

Interplay between Molecular Simulation and Neutron Scattering in Developing New Insights into the Structure of Water[†]

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For three decades, molecular models for water, nature's most important liquid, have been developed and refined by fitting to structure measured by neutron scattering. The decade-old widely accepted structure of water at room temperature and pressure was recently revised as a byproduct of attempts to understand the structure of high-temperature/high-pressure water for which, in a remarkable reversal of roles, molecular models successfully pinpointed inaccuracies in scattering data. Subsequent improvements in analyzing scattering data have led to reevaluation of water structure at normal conditions. This remarkable interplay between molecular modeling and experiment suggests molecular methods can effectively complement scattering experiments.

Introduction

Water is the most ubiquitous and intriguing fluid in nature, crucial for the existence of life and a central component in many industrial and most biochemical processes (Franks, 1972). Its significance hinges on its unusual properties, resulting from its ability to form short-ranged, strongly directional, and strongly attractive hydrogen bonds, which make water perhaps the most challenging of all fluids to understand (Stillinger, 1980). Over the years researchers have debated over the nature of the hydrogen bond interaction and its microstructural manifestation in ambient liquid water and supercooled water, as well as at extreme conditions of temperature and pressure. Using X-ray and neutron scattering techniques, researchers have been able to study the local structure of water, that is, to elucidate how water molecules are statistically distributed around each other.

For >25 years, attention has been focused mainly on water at ambient conditions (1 atm, 25 °C; Beveridge et al., 1983), though some controversy continues on the accuracy of the existing scattering data. A renewed interest in the structure of water was recently stimulated by Postorino et al. (1993) who reported new structural data for ambient and high-temperature water from neutron scattering with isotope substitution (NDIS). The new scattering data were controversial for several reasons (discussed later) and immediately generated an enthusiastic scientific discussion (Bellissent-Funel et al., 1997; Chialvo and Cummings, 1994; Chialvo and Cummings, 1996; Gorbaty and Kalinichev, 1995; Hoffmann and Conradi, 1997; Kalinichev and Bass, 1994; Löffler

et al., 1994; Mountain, 1995; Soper, 1996; Yamanaka et al., 1994). In what follows, we critically discuss the interplay that took place between simulation practitioners and neutron scattering experimentalists in quest of a reliable microstructural characterization of water at ambient and supercritical conditions. In particular, we highlight the most controversial features of the NDIS data through a direct comparison between the NDIS data, ab initio simulation results, and new "classical" simulation results based on nonpolarizable and polarizable water models. Finally, we summarize some of the outcomes and consequences of this fruitful interplay.

Microstructure of Water at High Temperature and the Hydrogen Bonding Controversy

The unusual behavior of high-temperature water is typically ascribed to the profound changes undergone by its hydrogen-bond network, and as a consequence, points to the need for a reliable microscopic characterization of the water structure as well as an adequate description of hydrogen bonding (Chialvo and Cummings, 1994; Chialvo and Cummings, 1996; Gorbaty and Kalinichev, 1995; Kalinichev and Bass, 1994).

Through a direct comparison between their NDIS data and our earlier simulation results at rather different state conditions (Cummings et al., 1991), Postorino et al. (1993) made two claims. First, they stated that hydrogen bonding disappeared at 400 °C; that is, (see Figure 1) as a result of the diminishing amplitude and changing position of the first peak of the oxygen–hydrogen radial distribution function, $g_{OH}(r)$ which they interpreted as a measure of hydrogen bonding. Second, they doubt the capability of the currently used simple water models to represent water structure at high temperature.

