf{\Omega}_1) - \beta \bar{u}_{ij}^r(r, \mathbf{\Omega}_2)), \quad (10)$$

and $\omega = \int d\mathbf{\Omega}$ is the normalization constant for the spherical average.

In practical use, the relative coordinates [7] for the *both* integrals may be easily reduced so that $\omega^2 = \int d\mathbf{\Omega}_{12}$, and we may take advantage of the symmetry of the *both* integrals,

$g_{ij}^b(r) = g_{ji}^b(r)$, to reduce the dimensionality of the overall problem. The coefficients g^b , g^l , g^r , and the related Φ integrals defined below, are trivially parallel as a function of r , since for

each value of r the functions are independent of one another, which allows application of multi-core computers.

In order to generate the vector coordinates needed in each of the angular integrations, i.e. for the potential functions with vector dependencies of the form $u(\mathbf{r} - \mathbf{d})$, we use the rotational matrices for passive rotations, $\mathbf{A}$, in the convention of Arfken [38], so that $\mathbf{d} = \mathbf{A}\mathbf{d}_0$, where the site vectors $\mathbf{d}_0$ are the initial coordinate vectors for the collective site set of each molecule in an arbitrary reference frame.

In equation (9), the pair correlation function, $h_{ij} = g_{ij} - 1$, is returned by the standard contraction,

$$c_{ij} = c_{ij}^o + c_{ij}^l + c_{ij}^r + c_{ij}^b,$$

$$\tau_{lj} = \tau_{ij}^o + \tau_{ij}^l + \tau_{ij}^r + \tau_{ij}^b, \quad (11)$$

and

$$h_{ij} = c_{ij} + \tau_{lj}.$$

These contractions of equation (9) to recover h_{ij} and g_{ij} are embedded in our matrix algebra below. As a final note on utility, the higher order projections, $g_{\mu\nu}^{mnl}$, are always available via equations (8) and (10), and are readily collected on each iteration. Thus, our first, low order approximation retains some of the information available from the complete molecular theory in practice.

In the matrix algebra of Rossky and Chiles [20], we construct the principle connectivity super-matrices, $\mathbf{P}$, as

$$\mathbf{P} = \begin{pmatrix} \boldsymbol{\rho} & \boldsymbol{\rho} \\ \boldsymbol{\rho} & \mathbf{0} \end{pmatrix}, \quad (12)$$

where the $\boldsymbol{\rho}$ sub-matrices are the standard diagonal site and species density matrices of an $N \times N$ site-site molecular mixture as used in RISM,

$$\boldsymbol{\rho} = \begin{pmatrix} \rho_1 & \cdots & 0 \\ 0 & \cdots & \rho_N \end{pmatrix}, \quad (13)$$

where N is the total number of sites in a mixture, $N = \sum_i^n m_i$, for m_i the total number of sites in a molecule of species i .

Note, for $\mathbf{P}$ and $\mathbf{p}$ alone, each site carries the full molecular density. The site–site origin degeneracy [27] is accounted for in our second connectivity matrix, $\mathbf{P}^{(b)}$,

$$\mathbf{P}^{(b)} = \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{p}^{(m)} \end{pmatrix}, \quad (14)$$

where $\mathbf{p}^{(m)}$ is the origin degeneracy-weighted site density matrix, diagonal as with $\mathbf{p}$ but with each element weighted by the total number of sites in the molecule the site is contained within, ρ_i/m_i .

To aid the reader, we give in full the connectivity matrices for a 3-site water molecule, and for a sodium chloride electrolyte mixture of a 3-site water molecule with single site ions. For the pure water case with a total molecular density of ρ ,

$$\mathbf{P}_w = \begin{pmatrix} \rho_w & \rho_w \\ \rho_w & 0 \end{pmatrix}$$

$$\mathbf{p}_w = \begin{pmatrix} \rho & 0 & 0 \\ 0 & \rho & 0 \\ 0 & 0 & \rho \end{pmatrix} \quad (15)$$

and

$$\mathbf{P}_w^{(b)} = \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{p}_w^{(m)} \end{pmatrix}$$

$$\mathbf{p}_w^{(m)} = \begin{pmatrix} \rho/3 & 0 & 0 \\ 0 & \rho/3 & 0 \\ 0 & 0 & \rho/3 \end{pmatrix}. \quad (16)$$

