SIMPLE TRANSFERABLE INTERMOLECULAR POTENTIAL FOR THE MOLECULAR SIMULATION OF WATER OVER WIDE RANGES OF STATE CONDITIONS

by

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ABSTRACT

We discuss new developments in our polarizable water model consisting of smeared charges and a self-consistent point dipole polarizability, and compare the structural and polarization results at ambient and a supercritical conditions with those obtained previously with the corresponding simple point charges counterpart. We discuss the outcome of this comparison and make contact with the structural data from neutron scattering with isotopic substitution.

1. INTRODUCTION

Since the introduction of the BNS [1] water model in the early seventies, the modeling of water and aqueous solutions has been mostly done by molecular force-fields based on fixed point charges in either rigid or flexible molecular geometry [2, 3]. All these models share a common feature, *i.e.*, they are unable to account explicitly for the polarization effects (many-body) but rather implicitly as two-body interactions through enhanced dipole moments. This feature, in turn, has at least two undesirable consequences for the modeling of aqueous solutions over wide range of state conditions. First, the pairwise additivity assumption cannot describe common situations where the actual polarization is anisotropic, *i.e.*, such as water near surfaces or charged species, and under external electric fields [3]. And second, as a result of the enhanced dipoles, the models cannot describe the two-body interactions of an isolated molecular pair, *i.e.*, the behavior at low density, without running into undesirably state dependence in the force-field parameters [4]. Consequently, these non-polarizable water models are non-transferable, *i.e.*, they are unable to describe properly the phase behavior at conditions away from those at which the parameterization was performed, even if the model parameters are defined as state dependent [5].

Recent neutron scattering results for the structure of water at ambient and supercritical water [6, 7] have fueled the interest in the development of more reliable

models for water [8-12], as a vehicle to improve our understanding of the complex behavior of water at ambient and supercritical conditions, through the interplay between molecular simulations and neutron scattering experiments [13]. In particular, as part of a wider investigation of high temperature solvation in aqueous solutions [14-17], we have recently developed a simple polarizable water model capable of reproducing the pressure, the configurational internal energy, and the site-site pair correlation functions at $T = 298K$ and $\rho = 1.0 g/cc$ while maintaining a permanent dipole moment of $\mu = 1.85D$ corresponding to the water dimer [18]. The model (SCPDP) was based on the rigid SPC geometry, *i.e.*, a planar configuration with an $\mathrm{H-O-H}$ angle of 109.5° and an $\mathrm{O-H}$ bond length of 1.0Å [19], with the negative charge located along the $\mathrm{H-O-H}$ bisector, a distance R_{OM} toward the H sites (see Figure 1 of Ref [12]), with a magnitude such that $\mu = 1.85D$ [12]. Its parameterization for $0 \le R_{OM} \le 0.25\mathring{A}$ resulted in total dipole moments between 2.88 and 3.03D, with polarization energies accounting for 40 to 57% of the total configuration internal energy of water. Those thermophysical results in conjunction with the short-range over structuring of the site-site correlation functions, pinpointed some shortcomings of the simple point charge approximation for the polarization behavior at short intermolecular distances, as well as the inadequacy (steepness) of the r^{-12}-repulsive part of the non Coulombic interactions [20].

In this paper, we present new developments aimed at correcting the mentioned shortcomings thorough the introduction of smeared, as opposed to point charges, and the replacement of the r^{-12} by an exponential dependence. For comparison purposes we use the original parameterization and the latest (revised) neutron scattering data. In Section 2 we describe the modification introduced to the original model, and describe briefly the parameterization and simulation methodology. In Section 3 we present the simulation results for the model's thermodynamics, force-fields, and structure at ambient and high

temperature conditions for a series of geometries. Finally, we highlight some relevant conclusions.

2. MODEL DESCRIPTION AND PARAMETERIZATION

2.1. Smeared Charges plus a Self Consistent Point Dipole Polarizability

According to the neutron diffraction investigation of the intramolecular structure of liquid water [21], the actual geometry of water lies between that of the SPC [19] and the TIP4P [22] geometry, *i.e.*, a planar configuration with an $\mathrm{H-O-H}$ angle between 109.5˚ and 104.5˚, and an $\mathrm{O-H}$ bond length between 1.0Å and 0.9572Å, respectively. In this work we study the two geometries for $R_{OM} = 0.25\mathring{A}$ from which the resulting effective quadrupole moments are close to those of real water.

