The solution of the reference hypernetted-chain approximation for water-like models

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In this paper we examine the dielectric and structural properties of hard polarizable multipolar models for liquid water. The theoretical results were obtained by solving the self-consistent mean field (SCMF) approximation together with the reference hypernetted-chain (RHNC) theory. The dielectric constants are in good agreement with experiment over a large range of temperatures and pressures. The rather poor agreement between the radial distribution functions determined for our water-like fluids at 25°C and those measured for liquid water is discussed.

1. Introduction

In recent articles [1-4] it has been shown that the reference hypernetted-chain (RHNC) integral equation theory can be solved for pure fluids in which the particles interact with angle-dependent pair potentials. However, these studies considered only systems of particles with linear symmetry. In very recent work [5] we have described how the RHNC approximation may be applied in general to mixtures and have employed it in the study of electrolyte solutions [5-7]. In the present article we will report RHNC results for systems of non-linear symmetry with particular attention being paid to simple models for water.

The water-like solvents considered in this work have been used in our recent studies [5, 6] of model aqueous electrolyte solutions. These relatively simple solvent models consist of hard spheres into which the low-order electrical multipole moments and the point polarizability tensor of the water molecule have been embedded. The influence of the many-body interactions due to the molecular polarizability are taken into account at the self-consistent mean field (SCMF) level [5, 8, 9]. In previous studies [9, 10] the reference linearized HNC (RLHNC) and reference quadratic HNC (RQHNC) theories were solved in conjunction with the SCMF approximation for these water-like fluids. However, in the earlier work [9, 10] only dipole and quadrupole moments were included and the quadrupole moment was assumed to have tetrahedral symmetry [9, 11]. The results obtained for the dielectric constant were found to be in good agreement with experiment over a large range of temperatures and pressures [9, 10].

In this paper we will report SCMF/RHNC results for hard polarizable multipolar models for water. We will examine two such water-like models in detail. The first contains only dipole and quadrupole moments (Model II as defined below) while the second includes multipole moments up to octupole order (Model III as

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defined below). Both models are of general $C_2v$ symmetry since it is the true quadrupole (and octupole) tensor of the water molecule which is employed. We will also examine the tetrahedral model (Model I as defined below) used in previous studies [9, 10] which assumes that the quadrupole moment of water has tetrahedral symmetry. This system proved particularly useful in exploring the basis set dependence of the RHNC theory for fluids of non-linear particles. Moreover, we will show that this model works extremely well as an effective system for the full quadrupole model with an appropriate choice of the tetrahedral quadrupole moment, $Q_T$. This model has also been used extensively in our study of model aqueous electrolyte solutions at finite concentration [5].

The remainder of this paper is divided into three parts. We very briefly outline the SCMF/RHNC theory in § 2. In § 3 we report our results for the specific models studied with particular attention being paid to the structural and dielectric properties. Finally, our concluding remarks are summarized in § 4.

2. Theory

The method of solution of the SCMF/RHNC theory for the present models has been described in previous articles [5, 12]. Therefore, here we will simply outline some of the basic definitions and essential relationships.

2.1. Integral equations

The HNC and the closely related RHNC theories consist of the Ornstein-Zernike (OZ) equation

$$h(12) = c(12) + \frac{\rho}{8\pi^2} \int h(13)c(32)d(3)$$

(1)

coupled with the appropriate closure approximation. In equation (1), $h(12)$ and $c(12)$ are the pair and direct correlation functions, respectively, between particles 1 and 2; $\rho = N/V$ is the number density and $d(3)$ indicates integration over all the positional and orientational coordinates of particle 3. The RHNC closure approximation can be written in the form

$$c(12) = h(12) - \ln g(12) - \beta u(12) + B_k(r),$$

(2a)
in which $g(12) = h(12) + 1$ is the pair distribution function, $u(12)$ is the pair interaction potential, $\beta = 1/kT$ where $kT$ is the Boltzmann constant times the absolute temperature, and $B_k(r)$ refers to the bridge function of some spherically symmetric reference system. If we separate the pair potential into reference and perturbation parts, $u_k(r)$ and $\Delta u(12)$, respectively, we can then define the function

$$Y_k(r) = B_k(r) - \beta u_k(r) = \ln g_k(r) - \eta_k(r),$$

(2b)

where $g_k(r)$ and $\eta_k(r) = h_k(r) - c_k(r)$ also refer to the spherically symmetric reference system. Following Fries and Patey [1], equation (2a) can be rewritten in the form

$$c(12) = \int h(12) \frac{\partial W^{RHNC}(12)}{\partial r} dr - \beta \Delta u(12) + Y_k(r),$$