For the sodium chloride mixture, the matrices are

$$\mathbf{P}_{sw} = \begin{pmatrix} \rho_{sw} & \rho_{sw} \\ \rho_{sw} & 0 \end{pmatrix}$$

$$\rho_{sw} = \begin{pmatrix} \rho & 0 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 & 0 \\ 0 & 0 & \rho & 0 & 0 \\ 0 & 0 & 0 & \rho_+ & 0 \\ 0 & 0 & 0 & 0 & \rho_- \end{pmatrix} \quad (17)$$

and

$$P_{sw}^{(b)} = \begin{pmatrix} 0 & 0 \\ 0 & \rho_{sw}^{(m)} \end{pmatrix}$$

$$\rho_{sw}^{(m)} = \begin{pmatrix} \rho/3 & 0 & 0 & 0 & 0 \\ 0 & \rho/3 & 0 & 0 & 0 \\ 0 & 0 & \rho/3 & 0 & 0 \\ 0 & 0 & 0 & \rho_+ & 0 \\ 0 & 0 & 0 & 0 & \rho_- \end{pmatrix}, \quad (18)$$

where we assume single-site models for the ρ_+ , ρ_- ions. Note, the closure in equation (9) is constructed so that the collection of terms ρ , l , r , b is transparent to the number of sites within a molecule. They are thus valid for single site molecules as well as m site molecules.

We next introduce two numerical methods or renormalizations for aiding convergence. First, for the Coulomb potential we require a practical means of treating the r^{-1} dependence. We have found the usual means of doing so [36] to be appropriate, if the topology of the molecular sites are taken into account. To illustrate, consider the general case for two molecules of arbitrary total charge on site-site Coulomb potentials,

$$u^C(\mathbf{R}, \Omega_1, \Omega_2) = \sum_{\gamma} \sum_{\nu} \frac{q_{\gamma} q_{\nu}}{|\mathbf{R} - \mathbf{d}_{\gamma} + \mathbf{d}_{\nu}|}, \quad (19)$$

where q_i is the charge of site i , and we have chosen $\mathbf{R}$ between two arbitrary points of molecules 1, 2. As we have pointed out previously [29], the Coulomb potential between molecules is inherently a *both* function. As a consequence, it is topologically consistent to treat the total charge potential function as a whole rather than separate into *none*, *left*, *right*, *both* form, due to the sum rules of electrostatics [4]. We may do so in special cases [30], but in general, so as to incorporate molecular ions, we retain u^C in the *both* functions, and renormalize the r -space functions by

$$\overline{u}^C = u^C \times (1 - y), \quad (20)$$

where

$$y(r) = \frac{1}{2}(1 + \text{erf}(\alpha(r - l))) \quad (21)$$

is the shifted error function or cumulative normal distribution function [39].

We use the slightly more general form of the error function here in order to help account for the intramolecular distributions which are ignored in the spherical basis averages as used, which assume rigid molecules. If we are to use the angular averages in this form without directly integrating over the distances of the $\mathbf{d}$ vectors, we must use functional approximations to account for the intramolecular bonds. If we assume that the l shift in the error function is sufficient for harmonic bond constraints, we have only to include similar forms for the Lennard-Jones potentials, $u^{\text{LJ}}(r)$. This scheme assumes Gaussian rotational-vibrational coupling of the intramolecular bonds. The error function approximation of the bond flex contributions to the Lennard-Jones potential follows as

$$u^{\text{LJs}}(r) = 4\varepsilon \times [R^{-12}(1 - \text{erf}((\lambda R)^{12})) - R^{-6}(1 - \text{erf}((\lambda R)^6))], \quad (22)$$

where here $R = r/\sigma$ for σ the usual distance scale of the 12–6 potential.