The first important modification to the original SCPDP model is the introduction of smeared charges, instead of the simple point charges, to improve the short-range polarization behavior. This is done using Gaussian distributions centered at the sites described by the simple point charge models, given by,

$$f_{i\alpha}(\mathrm{r}) = (2\pi\sigma_{i\alpha}^2)^{-3/2} q_i^{\alpha} \exp\left[-0.5\left(|\mathbf{r} - \mathbf{r}_{i\alpha}|/\sigma_{i\alpha}\right)^2\right] \tag{1}$$

where q_i^{α} is the magnitude of the charge in site α of the molecule i, and $\sigma_{i\alpha}$ is the width of the Gaussian charge distribution centered at $\mathbf{r}_{i\alpha}$. Thus, the charge-charge interaction contribution to the configurational energy becomes [23]

$$U_{qq} = 0.5\sum_{j\neq i}^{N}\sum_{\alpha,\beta}^{s} \frac{q_i^{\alpha} q_j^{\beta}}{|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}|} \mathrm{erf}\left(\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| \Big/ \left[2\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)\right]^{1/2}\right) \tag{2}$$

where erf is the error function. Note that this distribution (potential energy function) will render a finite value in the limit $\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| = 0$, *i.e.*, by recalling the behavior of the error function for small arguments,

$$\lim_{\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| \to 0} \left\{ \frac{q_i^{\alpha} q_j^{\beta}}{\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right|} \operatorname{erf}\left(\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| \Big/ \left[2\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)\right]^{1/2} \right) \right\} = \sqrt{2 \Big/ \pi\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)}\; q_i^{\alpha} q_j^{\beta} \tag{3}$$

where $\mathbf{r}_{i\alpha} = \mathbf{r}_i + \mathbf{r}_i^{\alpha}$ and $\mathbf{r}_i$ is the location of molecule i. Now, according to Thole's formalism [24], the electric field $\boldsymbol{E}_i^q$ at the center of mass of molecule i and the symmetric dipole tensor $\boldsymbol{T}_{ij}$ for smeared Coulombic charges are defined as

$$\boldsymbol{E}_i^q = -\frac{\partial \varphi}{\partial \mathbf{r}_i} \tag{4}$$

$$\boldsymbol{T}_{ij} = \frac{\partial^2 \varphi}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \tag{5}$$

where $\varphi \equiv \varphi\left(r, r_i, r_j, \sigma_{i\alpha}, \sigma_{j\alpha}\right)$ is the electrostatic potential of a system of smeared charges. Thus,

$$\boldsymbol{E}_i^q = \sum_{j \neq i, \beta}^{N} q_j^{\beta} \frac{\mathbf{r}_{i,j\beta}}{\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right|} \left\{ \left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right|^{-2} \operatorname{erf}\left(\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| \Big/ \left[2\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)\right]^{1/2} \right) - \sqrt{2 \Big/ \pi\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)}\; \exp\left(-\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right|^2 \Big/ \left[2\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)\right] \right) \right\} \tag{6}$$

and,

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$$\boldsymbol{T}_{ij} = \frac{1}{r_{ij}^3}\left(\frac{3\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^2} f - \boldsymbol{I} g\right) \tag{7}$$

where $\boldsymbol{I}$ is the unit tensor, and f and g are two coefficients dependent on $\left|\mathbf{r}_i - \mathbf{r}_j\right|$ and the Gaussian parameters whose precise forms are given elsewhere [23]. Finally, the induced electric field due to the point dipole polarizabilities is,

$$\boldsymbol{E}_i^p = \sum_{j \neq i}^{N} \boldsymbol{T}_{ij} \quad \boldsymbol{p}_j \tag{8}$$

so that the induced dipole moment on the center of mass of molecule i becomes,

$$\begin{aligned} \boldsymbol{p}_i &= \alpha \boldsymbol{E}_i \\ &= \alpha\left(\boldsymbol{E}_i^q + \boldsymbol{E}_i^p\right) \end{aligned} \tag{9}$$

