

## A POLARIZABLE THREE-SITE WATER MODEL WITH INTRAMOLECULAR POLARIZABILITY

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Received December 31, 2007

Accepted March 26, 2008

Published online April 25, 2008

*Dedicated to Professor William R. Smith on the occasion of his 65th birthday.*

The forgotten “atom dipole interaction model” in which several induced dipoles in a molecule can interact is investigated. This model leads to an anisotropic (tensor) polarizability of a molecule using only isotropic (scalar) atomic contributions. A three-site model of water reproducing the experimental tensor polarizability is developed and tested using molecular dynamics calculations.

**Keywords:** Polarizability; Water; Atom dipole interaction model; Tensor; Molecular dynamics.

For statistical-thermodynamical calculations on systems containing thousands of atoms we need a potential energy function (force field) which is both simple and accurate. Both requirements are apparently contradictory and one has to make compromises. The most common approximation simplifying the calculations is the assumption that the forces are pairwise-additive. This approximation is especially severe in systems with ions or highly polar molecules because the electrostatic field is strong enough to significantly distort electron clouds and to induce dipoles (or higher multipoles) in molecules. The induced charge distribution is again a source of electrostatic field which feeds back the source molecules and thus the resulting field is not pairwise-additive (it is not even given explicitly but as a self-consistent solution). The calculations with included polarizability demand more computer time, and, therefore, are not so popular. Nevertheless, the development and usage of polarizable models is a challenge which can give a better description and understanding of intermolecular forces.

A number of polarizable models for water have been developed, differing in the number of sites and other properties (flexibility, dissociability). In this paper we will deal with the simplest family of three-site models. These include the polarizable SPC model (PSPC)<sup>1</sup> with polarizable oxygen, several SPC-based models with Drude oscillators<sup>2</sup>, and the POL3 model<sup>3</sup> and its predecessors<sup>4,5</sup> with all atoms polarizable.

While the SPC family of models use the experimental polarizability (1.44–1.47 Å<sup>3</sup>), which is the common practice for most polarizable water models, the polarizability of the POL3 model is only 0.868 Å<sup>3</sup>, in contrast to experiment. The explanation is peculiar: the original idea<sup>4</sup> leading to this value was that the dipoles induced at all atoms can interact according to the atom dipole interaction model (ADIM)<sup>6</sup>. This interaction enhances the response to an electrostatic field and also leads to an anisotropic polarizability tensor. Indeed, the calculated effective isotropic polarizability is 1.465 Å<sup>3</sup>. This internal polarizability, however, was forgotten and the model was later reparametrized<sup>3,5</sup> to give good properties of water: the dipole moment was increased to account for its reduced polarizability and the Lennard–Jones (LJ) part was adjusted to the experimental density and vaporization enthalpy. The POL3 model is therefore a compromise between a non-polarizable effective model with enhanced charges and a true polarizable model.

Combination of interacting isotropic atomic polarizabilities in ADIM can be viewed as a technical trick to achieve an anisotropic polarizability using as simple code as possible. The same goal can be obtained directly by using explicit polarizability tensor<sup>7,8</sup>, or for flexible molecules by an additive (non-interacting) combination of axial tensors in the direction of chemical bonds<sup>9</sup>.

The original idea of atom-distributed polarizabilities was later used<sup>10</sup> with distance-dependent polarizabilities to avoid polarization catastrophe (divergence of the equations for the self-consistent field). Quadrupolar terms can be also added<sup>11</sup>.

There are two common approaches to avoid polarization catastrophe: the distance-dependent polarizability (see, e.g., ref.<sup>12</sup> for recent discussion) and the shell-core model<sup>13</sup> based on a mechanistic idea of negative electron clouds repelling each other at close separations. The former approach, with a realistic damping function, essentially reduces the intramolecular induction in water to zero. The latter approach was used<sup>14</sup> to develop a polarizable and dissociable model of water, but it is not applicable to intramolecular polarizability in rigid models.

The main aim of this paper is to investigate the internal polarizability using a three-site model of water as the case study. The isotropic atomic polarizabilities and partial charges are assigned to atoms to reproduce the experimental polarizability tensor and the dipole moment, respectively.

## METHODS

### *Polarizability and the Atom Dipole Interaction Model*

The polarizability  $\alpha$  (more precisely “polarizability volume”) is defined as a constant in the relation between the external field  $\mathbf{E}$  and the induced dipole,

$$\boldsymbol{\mu} = 4\pi\epsilon_0\alpha\cdot\mathbf{E}$$

where  $\epsilon_0$  is the permittivity of vacuum. We shall not consider higher-order terms (hyperpolarizability). The polarizability  $\alpha$  is generally a tensor, i.e.,  $\boldsymbol{\mu}$  need not be parallel to  $\mathbf{E}$ .