(2c)
where

$$W^{\text{RHNC}}(12) = -\eta(12) + \beta\Delta u(12) - Y_0(r). \quad (2d)$$

We remark that equation (2c) is equivalent to the original formulation of the RHNC equation (cf. equation (30) of [1]) employed in earlier work [1–3]. However, from a practical perspective equation (2c) represents a more convenient form since it is a more compact expression and hence is easier to solve numerically. The application of this closure approximation requires that the radial distribution function of the appropriate reference system be known ($\eta_k(r)$ can be determined from the OZ equation). In the present study the required hard-sphere radial distribution function was taken to be the Verlet–Weis [15] fit to computer simulation data.

The solution of the RHNC theory for pure fluids characterized by angle-dependent pair potentials is given in [1], while the generalization to multicomponent systems is described in [5]. This reduction of the RHNC equations is based upon the expansion of the pair potential and correlation functions in a basis set of rotational invariants [1, 16]. These expansions have the general form

$$a(12) = \sum_{\mu
u} a_{\mu\nu}^{mnl}(r)\Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \vec{r}), \quad (3a)$$

where $a(12)$ can be any correlation function or the pair potential, $\Omega_1$ and $\Omega_2$ represent Euler angles describing the orientations of particles 1 and 2, $r$ is the separation between the particles and $\vec{r}$ gives the direction of $r$. The rotational invariants are defined by

$$\Phi_{\mu\nu}^{mnl}(\Omega_1, \Omega_2, \vec{r}) = f^{mnl} \sum_{\mu'\nu'\lambda'} \left( \begin{array}{lll} m & n & l \\ \mu' & \nu' & \lambda' \end{array} \right) R_{\mu\nu}^{m}(\Omega_1)R_{\nu\lambda}^{n}(\Omega_2)R_{\lambda\nu}^{l}(\vec{r}), \quad (3b)$$

where $\left( \begin{array}{lll} m & n & l \\ \mu' & \nu' & \lambda' \end{array} \right)$ is a $3-j$ symbol, $R_{\mu\nu}^{m}(\Omega)$ is a generalized Wigner spherical harmonic and $f^{mnl}$ can be any non-zero constant. We remark that all the correlation functions presented in this article are for the choice $f^{mnl} = 1! \left( \begin{array}{llll} m & n & l \\ 0 & 0 & 0 \end{array} \right)$ in accord with previous studies [1–9].

Details of the reduction of the RHNC equations for systems of $C_{2v}$ symmetry along with the numerical methods used to find solutions to these equations can be found in [5].

2.2. Treatment of molecular polarizability: The SCMF theory

The SCMF theory was originally derived [9] for a pure fluid of particles of $C_{2v}$ or higher symmetry assuming that only dipole and quadrupole moments are included in the model. In [5] we have outlined a further generalization of this approach to multicomponent systems in which octupole and ion field contributions may also be present.

Within the SCMF approximation the many-body interactions of a multipolar polarizable system are replaced by effective pairwise-additive interactions by ignoring fluctuations in the local electric field. These effective pair potentials are obtained by replacing all instantaneous dipole moments by the effective permanent moment,
\[ m_e = \mu + C(m')\mu \cdot \alpha', \]

\[ \alpha' = \alpha + C(m')\alpha \cdot \alpha', \]

\[ m_e^2 = m^2 + 3\alpha'kT, \]

where \( \mu \) is the permanent dipole moment of the model, \( m' = \langle m \rangle \) is the average total (i.e. permanent plus induced) dipole moment as measured in the molecular frame of reference, \( \alpha \) is the polarizability tensor, \( \alpha' \) is a renormalized polarizability tensor, and \( \alpha' = \frac{1}{3} \text{Tr} \alpha' \). For particles of \( C_2v \) or higher symmetry the scalar \( C(m') \) in equations (4a) and (4b) is simply related to the total average local electric field, \( \langle E_i \rangle \), by

\[ \langle E_i \rangle = C(m')m'. \]