The second modification to the original SCPDP model is the replacement of the Lennard-Jones oxygen-oxygen interactions for a Buckingham-type potential, to improve the short-range water structure. Thus, the total potential energy for a system of N water molecules described by the self-consistent point dipole polarizability model (SCPDP) becomes,

$$\begin{aligned} U_{SCPDP} = {} & 0.5 \sum_{i,j=1}^{N} \sum_{\beta,\gamma=1}^{3} \frac{q_i^{\alpha} q_j^{\beta}}{\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right|} \operatorname{erf}\left(\left|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}\right| \Big/ \left[2\left(\sigma_{i\alpha}^2 + \sigma_{j\beta}^2\right)\right]^{1/2}\right) \\ & - 0.5 \sum_{i=1}^{N} \boldsymbol{p}_i \quad \boldsymbol{E}_i^q + \varepsilon_{OO} \sum_{i \neq j}^{N} \left[\exp\left[12\left(1 - \left|\mathbf{r}_{i4} - \mathbf{r}_{j4}\right| \Big/ \sigma_{OO}\right)\right] - C\left(\frac{\sigma_{OO}}{\left|\mathbf{r}_{i4} - \mathbf{r}_{j4}\right|}\right)^6\right] \end{aligned} \tag{10}$$

where the oxygen site is taken as the fourth site in the model's geometry, *i.e.*, $\beta = \gamma = 4$ for the non-Coulombic $O - O$ interactions.

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2.2. Simulation Methodology

All simulations were performed in the canonical-isokinetic (NVT) ensemble, with N=256 particles at the system density of ρ=1.0g/cm^3 and temperature T=298K, and were started from well equilibrated configurations from the original polarizable model. Gear's fourth order predictor-corrector algorithm [25] with a Gaussian thermostat was used to integrate Newton-Euler equations of motion, which are based on Evans-Murad quaternion formalism [26]. The force-field parameters ε_{OO} and σ_{OO} for either model were determined following the same strategy as described elsewhere [12]. Standard periodic boundary conditions were used along with the minimum image criterion, a spherical center-to-center cutoff for the truncated intermolecular interactions, and a Verlet neighbor list. Pressure and configurational internal energy were corrected for the truncation $r_c = 8.6\mathring{A}$ by adding the standard long-range contributions [27]. Long-ranged Coulombic interactions were handled by a molecular reaction field approach with a dielectric constant $\varepsilon_{rf} = 78$ [28] in an analogous way as described in Appendix A of Ref. [12].

In this work we have chosen $R_{OM} = 0.25\mathring{A}$ so that the resulting effective quadrupole moments are close to the actual values. For any model geometry the electrostatic charges were determined by setting the permanent dipole moment $\mu = 1.85D$ [18]. The implicit electrostatic equation (9) with a molecular polarizability $\alpha = 1.444\mathring{A}^3$ [18] was then solved to self-consistency as described in Ref [12]. With the resulting force-fields we performed additional simulations at $T = 573K$ and $\rho = 0.72 g/cc$ with $\varepsilon_{rf} = 20$.

3. SIMULATION RESULTS AND DISCUSSION

The model parameterization was performed to reproduce the experimental values of $-9.92 Kcal/mol$ and $0.0 Kbars$ for the configurational internal energy and pressure, respectively. The resulting force-field parameters for the model are $\varepsilon_{OO}/k = 70.6K$,

$\sigma_{OO} = 3.514 Å$, and $C = 1.34$. The simulated site-site radial distribution functions for water at ambient conditions are compared in Figures 1-3 with two sets of neutron scattering experimental results, *i.e.*, the *de facto* standard for water structure determined by Soper and Phillips [29] (hereafter referred to as the NDIS-86) and the latest (and revised) results [7] (hereafter denoted the NDIS-97). Similarly, in Figures 4-6 the simulated structure of water at the state condition of $\rho = 0.72 g/cc$ and $T = 573 K$ is compared with the NDIS-97.

Although we have discussed the subject elsewhere [13] we must point out that, if the NDIS-97 is the most accurate data set currently available, the NDIS-86 data set appears to overpredict the strength of the $O-O$ and $O-H$ pair correlation functions, even though both data sets fulfill thermodynamic consistency tests [30]. Moreover, because the two data sets were determined by the same research group, *i.e.*, they have not been reproduced by any independent group, for comparison purposes we include the NDIS-86 and the NDIS-97 to give a sense of the magnitude of the current uncertainties associated with the water microstructure.

Preliminary results indicated that the introduction of smeared charges into the original SCPDP model with $R_{OM} = 0.25 Å$ (and a Lennard-Jones potential) induces a small (though noticeable) decrease of the polarization at short distance, with a simultaneous shift of the first peak of the correlation functions [23]. Yet, this is not the sizable change of polarization we expected to obtain. We have also noticed that the first second peak of the $g_{OO}(r)$ still shows a distinctive change of curvature around $r \approx 4 Å$ (see Figure 5 of Chialvo and Cummings [12]) rather than the well defined and symmetric peak found by neutron scattering.