With the functions defined above, and the definitions of the connectivity matrices, the corresponding super-matrices for the Fourier transforms, $\hat{c}_{ij} = \int d\mathbf{r} r^2 c_{ij}(r) \sin(kr)/kr$, are

$$\mathbf{c} = \begin{pmatrix} \mathbf{c}^o & \mathbf{c}^r \\ \mathbf{c}^l & \mathbf{c}^b \end{pmatrix}, \quad (23)$$

which are composed from the $N \times N$ sub-matrices $\mathbf{c}^o$ with elements $\hat{c}_{ij}^o$, and similarly for the $\mathbf{c}^l$, $\mathbf{c}^r$, $\mathbf{c}^b$ sub-matrices. When combined with the corresponding super-matrix of intramolecular distribution functions with elements $S_{ij}^b = S_{ij}(k)$, $S_{ij}^o = S_{ij}^l = S_{ij}^r = 0$, the correct k -space distribution matrix between sites i and j on the same molecule, so that

$$\mathbf{S} = \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{S}^b \end{pmatrix}, \quad (24)$$

then the diagrammatically proper form of the molecular Ornstein–Zernike equation consistent with the closure in equation (9) is the coupled set

$$\chi = \mathbf{c} - \Phi + (\mathbf{c} - \Phi) \mathbf{P}^{(b)} \chi \quad (25)$$

$$\mathbf{H} = \chi + \mathbf{S} - \psi + (\chi + \mathbf{S} - \psi) \mathbf{P} \mathbf{H},$$

where the site–site intramolecular distributions are Gaussian forms,

$$S_{ij}(k) = \exp(-b_{ij}k^2) \frac{\sin(kl_{ij})}{kl_{ij}\rho_j} \quad (26)$$

for l_{ij} the bond distance between sites with bond constants b_{ij} , ρ_j the density of site j (we here assume that the density of site j is equivalent to the density of molecules containing site j and $\rho_i = \rho_j$ if i and j are on the same molecule, i.e. nonreactive fluids with no distinct handedness for the S -bonds) and Ψ the Fourier transforms of the Coulomb potential in a pre-conditioned form generated from a chain-sum [40] which takes advantage of the normalization of the S -bond.

Specifically, we may make chains of the S -bond, if we properly take into account the normalization of the final chain sum. The means of doing so for the site–site Coulomb interactions is provided by [34] the OZ equation in standard mixture form, so that we define the inverse s -bond by (note the sign and order of matrix multiplication)

$$s = S[I + \rho S]^{-1}, \quad (27)$$

which then allows us to generate the diagrammatically proper molecular chain sum of Coulomb bonds

$$\psi^{(b)} = [I - (\mathbf{Q} + s)\rho]^{-1} \mathbf{Q} - s. \quad (28)$$

All matrices in equations (27) and (28) are site–site submatrices, not the super-matrices, and the elements of $\mathbf{Q} = \Sigma \mathbf{q} \Sigma^t$ are given by

$$\Sigma = I + S\rho$$

$$\Sigma^t = I + \rho S$$

and

$$q_{ij} = \frac{4\pi q_i q_j}{k^2} \exp(-k^2/(2\alpha)^2). \quad (29)$$

Taking $\Psi^o = \Psi^I = \Psi_r \equiv 0$, we then insert the pre-conditioned Coulomb functions into equation (25) via

$$\psi = \begin{pmatrix} 0 & 0 \\ 0 & \psi^{(b)} \end{pmatrix}, \quad (30)$$

and the system of equations for the spherical approximation is complete, up to the definition of the Φ and ϕ_{ij} functions.

With the definitions of equation (10) and the closure projections of equation (9), we find [27] the self-consistent diagram series functions to be

$$\phi_{ij}^o = 0$$

$$\phi_{ij}^l = \sum_{\gamma \neq i} t_{\gamma j}^o (\mathbf{r}_{ij} - \mathbf{d}_\gamma)$$

$$\phi_{ij}^r = \sum_{\mu \neq j} t_{i\mu}^o (\mathbf{r}_{ij} + \mathbf{d}_\mu)$$

$$\phi_{ij}^b = \sum_{\gamma \neq i} \sum_{\mu \neq j} t_{\gamma\mu}^o (\mathbf{r}_{ij} - \mathbf{d}_\gamma + \mathbf{d}_\mu) + \sum_{\gamma \neq i} t_{\gamma j}^r (\mathbf{r}_{ij} - \mathbf{d}_\gamma) + \sum_{\mu \neq j} t_{i\mu}^l (\mathbf{r}_{ij} + \mathbf{d}_\mu), \quad (31)$$