The challenge of the new NDIS results prompted a thorough reevaluation of the simple models used in molecular simulations of water (Chialvo and Cummings, 1994; Chialvo and Cummings, 1996). The claim by Postorino et al. (1993) concerning the disappearance of hydrogen bonding ensured that the paper was widely read and carefully studied. Almost immediately it

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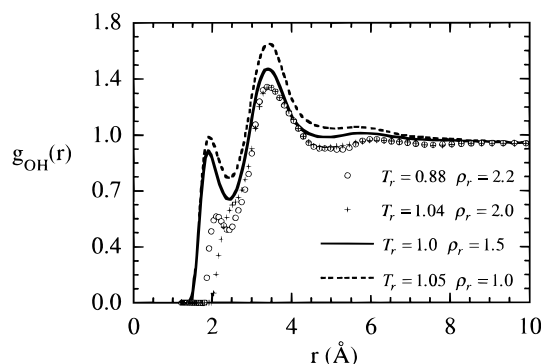


Figure 1. Comparison between the NDIS (o and +; Postorino et al., 1993) and the SPC-simulated intermolecular O—H radial distribution function (— and - - -; Cummings et al., 1991) of water at high temperature.

became clear that the new NDIS results were seriously flawed. Given the complexity of the NDIS experiments and the many possible sources of errors in the processing of the raw data, it was not unreasonable to suspect the possibility of artifacts (Löffler et al., 1994). For example, the experimental data exhibited unexpected behavior in the temperature dependence of the hard-core for the O—H interactions; that is, an increasing hard-core diameter with temperature (see Figure 1).

Initially it was unclear whether the disagreement between the predicted and measured correlation functions was a reflection of unrealistic intermolecular models, inadequate methods of processing the raw NDIS data, or a combination of both. Molecular simulations gave the first clues concerning the anomalies in the NDIS data. Chialvo and Cummings (1994 and 1996) pointed out the unphysical features of the new NDIS data and the unusual isothermal density dependence of the amplitude of the first peak of the oxygen—hydrogen radial distribution function, $g_{OH}(r)$. This quantity measures the ratio of the local density to the bulk density of hydrogen atoms in a spherical shell at a distance r from an oxygen atom. It is therefore a dimensionless quantity that goes to unity at large r and to zero at small r , reflecting exclusion at short distances. The amplitude of the first peak decreases with increasing density and the corresponding coordination number increases (Chialvo and Cummings, 1994; Chialvo and Cummings, 1996; Löffler et al., 1994). By analyzing an orientationally dependent version of $g_{OH}(r)$, Chialvo and Cummings also concluded that neither the height of the first peak of $g_{OH}(r)$ nor the corresponding coordination number, $n_{OH}(r) = 4\pi\rho_H \int_0^r g_{OH}(r')r'^2 dr'$, adequately measure the strength of the hydrogen bonding in water. This conclusion is consistent with the study of Kusalik and Svishchev (1994) who characterized water structure by unambiguous spatial distribution functions and pointed out the limitations of the radial distribution analysis of water structure.

Löffler et al. (1994) suggested that the observed unphysical features were the result of a rather large correction for inelastic scattering in the NDIS data for light water, and that the “bump” at the base of the left side of the first peak of the oxygen—oxygen radial distribution function, $g_{OO}(r)$, as well as the disappearance of the first peak of the $g_{OH}(r)$, had a common source as an artifact of the inelasticity corrections (see discussion of their Figure 4).

Interestingly, even though the neutron scattering experimentalist (Tromp et al., 1994) claimed that “it is

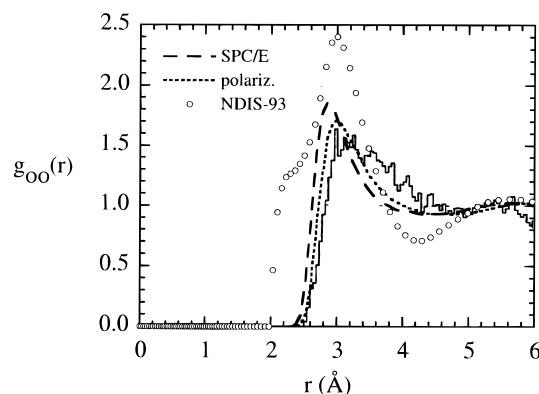


Figure 2. Comparison between the NDIS-93 (o; Postorino et al., 1993) at $\rho = 0.66$ g/cm³ and $T = 673$ K, the *ab initio* (choppy line; Fois et al., 1994), and the “classical” simulated O—O radial distribution function (— and - - -) of water at $\rho = 0.64$ g/cm³ and $T = 730$ K.