The introduction of the exponential (Buckingham-type) in place of the r^{-12} (Lennard-Jones) repulsive term induces a large decrease (approximately by one) in the observed strength of the first peak of $g_{OO}(r)$ for ambient water, without affecting the

definition of the second peak (compare Figure 5 of Chialvo and Cummings [12] and our Figure 1). Yet, while the simulated $g_{OH}(r)$ and $g_{HH}(r)$ are in remarkable better agreement with the NDIS data (specially with the NDIS-86) than the original SCPDP model (see Figures 6 and 7 of Ref. [12] for $R_{OM} = 0.25\AA$), there is still room for improvements which should be guided by analysing other experimental information such as phase diagram and dielectric constant.

For the water structure at high temperature, the new version of the SCPDP model gives a similar agreement with the NDIS-97 as the original model (note that in Ref. [12], Figures 8-10, this comparison was done with the NDIS of [6] which were later revised to become NDIS-97 [13]), though the strength of the first peak of the simulated $g_{OO}(r)$ is in almost perfect agreement with the experimental one.

In terms of thermophysical properties, the total dipole moment predicted by the model decreases from $2.87 \pm 0.02 D$ at ambient conditions to $2.39 \pm 0.05 D$ at the high temperature conditions (compare this value with the *ab initio* simulation result of 2.3±0.2D [31]), with a polarization energy decreasing from $-4.2 \pm 0.2\, Kcal/mol$ to $-1.6 \pm 0.1 Kcal/mol$, respectively.

In summary, the revised model is able to describe accurately the pressure and configurational energy of water at ambient conditions, while maintaining the experimental value for the permanent dipole moment. The resulting structure at ambient conditions shows a remarkable improvement over the original model, through the combined effects of smeared Coulombic charges and a more realistic repulsive term for the non-electrostatic $O-O$ interactions. Similar improvement is observed for the structure of water at high temperature.

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FIGURE CAPTIONS

Figure 1: Comparison between the experimental NDIS-97, NDIS-86, and the simulated $O-O$ radial distribution functions of ambient water.

Figure 2: Comparison between the experimental NDIS-97, NDIS-86, and the simulated $O-H$ radial distribution functions of ambient water.

Figure 3: Comparison between the experimental NDIS-97, NDIS-86, and the simulated $H-H$ radial distribution functions of ambient water.

Figure 4: Comparison between the experimental NDIS-97 and the simulated $O-O$ radial distribution functions of water at 573K and 0.72g/cc.

Figure 5: Comparison between the experimental NDIS-97 and the simulated $O-H$ radial distribution functions of water at 573K and 0.72g/cc.

Figure 6: Comparison between the experimental NDIS-97 and the simulated $H-H$ radial distribution functions of of water at 573K and 0.72g/cc.