and their spherical, exponentiated forms, Φ , in r -space,

$$\Phi_{ij}^o(r) = 0$$

$$\Phi_{ij}^l(r) = \omega^{-1} \int d\Omega_1 [\exp(-\beta \bar{u}_{ij}^l) - 1]$$

$$\Phi_{ij}^r(r) = \omega^{-1} \int d\Omega_2 [\exp(-\beta \bar{u}_{ij}^r) - 1]$$

$$\begin{aligned} \Phi_{ij}^b(r) = & \omega^{-2} \int d\Omega_1 d\Omega_2 \\ & \times [\exp(-\beta \bar{u}_{ij}^b - \beta \bar{u}_{ij}^l - \beta \bar{u}_{ij}^r) - \exp(-\beta \bar{u}_{ij}^l - \beta \bar{u}_{ij}^r) \\ & - (\exp(-\beta \bar{u}_{ij}^b) - 1)(\exp(-\beta \bar{u}_{ij}^l) - 1)(\exp(-\beta \bar{u}_{ij}^r) - 1)], \end{aligned} \quad (32)$$

which are then Fourier transformed to be used in equation (25).

Equations (9) and (25), together with the definitions of ϕ, Φ, ρ, ψ , and P , form the set of diagrammatically proper interaction site equations in the HNC approximation that are, through the χ chain sums and molecular convolution, diagrammatically equivalent [18, 21, 27] to the molecular HNC constructed via the Blum and Torruella expansions [6, 28]. In the form presented here, we have made no approximations based on the number of sites, and all equations are, within the spherical approximation, appropriate for molecules with any number of sites. Further, taking into account the normalization conventions and intramolecular degrees of freedom [31, 41], the equations are readily generalized for flexible and reactive fluids.

We solve in the spherically averaged approximation, equations (25), as

$$\chi = [I - (c - \Phi)P^{(b)}]^{-1}c \quad (33)$$

$$\tau = [I - (\chi + S - \psi)P]^{-1}(\chi + S) - S - c,$$

the diagrammatically and charge re-summed form [27, 29] generalized to mixtures with arbitrary sites, iteratively with the closures of equation (9) while the integrals of equations (32) and (10) for the Φ and g^l, g^r, g^b terms, respectively, are held fixed, until the τ functions converge. We use the re-summed potentials of equations (20) and (22) for the charge and Lennard-Jones potentials, respectively, in r -space, and the corresponding intramolecular S -bond, equation (26), and preconditioned chain sum of molecular Coulomb bonds of equation (30) in k -space.

We then integrate to obtain the next Φ and g^l, g^r, g^b functions, and feed them back into the OZ and closure equations for the next refinement cycle. This iterative solution cycle is, functionally and diagrammatically, equivalent [23–25, 27, 29–31] to the h -bonded bridge function methods [17, 42–46], where here the bridge functions being generated are the site–site bridge functions of order ρ^0 which would be part of the closure in the molecular OZ methods, and the site–site bridge functions of order ρ^1 that are part of the molecular convolutions of the molecular OZ equation, but are not otherwise generated by the original diagrammatically proper OZ matrices [20].

3. Methods

For this work, we report results using a numerical grid defined on 512 points in r with a range of 60 Angstroms, 8 points in the θ , 16 points in the ϕ, γ, α Euler angles required for the rotation matrices.

For the potentials, we use the standard model parameters for the SPC, SPC/E, and TIP3P models [47–49]. Though it is not strictly necessary given the exponential form of the closure equations, in order to assure continuity with the standard RISM results for these models, we include a Lennard-Jones potential for the hydrogen sites with $\sigma_{HH} = 0.4 \text{ \AA}$ and $\epsilon_{HH} = 1 \text{ K}$ for SPC and SPC/E, 23.153 K for TIP3P. For the NaCl ion parameters, we use the

thermodynamically rationalized parameters [50] for SPC/E and TIP3P. For the ion parameters for SPC, we use the SPC/E values. We use the standard Lorentz-Berthelot mixing rules for cross-species parameters.