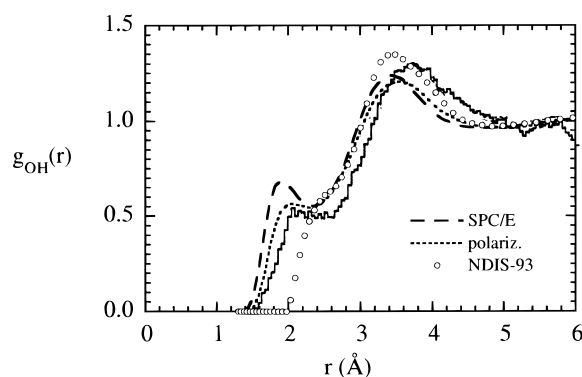


Figure 3. Comparison between the NDIS-93 (o; Postorino et al., 1993) at $\rho = 0.66$ g/cm³ and $T = 673$ K, the *ab initio* (choppy line; Fois et al., 1994), and the “classical” simulated intermolecular O—H radial distribution function (— and - - -) of water at $\rho = 0.64$ g/cm³ and $T = 730$ K.

a straightforward matter to compare the results with those of computer simulation. Indeed in our previous letter (Postorino et al., 1993), we showed that in so doing there exist a significant difference between SPC model and the experimental results.In passing we note that in private communication with the group of Parrinello (Fois et al., 1994), an *ab initio* computer simulation based on the Car-Parrinello method (Car and Parrinello, 1985) gives good agreement with our results...” the alluded comparison in fact was neither at the same state conditions as (see Figure 1), nor in any acceptable agreement with the NDIS experiment (see Figures 2–4).

The most convincing indications of inconsistencies in the NDIS data comes from the comparison between *ab initio* (Fois et al., 1994) and “classical” simulations of the microstructure of supercritical water at $T = 730$ K and $\rho = 0.64$ g/cm³ (the state conditions at which the *ab initio* calculations have been performed) contrasted with Fois et al. comparison between *ab initio* at $T = 730$ K and $\rho = 0.64$ g/cm³ and NDIS at $T = 653$ K and $\rho = 0.66$ g/cm³. *Ab initio* simulations provide a description of the fluid behavior without preassigning an interaction potential, rather by determining the interactions from electronic structure calculations within the Born–Oppenheimer approximation during the simulation (Car and Parrinello, 1985).

In terms of the hard-core diameters as well as the location and strength of the peaks of the site–site correlation functions, our direct comparison between

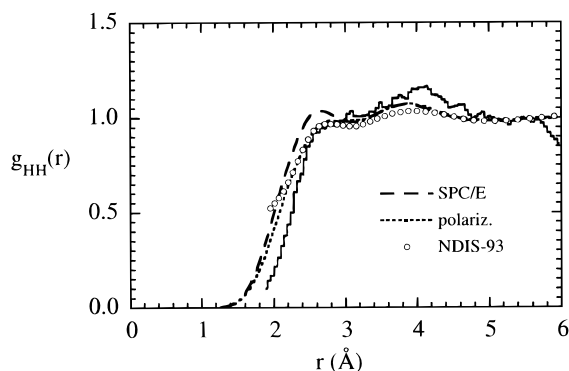


Figure 4. Comparison between the NDIS-93 (Postorino et al., 1993) at $\rho = 0.66 \text{ g/cm}^3$ and $T = 673 \text{ K}$, the *ab initio* (choppy line; Fois et al., 1994), and the “classical” simulated intermolecular H—H radial distribution function (— and - -) of water at $\rho = 0.64 \text{ g/cm}^3$ and $T = 730 \text{ K}$.