In order to determine an expression for \( C(m') \) in terms of the properties of the effective system, we decompose \( \langle E_i \rangle \) and \( C(m') \) into components dependent upon the various multipole moments. Ignoring fluctuations in the field it is then possible to show [5, 9] that for the water-like models being considered in this study

\[ C(m') = -\frac{2U_{DD}}{N m_e^2} - \frac{1}{N m_e m} (U_{BO}^D + U_{DO}), \]

where the superscript ‘e’ indicates the average energies for the effective system. In the present calculations \( U_{DD}^D, U_{BO}^D \) and \( U_{DO}^D \), the average dipole–dipole, dipole–quadrupole and dipole–octupole contributions, respectively, to the energy in the effective system, were determined using the RHNC theory. The solution of the SCMF approximation then consists of solving equations (4) and (6) to self-consistency.

### 3. Results and discussion

In the present calculations we have considered hard polarizable multipolar fluids with water-like parameters in which the permanent dipole moment, \( \mu \), is replaced by the effective permanent dipole moment, \( m_e \). The pair potentials for our models can then be written in the form

\[ u(12) = u_{HS}(r) + u_{el}(12), \]

where the hard-sphere interaction

\[ u_{HS}(r) = \begin{cases} \infty & r < d_s \\ 0 & r > d_s \end{cases}, \]

\( d_s \) being the hard-sphere diameter of the particles. In equation (7a), \( u_{el}(12) \) represents the electrostatic contribution to the pair potential and is given by the electrostatic multipole expansion (cf. equation (29) of [5]). Of importance here is the fact that we have only considered terms up to octupole order in this expansion, as in our previous work [5, 7].

In table 1 we have summarized the molecular parameters used for the water-like systems we have investigated. Our choice for the hard-sphere diameter, \( d_s \), is consistent with previous studies [9, 10] and with the experimentally measured structure...
Table 1. Values for molecular properties employed for the water-like models considered in the present study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_s$</td>
<td>$2.8 \text{Å}$</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>$1.501 \times 10^{-24} \text{cm}^3$</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>$1.390 \times 10^{-24} \text{cm}^3$</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>$1.442 \times 10^{-24} \text{cm}^3$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$1.855 \times 10^{-18} \text{esu cm}$ [22]</td>
</tr>
<tr>
<td>$Q_{xx}$</td>
<td>$2.63 \times 10^{-26} \text{esu cm}^2$ [21]</td>
</tr>
<tr>
<td>$Q_{yy}$</td>
<td>$-2.50 \times 10^{-26} \text{esu cm}^2$ [21]</td>
</tr>
<tr>
<td>$Q_{zz}$</td>
<td>$-0.13 \times 10^{-26} \text{esu cm}^2$ [21]</td>
</tr>
<tr>
<td>$Q_{xy}$</td>
<td>$2.30 \times 10^{-34} \text{esu cm}^3$ [23]</td>
</tr>
<tr>
<td>$Q_{xz}$</td>
<td>$-0.96 \times 10^{-34} \text{esu cm}^3$ [23]</td>
</tr>
<tr>
<td>$Q_{yz}$</td>
<td>$-1.34 \times 10^{-34} \text{esu cm}^3$ [23]</td>
</tr>
</tbody>
</table>

† $1 \text{C}^2 \text{m}^2 \text{J}^{-1} = 8.988 \times 10^{15} \text{cm}^3$; $\mu$, $1 \text{C.m} = 2.9979 \times 10^{11} \text{esu cm}$; $Q$, $1 \text{C}^2 = 2.9979 \times 10^{13} \text{esu cm}^2$; $\Omega$, $1 \text{C}^2 = 2.9979 \times 10^{15} \text{esu cm}^3$.

The elements of the polarizability tensor were determined using the experimental results of Murphy [19] weighted to give the average polarizability reported by Eisenberg and Kauzmann [20].