The values used here for the convergence parameters are $\alpha = 1.08$ throughout, α the standard error function parameter. For the bond constants, we use the same value for all intramolecular bonds, a harmonic constant of $b = 1 \times 10^{-3} \text{ \AA}^2$. For the Lennard-Jones intramolecular distribution parameter, we use the same value for all sites, $\lambda = 1.13$. The I parameter for the displaced error function in the charge-charge potentials varies slightly for each water model, due to the geometry difference between the SPC family and TIP3P. For both SPC and SPC/E, we use $I = 0.54$, for TIP3P we use $I = 0.6$. These values were found to be the best combination for consistent numerical behavior for both the pure water and salt-water mixtures, taking into account structure, dielectric, and thermodynamic behavior across the phase points investigated. We detail this process further in the Discussion section below.

The simulation results for SPC and SPC/E are taken from NVT ensemble simulations at 298.15 K with 512 molecules using the Nosé thermostat and Ewald summation [51]. The TIP3P simulation results were taken from a recent study of decalanine solvation [52].

4. Results

4.1. Water

We report results for the 3-site water models at $T = 298.15 \text{ K}$ and $\rho = 0.03346 \text{ molecules \AA}^{-3}$. The SPC results for the site-site radial distribution functions are given in figure 1.

Overall, we find that the structural predictions are qualitative but not quantitative. The typical hydrogen-bonding structure of liquid water appears to be overly damped in the hydrogen-hydrogen and hydrogen-oxygen functions, with the spherical packing components of the oxygen-oxygen $g_{OO}(r)$ at $\sim 6 \text{ \AA}$ over-emphasized, similar to the results of extended RISM.

The slight phase mismatch of the SPC $g_{OO}(r)$ function in comparison to simulation is model dependent. To demonstrate, in figure 2 we plot the $g_{OO}(r)$ for the TIP3P model in comparison to simulation. The agreement with simulation is clearly sensitive to model details.

We may collect the $h^{110}(r)$ projections using the n^{nnl} normalization convention of the molecular HNC theory [28], so that the dielectric constant for a dipolar fluid is given in the usual Kirkwood [5] route as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = y \left(1 + \frac{\rho}{3} \int d\mathbf{r} h^{110}(r) \right) = y g_K, \quad (34)$$

defining the Kirkwood g -factor, g_K , and $y = 4\pi\beta\mu^2\rho/9$ is the dipole density. We write the integral without respect to the site labels, h_{ij}^{110} , since for pure fluids the results as measured

from different origins within the molecules 1, 2 should be equivalent. This serves as a check on numerical consistency and convergence for the theory and implementation.

The results for $h_{\text{OO}}^{110}(r)$, the dipole–dipole correlation function as measured relative to the displacement vector pointing between the oxygen sites on each molecule, for the TIP3P model are given in figure 3.

The $h_{\text{OH}}^{110}(r)$ dipole–dipole functions, the dipole correlations as measured relative to the displacement between the oxygen site on molecule 1 and either hydrogen site on molecule 2, are of similar quality. We plot the results for the TIP3P model in figure 4.

For completeness, we also give, in figure 5, the $h_{\text{HH}}^{110}(r)$ dipole–dipole functions. The difference between these results and those for the h_{OH}^{110} and h_{OO}^{110} functions indicate the nonlinearity of the molecules, and where the spherical basis approximation breaks down.

The dielectric constant predicted by the theory for the three different water models is given in table 1 in comparison to the literature results for each model.

For the thermodynamic results for the three water models, in anticipation of solution thermodynamics work, we report results for the Kirkwood G integrals and the excess chemical potentials. The Kirkwood G integrals [32] for each site–site distribution are given by

$$G_{ij} = \int d\mathbf{r} h_{ij}(r). \quad (35)$$

The G_{ij} integrals for each site–site pair of the same molecular species should be the same, and serve as an indication of the convergence and numerical consistency of the theory and calculation. The results for the 3-site models are given in table 2, in comparison to the simulation results for the same models [53].