In the ADIM<sup>6</sup>, isotropic (scalar) polarizabilities  $\alpha$  are assigned to interaction sites (atoms). All induced dipoles can interact; in contrast, the intramolecular partial charges do not interact. Hence, the total polarizability of a single molecule is not the sum of atomic contributions. The formula for the total polarizability tensor was derived in ref.<sup>6</sup>; we briefly review the results here. Let us first define the dipole field tensor

$$\mathbf{T} = -\frac{3}{r^5} \begin{pmatrix} x^2 - r^2/3 & xy & xz \\ yx & y^2 - r^2/3 & yz \\ zx & zy & z^2 - r^2/3 \end{pmatrix} \quad (1)$$

where  $\mathbf{r} = (x, y, z)$  is the vector from site  $i$  to site  $j$ . Matrix  $\mathbf{A}$  is a  $3N \times 3N$  matrix ( $N$  is the number of atoms) written in  $3 \times 3$  blocks as

$$\mathbf{A} = \begin{pmatrix} \alpha_1^{-1} & \mathbf{T}_{12} & \dots & \mathbf{T}_{1N} \\ \mathbf{T}_{21} & \alpha_2^{-1} & \dots & \mathbf{T}_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{T}_{N1} & \mathbf{T}_{N2} & \dots & \alpha_N^{-1} \end{pmatrix} \quad (2)$$

where  $\alpha^{-1}$  is for scalar  $\alpha$  simply a diagonal matrix  $\text{diag}(1/\alpha, 1/\alpha, 1/\alpha)$ . The total polarizability tensor is then the sum of  $3 \times 3$  blocks of inverted matrix  $\mathbf{A}$ :

$$\alpha = \sum_{i=1}^N \sum_{j=1}^N (\mathbf{A}^{-1})_{ij} . \quad (3)$$

### Water Models

The intermolecular potential is composed of the Lennard–Jones oxygen–oxygen term and electrostatic interactions. In accordance with common force fields, we write the Lennard–Jones term as

$$u_{\text{LJ}} = -E_{\text{min}} \left[ \left( \frac{R_{\text{min}}}{r} \right)^{12} - 2 \left( \frac{R_{\text{min}}}{r} \right)^6 \right] \quad (4)$$

where  $r$  is the oxygen–oxygen separation,  $E_{\text{min}}$  is the minimum energy (a negative number), and  $R_{\text{min}}$  the separation at the minimum. The geometry of our models is the same as of the popular SPC model<sup>15</sup>: the H–O–H angle is tetrahedral (109.47°) and the H–O distance is 1 Å. Partial charges and linear dipolar polarizabilities are assigned to the atoms; the induced dipoles are point dipoles by definition. The electrostatic interactions then consist of the direct Coulombic interactions, induced dipole–charge terms, induced dipole–induced dipole contributions, and the self-energy terms.

### Isotropic Models

In standard isotropic polar (IPOL) models the intramolecular induced dipoles do not interact; the total polarizability is the sum of atomic contributions and therefore it is a scalar. As a benchmark, we simulated five models (Table I). One is the original POL3 model<sup>3</sup>. It has an enhanced dipole moment and reduced total polarizability. Four isotropic models have partial charges determined to reproduce the experimental dipole moment and we test two versions differing in the Lennard–Jones attraction. A pair of PSPC-like models have oxygen-based polarizability 1.44 Å<sup>3</sup> and non-polarizable hydrogens. A pair of POL3-like models have realistic values of polarizability distributed between oxygen (1.22 Å<sup>3</sup>) and hydrogen (0.1 Å<sup>3</sup>); significantly larger values at hydrogen cause a polarization catastrophe. Note that the model symbols are derived from  $E_{\text{min}}$  in kcal mol<sup>-1</sup> and  $\alpha_{\text{H}}$  in Å<sup>3</sup>.

The efficiency of the models differs. The pair potential of two molecules without polarizable hydrogens contains 16 charge-charge terms while adding hydrogen polarizability increases the cost to 36 such terms. The real speed ratio was about 1.5:1.