Calculations were carried out for three different water-like systems which for convenience we shall refer to as Models I, II and III. All three models have the same hard-sphere diameter and include the polarizability tensor $\alpha$ and the dipole moment $\mu$ as given in Table 1, but differ at the quadrupole and/or octupole levels. The models can be summarized as follows:

- **Model I**: ($\alpha$, $\mu$, tetrahedral-$Q$),
- **Model II**: ($\alpha$, $\mu$, $Q$),
- **Model III**: ($\alpha$, $\mu$, $Q$, $\Omega$),

where the parameters enclosed in parentheses are those included in determining the electrostatic interaction, $u_{el}(12)$. $Q$ and $\Omega$ are the full quadrupole and octupole tensors, respectively, given in Table 1. The expression 'tetrahedral-$Q$' refers to a quadrupole moment of tetrahedral symmetry (cf. equation (32) of [5]) which is a result of setting $Q_{zz} = 0$. Such a quadrupole moment can be specified by the single parameter $Q_T$, the tetrahedral quadrupole moment. We point out that for a dipole-tetrahedral quadrupole model, such a Model I, the rotational invariant basis set is subject to an additional symmetry condition [9, 11]

$$(\mu + v + 2l) \mod 4 = 0,$$

which further restricts the basis set.

In this study we have examined these water-like models at several different temperatures and pressures. The temperature and pressure points at which calculations were performed are given in Table 2 along with the corresponding experimental densities. The points sample a relatively large portion of the phase diagram of liquid water and correspond with those examined in earlier work [9, 10]. Of
Table 2. Experimental densities of water at the temperatures and pressures examined in the present study.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure</th>
<th>Density (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1 atm.</td>
<td>0.99707 [25]</td>
</tr>
<tr>
<td>90</td>
<td>1 atm.</td>
<td>0.9653 [24]</td>
</tr>
<tr>
<td>200</td>
<td>Vapour pressure</td>
<td>0.865 [24]</td>
</tr>
<tr>
<td>300</td>
<td>Vapour pressure</td>
<td>0.710 [24]</td>
</tr>
<tr>
<td>370</td>
<td>Vapour pressure</td>
<td>0.452 [26]</td>
</tr>
<tr>
<td>100</td>
<td>5000 bars</td>
<td>1.106 [26]</td>
</tr>
<tr>
<td>200</td>
<td>5000 bars</td>
<td>1.051 [26]</td>
</tr>
<tr>
<td>300</td>
<td>5000 bars</td>
<td>0.993 [26]</td>
</tr>
<tr>
<td>400</td>
<td>5000 bars</td>
<td>0.931 [26]</td>
</tr>
</tbody>
</table>

1 atm. = 1.01325 × 10^5 Nm^-2.

importance here is the fact that the dielectric constant has been measured [24-26] at all these temperatures and pressures. We shall refer to the points at 1 atm. or at vapour pressure as being at ‘normal’ pressure, while those at 5000 bars shall be referred to as ‘high’ pressure points.

In our calculations and in some of the following discussion it is convenient to express the molecular and state parameters in reduced units. The water-like fluids we have considered can be characterized by the following reduced parameters:

\[
\rho^* = \frac{\rho}{d_0^3}, \quad \alpha^* = \frac{\alpha}{d_0^3}, \quad \mu^* = \left(\frac{\mu}{d_0^3}\right)^{1/2},
\]

\[
Q^* = \left(\frac{Q^2}{d_0^5}\right)^{1/2}, \quad \Omega^* = \left(\frac{\Omega^2}{d_0^7}\right)^{1/2},
\]

where \(\rho^*, \alpha^*, \mu^*\) and \(Q^*, \Omega^*\) are the reduced density, polarizability and dipole moment, respectively. \(Q^*\) and \(\Omega^*\) represent the reduced elements of the quadrupole and octupole tensors, respectively, and again \(\beta = 1/kT\).

3.1. Choice of RHNC basis sets

In order to perform numerical calculations we must truncate the rotational invariant expansion (as given by equation (3a)) at some point. Following previous studies [1–3] we have used the restriction \(m, n \leq n_{\text{max}}\) to generate finite RHNC basis sets. We note that a further truncation was explored for the present systems by requiring that \(l \leq l_{\text{max}}\), but this was found [12] to be an unsatisfactory means of limiting the size of the basis sets.