For the excess chemical potential, since by construction the h , c , τ functions are molecularly complete, we use the integral form for the HNC approximation [33, 54] of each site of a mixture,

$$\beta\mu_i^{\text{ex}} = \sum_j^N \int d\mathbf{r} \left(\frac{1}{2} h_{ij}^2(r) - \frac{1}{2} h_{ij}(r) c_{ij}(r) - c_{ij}(r) \right) \rho_j, \quad (36)$$

where the sum over j is for all sites in the liquid. The total excess chemical potential for a given molecule [11, 33] is the sum over sites m for an individual molecule, $\beta\mu^{\text{ex}} = \sum_{\gamma}^m \beta\mu_{\gamma}^{\text{ex}}$. We give the results for each model, in comparison to the simulation results [55, 56], in table 3. Note, the results of [55] table III are in kJ mol^{-1} , not kcal mol^{-1} . Our sign convention here is chosen in the usual way [33] for the the charging integral in equation (36), as opposed to the convention in the simulations [55, 56].

4.2. Salt water

The phase points for the NaCl solutions were taken from the IUPAC-NIST solubility tables [57], and are given explicitly in table 4.

For the solvation free energy, following the literature [58, 59], we use the pure NaCl crystal as the thermodynamic reference state for the free energy, and report the results for the different water/salt models [50] at infinite dilution in table 5 in comparison to the experimental results [58, 60, 61]. We use the Born–Landé crystal value as the reference value.

For the dielectric constant of conducting electrolyte solutions, the Kirkwood form used for pure, polar fluids must be changed [34] to accommodate the change of boundary conditions [62]. The exact form [63] involves the dipole projections of the direct correlation functions, $c(r, \Omega_{12})$, which in our case are less well approximated than the total correlation functions. We follow Patey *et al* [64] with a modification to the reference state of the fluctuation formula [62]. The modification we make here is to take advantage of Kirkwood–Buff fluctuation theory [32], so that if we assume a fluctuation correction $\delta\rho$ of the form

$$\varepsilon = 1 + 3 \frac{4\pi\beta\mu^2}{9} \left(\rho + \delta\rho + \frac{\rho^2}{3} \int d\mathbf{r} h^{110}(r) \right), \quad (37)$$

for ρ the dipolar solvent density, then from the Kirkwood G integral definition we find the correction $\delta\rho = \rho (1 - G_w \rho)$ provides the limit required, where G_w is the water–water G integral. Use of equation (37) with the theory here matches the pure fluid result in the infinite dilution limit.

The dielectric constant of a saline mixture as a function of the salt concentration [65] is known to be lower than that of the pure solvent. This is known as the dielectric decrement. The dielectric decrement results for the theory of this work are reported in figure 6 in comparison to the experiments [66] and simulations for the SPC/E model [67].

For clarity, in figure 7 we plot separately the dielectric decrement results of the theory for the SPC and TIP3P models in comparison to the experimental results.

5. Discussion

We explored convergence on the numerical grids. The results we report are on a grid that is reasonably well converged for the properties reported. The operation count for the grid used is $O(r \times \theta^2 \times \phi^3) = 512 \times 8^2 \times 16^3 = 2^9 \times 2^6 \times 2^{12} = 2^{27}$ for the complete angular integrations of a single function. More detailed grids, up to $2048 \times 16^2 \times 32^3$ total points, were calculated so as to assure numerical convergence. The numerical results were essentially the same as those reported above, and thus served as a self-consistency check. On 4 cores of our current desktop machines, with the site–site symmetry of the angular integrals accounted for, each iteration takes approximately 7 min of wall clock time on the $512 \times 8^2 \times 16^3$ grid.

The convergence methods and renormalizations introduced above greatly enhance the grid refinement without changing the fundamental results of the systems examined, by allowing for quicker convergence and more stable numerical results. For the pure water case, this may be checked directly, by simply using the standard Lennard-Jones form for the potential and rigid bonds in the S matrix. The numerical results for the thermodynamic measures are essentially the same, what changes is the convergence behavior. Without the intramolecular functional approach, the equations are numerically more stiff, and require significantly more computational work to generate stable solutions at ~ 300 K. Similarly, the electrolyte solutions may be checked in the same way, though the convergence behavior is worse, and typically requires using the Debye–Hückel form of the ionic potential, or similar convergence methods, as a starting point. We also find that it is often necessary to gradually scale the ϕ functions in the closure on first finding an initial solution. A related finding is that the 1 M salt solution can be used to generate all of the other concentration points, down to infinite dilution, 0 M salt, and up to the high concentration salt points investigated.