### Anisotropic Models

If we return the intramolecular polarization to the POL3 model, we get the polarization tensor  $\alpha = \text{diag}(1.1189, 2.6605, 0.6161) \text{ \AA}^3$  (see Fig. 1 for the axes convention). While the isotropic polarizability,  $\alpha = \text{Tr}(\alpha)/3 = 1.4652 \text{ \AA}^3$ , matches the experiment (the parameters of the model were originally de-

TABLE I  
Parameters of water models (the values in parentheses are standard errors in the last significant digit)

Models	$q_{\text{O}}$ $e$	$\alpha_{\text{O}}$ $\text{\AA}^3$	$\alpha_{\text{H}}$ $\text{\AA}^3$	$E_{\text{min}}$ $\text{kJ mol}^{-1}$	$R_{\text{min}}$ $\text{\AA}$
POL3	-0.73	0.528	0.17	-0.652704	3.596
IPOL-0.13	-0.669	1.44	0	-0.54392	3.65750(23)
IPOL-0.16	-0.669	1.44	0	-0.66944	3.61636(19)
IPOL-0.13-0.1	-0.669	1.24	0.1	-0.54392	3.68326(13)
IPOL-0.16-0.1	-0.669	1.24	0.1	-0.66944	3.63822(20)
APOL-0.13	-0.669	1.4122	0.0056	-0.54392	3.67112(13)
APOL-0.16	-0.669	1.4122	0.0056	-0.66944	3.62890(16)

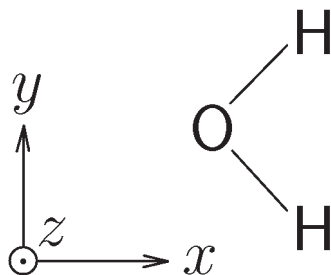


FIG. 1  
Definition of coordinate axes in water molecule

vised to do so), the tensor is much more anisotropic than the real water molecule. Our attempt to simulate bulk water with this model failed even when the molecule size was rescaled up to unrealistic values. The polarizability in the  $y$ -direction is so large that the equations for the SCF diverge (polarization catastrophe). A dimer exists, but its O–O distance is 2.5854 Å and energy  $-32.21$  kJ mol $^{-1}$ , far from real values. The polarization catastrophe could be avoided by using a distance-dependent polarizability.

In our anisotropic polar (APOL) model, the scalar atomic polarizabilities are determined so that the experimental polarizability tensor<sup>16</sup>,  $\alpha = \text{diag}(1.4679(13), 1.5284(13), 1.4146(3))$  Å<sup>3</sup>, is best reproduced (i.e., the sum of squared differences of the model and experimental polarizability components is minimized). The result is given in Table I. The model polarizability tensor is  $\text{diag}(1.4694, 1.5274, 1.4141)$  Å<sup>3</sup>; ADIM is therefore able to describe the anisotropic polarizability very accurately. The partial charges in this model are set according to the dipole moment. Once again, we try two versions differing in the attractive Lennard–Jones term while the radius is always set to give correct density at ambient conditions.

The pair potential of two APOL molecules contains 36 charge–charge terms such as POL3 or IPOL-0.13-0.1. The modified intramolecular terms do not affect the calculation speed.

### *Molecular Dynamics*

Our molecular dynamics experiment was performed using the MACSIMUS package<sup>9</sup>. The periodic simulation box contained 1000 water molecules; the size of the box was calculated to reproduce the experimental density at 298.15 K, which is 0.997048 g cm $^{-3}$ . Temperature was kept constant by the Berendsen (friction) thermostat with a correlation time of 1 ps.

Induced dipoles were replaced by two large charges (of  $-1000 e$ ) in close proximity (this trick is sometimes called the Drude oscillator because we can imagine the charges as connected with a spring). The systematic error of this approximation is negligible; e.g., the true equilibrium O–O distance in a dimer is by ca.  $8 \times 10^{-6}$  Å longer and the energy by 0.16 J mol $^{-1}$  larger. One of the charges sums up with the atomic partial charge. We thus have to evaluate four charge–charge interactions which is faster than four combined terms (charge–charge, two charge–induced dipole, and the induced dipole–induced dipole).

The electrostatic forces were calculated by the Ewald summation. The implementation is a bit tricky. The Ewald summation method<sup>17</sup> expresses the electrostatic energy as a sum of an  $r$ -space part and a  $k$ -space part. A raw sum

based on all charges in the system would contain also intramolecular charges that should not (directly) interact, like both auxiliary charges approximating the point dipole; these are very close together. Such charge-charge terms should be excluded. This is done by replacing the terms  $q_1 q_2 \operatorname{erfc}(\alpha r)/r$  appearing in the  $r$ -space sum ( $q_1$ ,  $q_2$  are both charges and  $\alpha$  stands here for the separation parameter) by terms  $q_1 q_2 [\operatorname{erfc}(\alpha r) - 1]/r$  whenever the charges do not interact directly (interaction via periodic images is preserved). The set of excluded interactions is different for the IPOL and APOL models. The efficiency, however, is not affected.