In table 3 we have summarized the number of unique terms which must be included in the RHNC basis sets for Model I and for Models II and III for \(n_{\text{max}} = 2, 3, 4, 5\). We have explicitly given the unique projections for the \(n_{\text{max}} = 2\) basis sets in table 4. A set of unique projections consists of all terms which cannot be related by some symmetry requirement of the model. As mentioned above the basis sets for Models II and III must satisfy the requirements dictated by \(C_{2v}\) symmetry (cf. equations (21) of [5]), whereas Model I has the additional condition given by
Table 3. Numbers of unique projection terms required in RHNC basis sets. Models I, II and III are considered.

<table>
<thead>
<tr>
<th>$n_{\text{max}}$</th>
<th>Model I</th>
<th>Models II and III</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>74</td>
<td>130</td>
</tr>
<tr>
<td>5</td>
<td>144</td>
<td>262</td>
</tr>
</tbody>
</table>

equation (8). Clearly this additional symmetry condition reduces the number of terms in the basis set for Model I by a factor of nearly two. Even so, the RHNC basis set for Model I still has far more projections than for systems of linear symmetry [1-3], particularly when $n_{\text{max}}$ is large (i.e. $\geq 4$).

The basis set dependence of the RHNC results for the dielectric constant, $\varepsilon$, the average energies and the contact value of the radial distribution function, $g(r = d_s)$, for Models I and III is summarized in tables 5 and 6, respectively. The parameters of the systems examined were chosen to be essentially those of the water-like fluids at 25°C. It is obvious from tables 5 and 6 that there is generally strong basis set dependence for both systems up to $n_{\text{max}} = 4$. Fortunately, we find that the basis set dependence is greatly reduced when going from $n_{\text{max}} = 4$ to $n_{\text{max}} = 5$ for Model I, although to a slightly lesser extent for Model III. For all the properties considered in table 5 the differences between the $n_{\text{max}} = 4$ and $n_{\text{max}} = 5$ results are at most 2 percent and are only slightly larger than the inherent inaccuracy (i.e. grid width dependence, etc.) in the numerical calculations. The difference between the $n_{\text{max}} = 4$ and $n_{\text{max}} = 5$ results for Model III are generally somewhat larger, as can be seen from table 6. This is not surprising since we would expect the octupole moment to increase the magnitudes of the higher order projections thereby increasing their importance. We remark that the basis set dependence we observe for these two non-linear models is similar to that reported for hard-sphere systems with dipoles and linear quadrupoles [3].

We have already seen that for the present models the number of unique projections in a given basis set increases very rapidly with $n_{\text{max}}$. Consequently, the $n_{\text{max}} = 4$ basis sets would seem to be a reasonable compromise between accuracy and computational requirements, and therefore these basis sets were used exclusively to obtain all the results presented below for all three water-like fluids. We also point out that $n_{\text{max}} = 4$ basis sets were employed in our recent studies [5, 6] of aqueous electrolyte solutions using similar solvent models.

Table 4. Projection terms included in $n_{\text{max}} = 2$ basis sets.

<table>
<thead>
<tr>
<th>Model</th>
<th>Number of unique terms</th>
<th>Projections included ($mnl; \mu\nu$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>12</td>
<td>(000; 00), (022; 00), (110; 00), (112; 00), (121; 02), (123; 02), (220; 00), (220; 22), (222; 00), (222; 22), (224; 00), (224; 22)</td>
</tr>
<tr>
<td>II and III</td>
<td>19</td>
<td>All those above plus</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(011; 00), (022; 02), (121; 00), (123; 00), (220; 02), (222; 02), (224; 02)</td>
</tr>
</tbody>
</table>
Table 5. Basis set dependence of $\varepsilon$, the average energies and $g(r = d_s)$ for Model I. A system for which $\rho^* = 0.7317$, $\mu^* = 2.75$ and $Q^*_f = 0.94$ is considered.