“classical” simulations, *ab initio* simulations, and the Postorino et al. NDIS data (see Figures 2–4) actually supports the accuracy of the prediction of the “classical” water models rather than the NDIS data. First, and most noticeable, are the hard-core diameters (excluded volumes) from the *ab initio* radial distribution functions $g_{\text{OO}}(r)$ and $g_{\text{OH}}(r)$; that is, ~ 2.5 and $\sim 1.5 \text{ Å}$, respectively, in comparison with ~ 2.4 and $\sim 1.5 \text{ Å}$, respectively, as predicted by most water models, and in sharp contrast to ~ 2 and $\sim 2 \text{ Å}$, respectively, as indicated by the NDIS. Second, the “classical” simulations predict $g_{\text{OO}}(r)$ with a first-peak height of ~ 1.8 in comparison with the *ab initio* value of ~ 1.6 and in contrast to ~ 2.4 from NDIS. Note also the formation of a flat first peak for the *ab initio* $g_{\text{OH}}(r)$ at $2 \text{ Å} < r < 2.5 \text{ Å}$, in remarkable agreement with the “classical” water model (especially the polarizable model). Third, the *ab initio* total (permanent + induced) dipole moment (*i.e.*, $2.3 \pm 0.2D$) is in very good agreement with $2.27 \pm 0.01D$ from our polarizable model (note that the extended SPC model has an effective permanent dipole moment of $2.35D$).

Further evidence of these unphysical features were given later by Jedlovsky and Vallauri (1996) through their reverse Monte Carlo simulation study, which also does not rely on any intermolecular potential model (McGreevy and Pusztai, 1988). Their results showed that the NDIS correlation functions could not represent simultaneously any real three-dimensional (3D) distribution of water molecules.

Interplay and Its Consequences on the Characterization of Water Structure

In this interesting interplay between modeling and experiment, the mounting challenges (Chialvo and Cummings, 1994; Chialvo and Cummings, 1996; Gorbaty and Kalinichev, 1995; Jedlovsky and Vallauri, 1996; Löffler et al., 1994; Mountain, 1995; Yamanaka et al., 1994) prompted Soper et al. (1997) to reexamine their high-temperature NDIS experiments with greater attention to the inelasticity correction. This correction becomes a large source of uncertainty at high temperature and remarkably difficult to estimate for light isotopes (Montague, 1991; Postorino et al., 1995). Realistic constraints were also imposed on the hard-core diameters of the pair correlations to avoid unphysical behavior at short range. The new method of analysis of the raw data better represents the inelasticity corrections, according to these authors (Bruni et al., 1996;

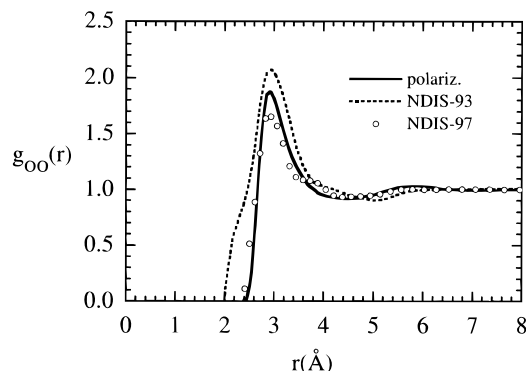


Figure 5. Comparison between the NDIS and simulated O—O radial distribution function of water at $\rho = 0.72 \text{ g/cm}^3$ and $T = 573 \text{ K}$. The SPC model with a permanent dipole moment of $2.15D$ superimposes its representation with the polarizable model.

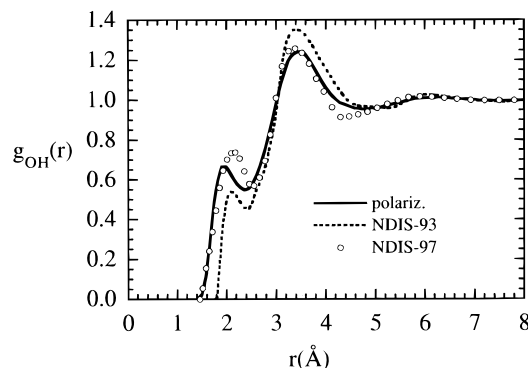


Figure 6. Comparison between the NDIS and simulated intermolecular O—H radial distribution function of water at $\rho = 0.72 \text{ g/cm}^3$ and $T = 573 \text{ K}$. The SPC model with a permanent dipole moment of $2.15D$ superimposes its representation with the polarizable model.