The equations of motion were integrated by the Verlet method with the always-stable predictor-corrector (ASPC) method<sup>18</sup> with  $k = 2$  for the induced dipoles. The time step was 0.001 ps. Bond lengths were constrained by the SHAKE algorithm (the H-O-H angle is replaced by an H-H "bond").

## RESULTS AND DISCUSSION

### *Simulation Results*

Seven models defined in Table I were investigated at ambient conditions (298.15 K and 0.997048 g cm<sup>-3</sup>). As a rule, we always ran several simulations (at least 400 ps long) differing in the molecular size ( $R_{\min}$ ) and determined the value of  $R_{\min}$  such that the pressure reached 101.325 kPa. That is why the  $R_{\min}$  is given with statistical uncertainty. The results are collected in Tables II and III, radial distribution functions (RDF) in Fig. 2. The pressure of the POL3 model is negative; the error is equivalent to the error in density 0.4%. This relatively small discrepancy can be explained by less accurate simulation methods used 15 years ago.

Our six models come in three pairs differing in the minimum of the potential,  $E_{\min}$ . The influence of  $E_{\min}$  on the results seems to be counter-intuitive: the smaller  $E_{\min}$ , the higher averaged energy. This paradox is a consequence of simultaneous adjustment of the size of the molecule,  $R_{\min}$ . The equilibrium water-water distance is shorter than  $R_{\min}$  because of O-H charge-charge attraction which is compensated by the repulsive part of the Lennard-Jones potential. Bigger  $E_{\min}$  (this means smaller  $|E_{\min}|$ , i.e., shallower potential well because  $E_{\min}$  is negative) then requires a longer  $R_{\min}$  to compensate. As follows from optimized dimer geometry and energy, the hydrogen bond is then deeper and narrower. The first peak on the O-O and H-O distribution functions is higher and lies at closer separations. Consequently, breaking hydrogen bonds is less likely and the diffusivity decreases.

TABLE II

Optimized dimer geometry and energy ( $r_{\text{OO}}$  is the oxygen–oxygen separation,  $\theta_a$  ( $\theta_d$ ) is the angle between the acceptor (donor) molecule axis and the donor–acceptor O–O vector,  $E$  is the dimer energy)

Models	$r_{\text{OO}}$ Å	$\theta_a$ °	$\theta_d$ °	$E$ kJ mol <sup>-1</sup>
POL3	2.7885	19.72	52.11	-22.772
IPOL-0.13	2.8492	19.27	51.64	-18.137
IPOL-0.16	2.8656	19.22	51.56	-18.070
IPOL-0.13-0.1	2.8619	18.85	51.67	-17.950
IPOL-0.16-0.1	2.8748	18.82	51.60	-17.972
APOL-0.13	2.8595	18.77	51.64	-17.980
APOL-0.16	2.8751	18.74	51.56	-17.939
Experiment <sup>24,25</sup>	2.98	57–59	51–53	-22.6

TABLE III

Properties of water models at temperature 298.15 K and density 0.997048 g cm<sup>-3</sup> ( $P$  is pressure,  $E$  averaged internal energy,  $D$  diffusivity,  $\mu$  averaged total dipole moment; errors in  $\mu$  are less than 0.001 D, 1 D = 3.33564 × 10<sup>-30</sup> C m)

Models	$P$ MPa	$E_{\text{pot}}$ kJ mol <sup>-1</sup>	$D$ 10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup>	$\mu$ D
POL3	-9.7(8)	-41.184(7)	2.52(5)	2.606
IPOL-0.13	0.1	-36.996(27)	2.51(5)	2.863
IPOL-0.16	0.1	-36.612(19)	3.01(6)	2.809
IPOL-0.13-0.1	0.1	-37.853(19)	2.04(4)	2.970
IPOL-0.16-0.1	0.1	-37.538(29)	2.37(4)	2.903
APOL-0.13	0.1	-37.602(17)	2.14(2)	2.932
APOL-0.16	0.1	-37.189(19)	2.61(5)	2.872
Experiment <sup>26,27</sup>	0.1	-41.5	2.3	2.6



Redistributing a part of the polarizability to hydrogens in the isotropic models enhances the hydrogen bond. Energy therefore decreases towards the correct value. The diffusivity decreases, too; if we take the diffusivity as the criterion of hydrogen bond strength, the optimum  $E_{\min}$  decreases. One might expect that increasing the hydrogen polarizability further would improve the model, but the set of induced dipoles soon becomes divergent.