<table>
<thead>
<tr>
<th>Property</th>
<th>$n_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>200.6</td>
</tr>
<tr>
<td>$U_{DD}/NkT$</td>
<td>-12.28</td>
</tr>
<tr>
<td>$U_{DQ}/NkT$</td>
<td>-6.27</td>
</tr>
<tr>
<td>$U_{QQ}/NkT$</td>
<td>-1.70</td>
</tr>
<tr>
<td>$g(r = d_s)$</td>
<td>12.03</td>
</tr>
</tbody>
</table>

3.2. Results for water-like fluids

Calculations using the $n_{\text{max}} = 4$ basis sets were carried out at all the temperatures and pressures listed in table 2. Model II was studied at all points, while Model III was examined only at 25°C at normal pressure and at 300°C at normal and high pressure. A calculation at 25°C was also performed with Model I taking $Q^*_f = 0.94$, this value being consistent with earlier work [9, 10].

The average dipole moments, $m'$, as determined by the SCMF approximation are shown in figure 1. Not surprisingly, we find that $m'$ decreases with increasing temperature but increases with increasing pressure. Yet even at high temperature the values of $m'$ are still well above the permanent dipole moment of water. The presence of the octupole moment in Model III affects only a slight increase in the average dipole moment. The results obtained here are in striking agreement with previous RLHNC studies [9, 10] in which Model I was examined over the same range of temperatures and pressures. We note that at 25°C Model I gave a value of $m'$ almost identical to that calculated for Model II. The average dipole moments we have determined at 25°C compare well with values that have been calculated for ice [27] or reported for another polarizable water-like model [28].

The dielectric constants obtained for the polarizable fluids being investigated here are shown in figure 2. We remark that at 300°C the points for Models II and III are virtually indistinguishable both at normal and at high pressure. From figure 2 we see that at higher temperatures (i.e. > 100°C) the simple hard-sphere models we have considered give results which are in good agreement with experimental data.

Table 6. Basis set dependence of $\varepsilon$, the average energies and $g(r = d_s)$ for Model III. The system considered is one for which $\rho^* = 0.7317$, $\mu^* = 2.75$ and the values of the reduced quadrupole and octupole moments correspond to a temperature of 25°C.

<table>
<thead>
<tr>
<th>Property</th>
<th>$n_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>91.3</td>
</tr>
<tr>
<td>$U_{DD}/NkT$</td>
<td>-11.94</td>
</tr>
<tr>
<td>$U_{DQ}/NkT$</td>
<td>-7.71</td>
</tr>
<tr>
<td>$U_{QQ}/NkT$</td>
<td>-1.21</td>
</tr>
<tr>
<td>$U_{OQ}/NkT$</td>
<td>-1.85</td>
</tr>
<tr>
<td>$U_{OO}/NkT$</td>
<td>-0.41</td>
</tr>
<tr>
<td>$U_{OO}/NkT$</td>
<td>0.35</td>
</tr>
<tr>
<td>$g(r = d_s)$</td>
<td>14.66</td>
</tr>
</tbody>
</table>
Figure 1. The average total dipole moment as a function of temperature and pressure. The values given are in Debyes. The solid and dashed lines are SCMF results for Model II at normal and high pressure, respectively. The solid and open squares, respectively, are values obtained for Model III at normal and high pressure. The dotted line represents the permanent dipole moment of water.

both at normal and at high pressure. However, at low temperatures we find that these models consistently overestimate $\varepsilon$. This was not the case in previous RLHNC investigations [9] of Model I where good agreement with experiment was found even at 25°C. Using the RHNC theory we obtain $\varepsilon = 101$ at 25°C for Model I (not shown in figure 2) even though the effective dipole moment is essentially the same. In previous comparisons [1–3] with computer simulation the RHNC has been generally found to be the more accurate theory and hence we would expect it to give the better estimates for the dielectric constant for the present water-like systems.