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Figure 1

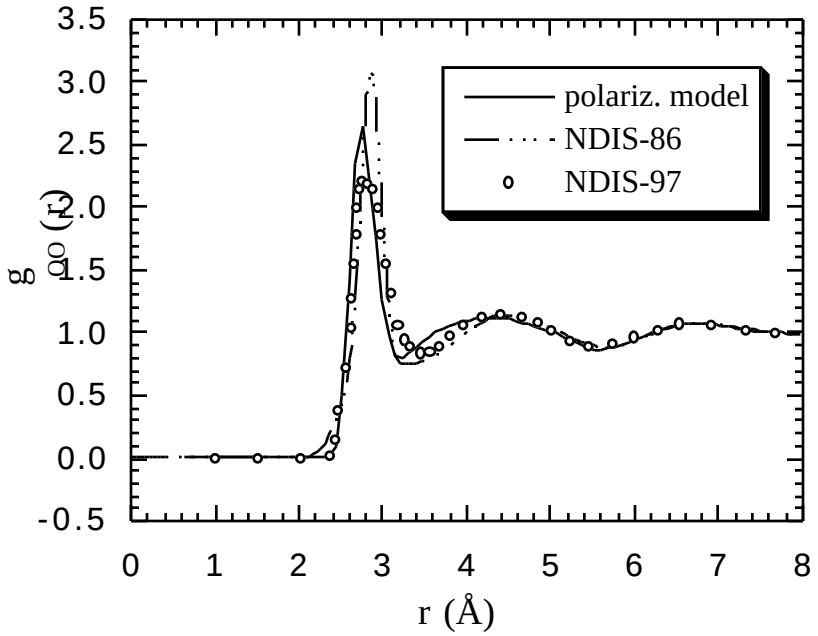

Figure 2

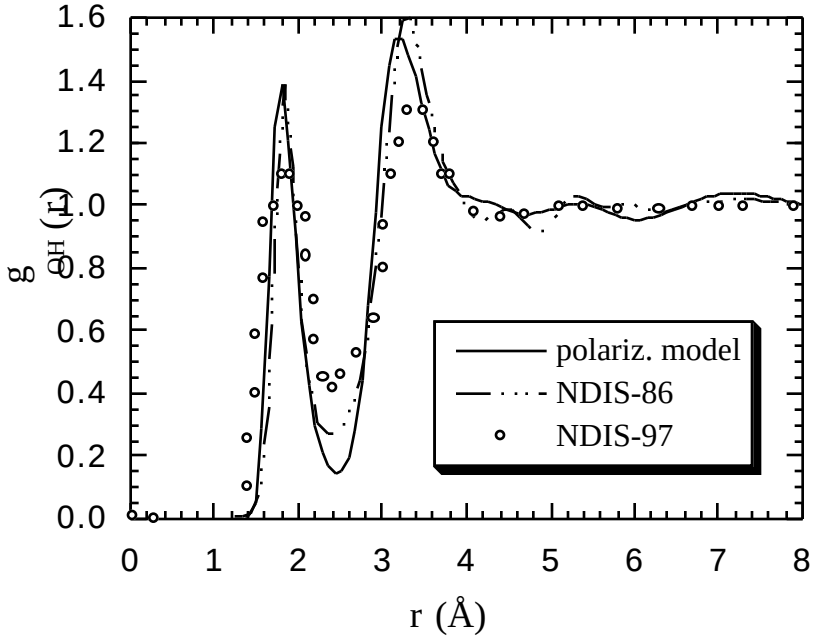

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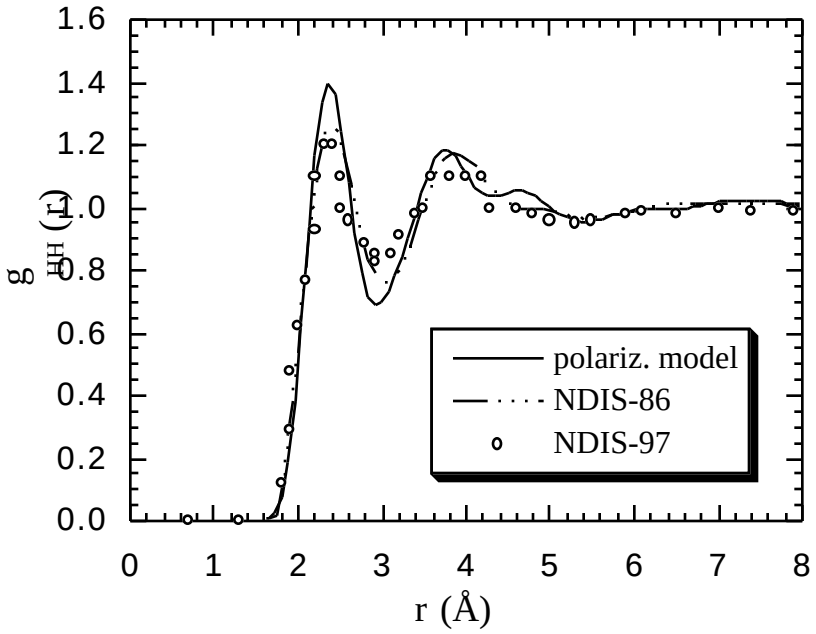
Figure 3