In the APOL models the hydrogen polarizability is not a free parameter. Although it is very small, its influence is apparent. According to diffusivity, the best model would be in between APOL-0.13 and APOL-0.16.

### Caveats

The proposed models suffer from the same caveats as all three-site models constructed under similar principles:

1) the dimer energy and internal energy of liquid are too high (in other words, the heat of vaporization is too low),

2) a wrong orientation of the acceptor molecule in the dimer and not well developed second peak in the O–O RDF (in other words, not enough tetrahedral structure),

3) the O–O distance both in the dimer and in the liquid is too short,

4) the total dipole moment of a molecule in bulk liquid is too large.

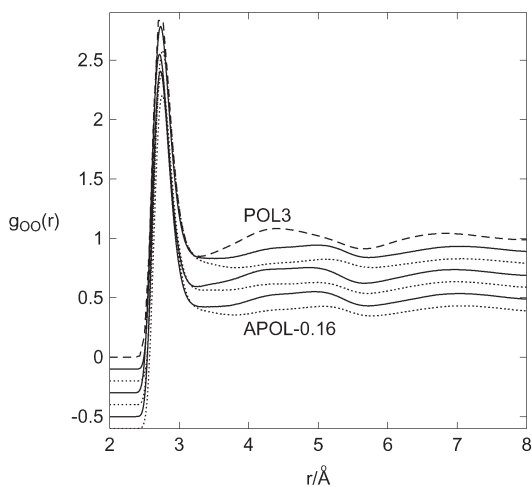


FIG. 2

Oxygen–oxygen distribution functions. The curves are shifted by multiples of 0.1. The order of curves is the same as in the tables

Caveat 1 cannot be fixed without rescaling charges because changing the Lennard–Jones energy term ( $E_{\min}$ ) requires rescaling the size ( $R_{\min}$ ) so that the experimental density is reproduced; the combined effect on the energy is marginal. The rescaled model cannot simultaneously describe electric properties both in the vapor and liquid phase. Model POL3 can be viewed as a compromise lying in between a fully effective pairwise potential (like SPC) and a “pure” polarizable one (like IPOL or APOL) where polarizability, and not rescaling charges, should suffice to describe all electric properties of a molecule irrespective of its environment.

Caveat 2 is commonly solved by moving the negative charge center in the direction of the dipole as in the popular TIP4P models (see ref.<sup>19</sup> and references therein) and their polarizable counterparts<sup>20–22</sup>. At the same time, caveat 1 is improved.

The least important caveat 3 is related to the too steep  $r^{-12}$  term in the Lennard–Jones potential and quantum effects.

Caveat 4 suggests a smaller effective polarizability of a water molecule in the environment of bulk water (the approach of POL3) or some other effects (quantum calculations on clusters do not predict such dramatic decrease in the effective polarizability<sup>23</sup>).

#### CONCLUDING REMARKS

The goal of polarizable models is much more ambitious than that of effective pair potentials. The models should correctly describe electric properties of a single molecule (in gas phase): dipole moment, quadrupole moment, and perhaps, as investigated in this paper, the tensor polarizability. The interaction of molecules should lead – without any rescaling – to correct description of condensed phases including phase equilibria. The experience with more sophisticated (four-site) models says that in spite of improvement in comparison with effective potentials, the above goal cannot be fully realized. Introducing fine effects such as anisotropic polarizability into crude three-site models, with constraints set up by the goal, cannot therefore significantly improve their performance and the resulting model can hardly be useful. It may, however, pave the way to more sophisticated (probably four-site) polarizable models.

In development of polarizable models of more complex compounds (e.g., ionic liquids), one has to solve the question which intramolecular induced dipole–induced dipole interactions to include and which not. The standard approach excludes all 1–2 and 1–3 non-bonded interactions (Lennard–Jones and all Coulombic interactions) and always includes 1–5,

1–6, etc. The 1–4 interactions (described by dihedral potentials) are often amended by rescaled non-bonded terms (a typical scaling factor is 0.5). The present contribution suggests that including all induced dipole–induced dipole interactions may be in some cases an advantage.

*We gratefully acknowledge support of the Czech Science Foundation (project 203/07/1006) and the computing facilities of the Czech Ministry of Education, Youth and Sports of the Czech Republic (Center for Biomolecules and Complex Molecular Systems, project LC512).*

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