Figure 2. The dielectric constants of water and of the present water-like fluids as functions of temperature and pressure. The solid triangles and dots are SCMF results for Model II at normal and high pressure, respectively, while the solid and open squares are as in figure 1. The solid and dashed lines represent experimental values [24–26] at normal and high pressure, respectively.
The importance of the polarizability in the water-like models we have considered can be easily demonstrated. If we ignore the polarizability in Model II and take the effective dipole moment to be simply the gas phase value, we obtain \( \varepsilon = 27.7 \) at 25°C. It is also interesting to point out that the MCY [29] and TIP4P [30] models, two popular models for water, have been shown [31] to give dielectric constants of 34 and 53, respectively, at 20°C. Both these fluids are non-polarizable and have dipole moments of about 2.2D. In comparison with these results, the values for \( \varepsilon \) obtained here at 25°C for our polarizable multipolar models appear quite respectable.

In general we find that the incorporation of the octupole moment in the model causes a noticeable drop in \( \varepsilon \) for a fixed dipole moment. We also see from figure 1 that the addition of the octupole results in a larger average dipole moment. These two effects tend to cancel one another and consequently Models II and III give quite similar dielectric constants (see figure 2).

As mentioned above, we obtained a dielectric constant of 101 for Model I at 25°C which is significantly larger than the result for Model II, despite the fact that their effective dipole moments are almost identical. For Model I the value of the parameter \( Q_T \) was the same as that used in earlier work [9-11] where it was somewhat arbitrarily set to \( 2.5 \times 10^{-26} \text{ esu cm}^2 \). The present calculations clearly indicate that this value of the tetrahedral quadrupole moment underestimates the effect of the full quadrupole tensor of the water molecule included in Model II. However, we do find that \( Q_T = 2.57 \times 10^{-26} \text{ esu cm}^2 \), which is just slightly larger than half the sum of the magnitudes of \( Q_{xx} \) and \( Q_{yy} \) (see table 1), works very well as an effective tetrahedral quadrupole moment. In this case Models I and II give almost identical results for all average properties examined, including \( \varepsilon \) and the average energies. Thus, it is this value of \( Q_T \) which was used in Model I in our recent study [5] of model aqueous electrolyte solutions at finite concentration.

The total average configurational energies, \( U_{\text{tot}}/NkT \), can be computed for our polarizable fluids using equation (42) of [5]. At 25°C Models II and III give values of \(-17.7\) and \(-18.7\), respectively, which compare well with the experimental result [30] of \(-16.7\). This agreement is perhaps somewhat fortuitous since we might expect some of the terms (e.g. dispersion and short-range repulsions) which we have ignored in the potential to make fairly large contributions to the energy.

The radial distribution functions, \( g(r) = g_{\text{oo}}(r) \), for Models II and III at 25°C are shown in figure 3. Both systems have the same effective dipole moment, \( m^* = 2.75 \), and hence any differences in structure are due solely to the influence of the octupole moment. We note that this value is very close to the SCMF results (2.768 and 2.787) for \( m^* \) for both these polarizable fluids. Included in figure 3 is the radial distribution function of the hard-sphere reference system [which would also be the RLHNC result for \( g(r) \)]. The effects of the strong multipolar interactions are clearly evident. For the two multipolar fluids the contact value of \( g(r) \) has increased dramatically from the hard-sphere result, while the position of the first minimum has moved inward. The second peak has also sharpened and shifted inward for both multipolar systems. However, its maximum still occurs at a separation of \( ~2d_s \), whereas for real water the maximum in the second peak appears at \( ~1.65d_s \), corresponding to the "tetrahedral" distance [17, 18]. If we compute coordination numbers,

\[
\text{CN} = 4\pi \rho \int_{d_s}^{R} r^2 g(r) \, dr, \tag{10}
\]
where $R$ represents the separation corresponding to the first minimum of the integrand, we find that both Models II and III give values of $\sim 5.8$ at $25^\circ C$. Again, these do not compare well with the result for liquid water at $25^\circ C$ where $CN \approx 4.5$ [18]. Thus, even accounting for the structural effects of the unrealistic hard cores of Models II and III, the RHNC results for $g(r)$ for these fluids are still quite different from that of real water.

The influence of the octupole moment on the radial distribution function can also be seen in figure 3. As might be expected, the contact peak becomes somewhat steeper due to the additional terms in the electrostatic potential. The maximum in the second peak of $g(r)$ remains virtually unchanged, although a small shoulder has developed on the second peak at the tetrahedral distance. Clearly, the presence of the octupole moment does influence the packing structure but the magnitude of these effects is relatively small.