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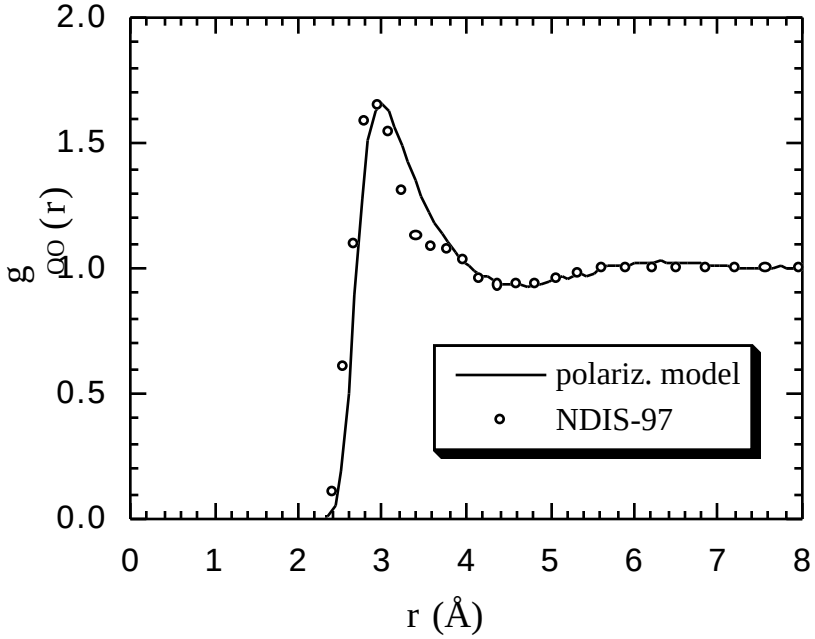

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Figure 5

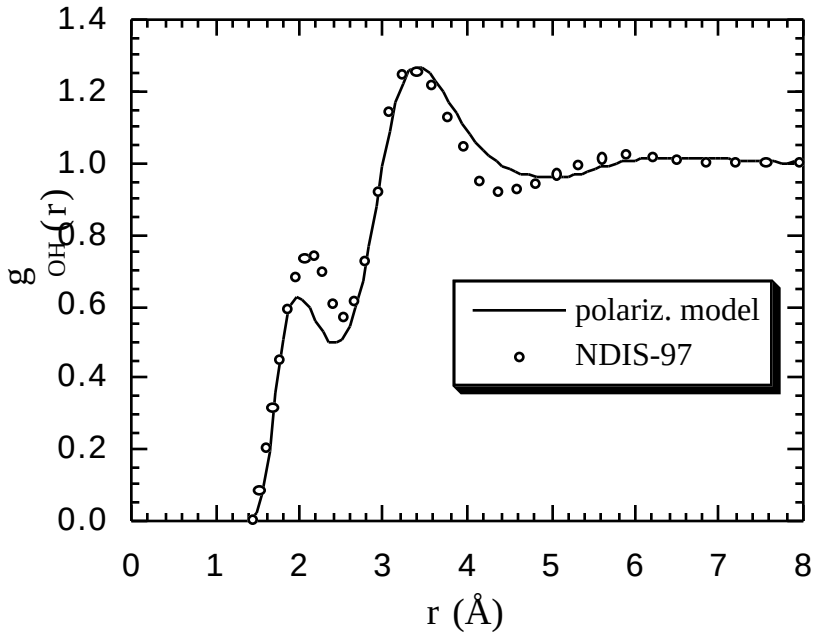
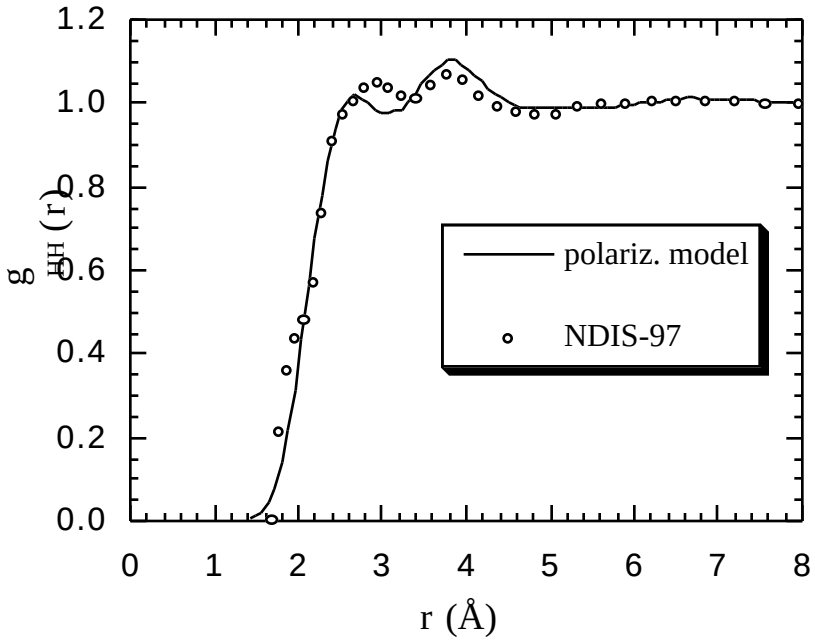


Figure 6



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