We fixed the b and α parameters according to standard usage or physical plausibility, and then chose λ and l , the intramolecular Lennard-Jones and charge coupling parameters in the scheme proposed, according to the overall thermodynamic results. The rule of thumb followed for the Coulomb term, according to the form of the functions, is that l should be as large as possible without destabilizing the numerical solutions, since $l \rightarrow \infty$ corresponds to the bare Coulomb potential.

Similarly, $\lambda \rightarrow 0$ corresponds to the bare Lennard-Jones potential, with no coupling to the intramolecular distribution. The rule of thumb used here, since we can use the $\lambda = 0$ value for the pure water case as a test, is to let λ be the largest value that does not change the thermodynamic results for the pure fluid. Further, the values of both terms chosen should be the same across all phase points investigated. The l values used are approximately $d_{\max}/3$, where $d_{\max}$ is the largest bond length in a given water molecule, corresponding well with the previous diatomic model results. The results for different λ values are much less sensitive to the value chosen than for the Coulomb renormalization. The $\lambda = 1.13$ value for all of the models was found to give the best convergence enhancement across the phase diagrams investigated.

The overdamping of the structure of the fluid in going from $g(r, \Omega_{12})$ to the site–site distributions suggests that there may be some utility in exploring alternate integration methods, including nonlinear sampling methods.

Overall, the h^{110} and $g(r, \Omega_{\max})$ functions demonstrate that the combination of the HNC approximation and the spherical basis set approximation lead to overcorrelated structure in $g(r, \Omega_{12})$ at short range, at the expense of the mid range order exhibited in the simulation results. If we understand the thermodynamic integrals as general sum rules, then we find that the integrals can be consistent with the measured thermodynamic results while subtle changes in the local structure of the integrands may still vary. Given the complexity associated with introducing bridge functions into a molecular theory, the most likely path forward for investigating the effect of the closure and the basis set approximation is to incorporate higher order basis set approximations systematically.

The same tendency in the structure may be the origin of the different model results for the Kirkwood G integrals versus the dielectric constant integrals. The difference between the models even for pure water do not follow the trends for simulation as we find SPC/E to be less structured in the region of the second OO solvation shell than TIP3P.

For the salt-water free energies of solution, better agreement with experiment in absolute terms may be had by using the experimental crystal energies rather than the theoretic result of the Born–Landé energy. We use here the more accessible theoretic result as a baseline for comparison, and point out that the most important result, in comparison to our previous work, is that the experimentally observed gap of $\sim 10 \text{ kcal mol}^{-1}$ between the different ions is more closely reproduced in this work.

The saline dielectric decrement results trend with the experiment and with the simulation results at all but the highest concentration in the case of the SPC/E results. The SPC and SPC/E models demonstrate an early saturation of the dielectric constant, exaggerated in the case of the theory used here but roughly confirmed by the simulation results. We do not generally expect an HNC approximation to directly predict the most concentrated solutions near saturation. In light of the simulation results we suggest that, even though the SPC and SPC/E models saturate the dielectric constant at a lower salt concentration than experiment or the TIP3P model results, further analysis of the reason why this occurs may be useful for the general process of molecular model development.

6. Conclusions

The diagrammatically proper and angularly dependent interaction site model theory was extended in this work to mixtures of nonlinear molecules with an arbitrary number of sites, and to polar and charged molecular species. We applied the theory to the SPC, SPC/E, and TIP3P models of pure water, and sodium chloride solutions of the same models of water, from infinite dilution to the experimental saturation density of NaCl. For the pure water cases, the dielectric constant, chemical potential, and Kirkwood G integrals were all in good agreement with the known simulation results for each model. For the electrolyte solutions, the free energy of solution of NaCl and the dielectric decrement as a function of salt concentration were also in qualitative agreement with both experiment and simulation for the same models.