In an attempt to try and improve our results for the radial distribution function, we examined the effects of increasing the values of the quadrupole and octupole moments. We found that increments as large as 50 per cent produced very little change in $g(r)$ except to generate an even steeper contact peak. Therefore, at least within the RHNC theory, hard-sphere models containing only the low-order multipole moments of water appear unable to give a tetrahedral structure similar to that of liquid water. Hence, a fourth water-like model which incorporated a soft spherical potential [12] was examined. It was found [12] that the 'correct' structure for water at $25^\circ C$ could be obtained by the addition of this empirical short-range isotropic interaction to Model III. Moreover, the dielectric constant determined [12] for this fluid was in very good agreement with experiment. What is not entirely clear, however, is whether this short-range potential is simply correcting for inadequacies in the hard-sphere model, or whether it is also compensating for a deficiency in the RHNC theory. Very recent work [32] suggests that part of the problem does lie with the RHNC theory.

Finally, in figures 4–10 we have shown some of the projections of the pair correlation functions for Models II and II. The projections which have been
Figure 4. The projection $h_{00}^{110}(r)$. The solid and dashed lines represent RHNC results for Models II and III, respectively, at 25°C and $m^*_s = 2.75$.

Figure 5. The projection $h_{00}^{112}(r)$. The curves are defined as in figure 4.

Figure 6. The projection $h_{00}^{123}(r)$. The curves are defined as in figure 4.
Figure 7. The projection $h_{02}^{123}(r)$. The curves are defined as in figure 4.

Figure 8. The projection $h_{00}^{224}(r)$. The curves are defined as in figure 4.

Figure 9. The projection $h_{02}^{224}(r)$. The curves are defined as in figure 4.
Figure 10. The projection $h_{22}^{224}(r)$. The curves are defined as in figure 4.

included are all those which contain potential terms for both systems as well as $h_{00}^{110}(r)$. In general the projections reflect the same oscillatory behaviour found in $g(r)$. Most of the correlation functions are at least moderately effected by the presence of the octupole moment; $h_{00}^{123}(r)$ and $h_{00}^{224}(r)$ change most markedly, while $h_{02}^{123}(r)$ and $h_{22}^{224}(r)$ appear to be the least effected. However, we find no systematic variation in the correlation functions.

The dipole–dipole correlations as given by $h_{00}^{110}(r)$ and $h_{00}^{112}(r)$ (see figures 4 and 5) are of particular interest. In both cases we find that the correlation functions become less structured with the addition of the octupole moment to the model. This is consistent with the observed drop in the dielectric constant and the decrease in the average dipole–dipole energy. Clearly, the octupolar forces act to disrupt the dipolar structure within the fluid. This is, of course, also true of the quadrupole [9].

4. Conclusions

In this article we have examined the dielectric and structural properties of simple models for liquid water. The models employed were hard-spheres embedded with the low-order multipole moments and polarizability tensor of the water molecule. The RHNC integral equation theory was used to study these fluids with the polarizability being treated at the SCMF level.

The RHNC basis set dependence for these non-linear models was observed to be quite similar to that previously reported [3] for hard-sphere systems with dipoles and linear quadrupoles. The basis sets corresponding to $n_{\text{max}} = 4$ were found to represent a reasonable compromise between convergence and computational requirements and were used exclusively in the present study of water-like fluids.

Model systems for liquid water were investigated over a large range of temperatures and pressures. The dielectric constants of these water-like fluids were found to be in good agreement with experiment, particularly at high temperatures. At low temperature the RHNC results for the radial distribution functions for the present hard-sphere systems are in rather poor agreement with those measured for liquid water. The octupole moment was shown to have relatively little effect upon...
the dielectric constant and its influence upon the structure within the model fluids was only slightly larger.

In the present study we have observed an apparent inability of hard multipolar water-like systems to give a tetrahedral structure similar to that of liquid water, however, it is not clear whether this problem is inherent in the model, or whether at least part of the problem lies with the approximate theory employed. In order to explore this question further we have undertaken a systematic study [32] of water models for which computer simulation results are available and which are known to sustain a tetrahedral structure.

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References