The pair molecular distribution functions, as measured by the angular projections, were slightly overstructured at the short length scales. This was reflected in the site–site distributions, which are overdamped slightly in comparison to the simulation results. The qualitative agreement, for both the full molecular distribution function and the radial distribution functions, was good overall.

The results of this work demonstrate that this site–site theory is practically, as well as formally, capable of predicting the liquid state structure, thermodynamics, and dielectric properties of polar and electrolyte mixtures for molecular models with general internal complexity, at least for small molecules with relatively fixed internal geometries, such as water and small ions. This is a step in the progression from the formal theoretic

demonstrations [19, 22] through the diatomic and linear cases [20, 24, 27] to more complex cases of general utility [23, 29, 31].

The most immediate general result is that the theory has been generalized to the point where it provides a practical computational as well as formal basis for understanding complex fluid behavior of more general practical and theoretic importance than previously considered. Future work will use the implementation extended here to take into account molecular ions, conformational distributions, and more complex mixtures.

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Figure 1.

Site-site radial distribution functions, $g_{ij}(r)$, for the SPC model of water as predicted by the proper ISM theory used in this work, in comparison to the results from simulation and those of the RISM theory. In these plots, the solid black line is the simulation result, the dashed line is the result from the theory of this work, and the dotted line is the RISM result.

Figure 2.

Results for the TIP3P oxygen radial distribution function, $g_{OO}(r)$, in comparison to simulation. The dashed line is for the result of the theory of this work, the solid black line is from simulation.

Figure 3.

Results for the dipole–dipole correlation functions, $h_{oo}^{110}(r)$, as measured relative to the oxygen–oxygen displacement vector for the TIP3P model, in comparison to simulation. The dashed line is for the theory of this work, the solid line for the result from simulation.

Figure 4.

Results for the dipole–dipole correlation functions, $h_{OH}^{110}(r)$, as measured relative to a oxygen–hydrogen displacement vector for the TIP3P model, in comparison to simulation. The dashed line is for the theory of this work, the solid line for the result from simulation.

Figure 5.

Results for the dipole–dipole correlation functions, $h_{\text{HH}}^{110}(r)$, as measured relative to a hydrogen–hydrogen displacement vector for the TIP3P model, in comparison to simulation. The dashed line is for the theory of this work, the solid line for the result from simulation.

Figure 6.

Results for the dielectric decrement of NaCl solution at the concentration points given in table 4 for the SPC/E model in comparison to simulation [67] and experiment [66]. The circles are the experimental results, the diamonds are the simulation results [67], and the stars are the SPC/E results from this work.

Figure 7.

Results for the dielectric decrement of NaCl solution at the concentration points given in table 4 for the SPC and TIP3P models in comparison to experiment [66]. The circles are the experimental results, the squares are the SPC results for this work, and the triangles are the TIP3P results from this work.

Table 1

Results for the dielectric constant, ϵ , of the pure fluid, 3-site water models, in comparison to our simulation results and the RISM-III closure for SPC/E.

Model	Simulation	This work	RISM-III [14]
SPC	63	66	
SPC/E	74	71	70
TIP3P	83	76	

Table 2

Results for the Kirkwood G integrals of the pure fluid 3-site water models.

Model	Simulation [53]	This work
SPC	−29.92	−29.3
SPC/E	−29.60	−28.9
TIP3P	−29.18	−27.0

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Table 3

Results for the excess chemical potential, μ^{ex} , of the 3-site water models, in kcal mol⁻¹.

Model	Simulation [55]	This work
SPC	5.5	5.5
SPC/E	6.2	5.7
TIP3P	5.5	5.7

Table 4

NaCl-water density points investigated in this work.

NaCl number density (molecules Å ⁻³)	NaCl molarity	Water number density
0.00028	0.46	0.0331
0.00056	0.9	0.0328
0.00117	1.9	0.0322
0.00175	2.9	0.031 48
0.00280	4.7	0.030 14

Note: 4.7 M NaCl is the standard saturation concentration.

Table 5

NaCl solvation free energies for this work and from experiment, for the different models examined.

	Na ⁺	Cl ⁻
TIP3P	83	77
SPC/E	83	73
SPC	83	73
Experiment [58]	90	80

Note: All energy values are in kcal mol⁻¹.