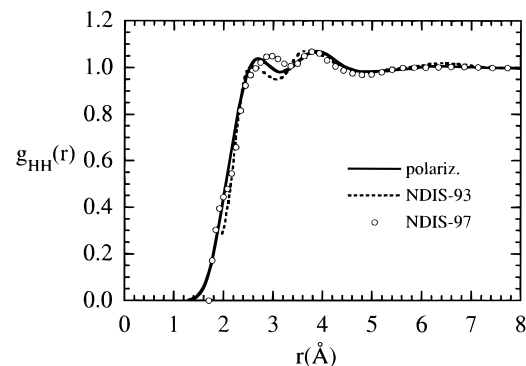


Figure 7. Comparison between the NDIS and simulated intermolecular H—H radial distribution function of water at $\rho = 0.72 \text{ g/cm}^3$ and $T = 573 \text{ K}$. The SPC model with a permanent dipole moment of $2.15D$ superimposes its representation with the polarizable model.

Soper et al., 1997), and consequently, the resulting microstructures from different experiments become consistent with one another.

The reanalyzed scattering data (here referred to as NDIS-97) are compared in Figures 5–7 with simulation results with a new polarizable model (Chialvo and Cummings, 1996) and modified SPC model with permanent dipole of $2.15D$ (Chialvo and Cummings, 1997). For illustration purposes, we also include in these figures the original NDIS data of Postorino et al. (1993), here referred to as NDIS-93. Perhaps the most revealing features of the NDIS data are related to $g_{\text{OO}}(r)$ and $g_{\text{OH}}(r)$. In particular, note in Figure 5 the shift of the

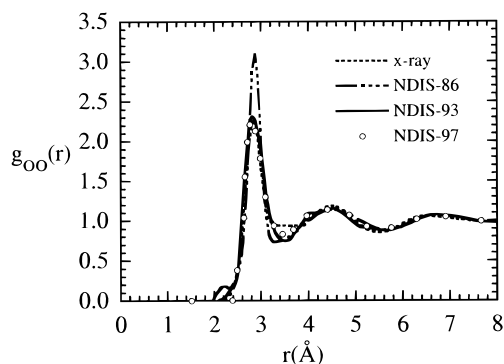


Figure 8. Comparison between scattering results from Soper and Phillips (1986; NDIS-86), Postorino et al. (1993; NDIS-93), Soper et al. (1997; NDIS-97), and X-ray results from Gorbaty and Demianets (1985) for the O-O radial distribution function of water at ambient conditions.

hard-core diameter in the $g_{OO}(r)$ from ~ 2.0 Å (NDIS-93) to ~ 2.5 Å (NDIS-97), and the decreased amplitude of the first peak from 2.1 to 1.75. Likewise, note in Figure 6 the shift of the hard-core diameter in $g_{OH}(r)$ from 1.75 Å (NDIS-93) to 1.5 Å (NDIS-97), and the simultaneous increase in the amplitude of the first peak from 0.55 to 0.75. These NDIS-97 results are in very good agreement with the corresponding results from *ab initio* simulations, from the modified SPC model, and from the new polarizable model.

The revised NDIS results have a few unexpected consequences. By comparison with earlier NDIS structural data for ambient water by Soper and Phillips (1986), NDIS-86, we find that the earlier NDIS results actually overpredict the amplitude of the $g_{OO}(r)$ and $g_{OH}(r)$ correlations, even though they satisfy some essential thermodynamic constraints (Lie, 1986). In turn, this means that most current water models included in commercial simulation packages, whose parametrization was guided by Soper and Phillips data (the *de facto* standard NDIS-86), might also fail to reproduce the actual structure of water. However, because these models exhibit qualitatively the main features of the three pair correlation functions, and give realistic trends for the temperature and density effects of many thermophysical properties of water, is possible that only minor adjustments are required. In addition, as shown in Figure 8, the new NDIS data suggests that earlier X-ray and neutron scattering determinations of $g_{OO}(r)$ of water at ambient conditions by Narten et al. (1982) and Gorbaty and Demianets (1983) are in fact more accurate than has been generally accepted over the past decade.

Because the comparison between simulation results and experimental data is at the heart of the validation of any molecular-based modeling effort, this interplay suggests a few important items to bear in mind. First, because of the experimental complexity and likelihood of undesirable numerical artifacts in the raw data processing, we need independent verification of the current NDIS. Fortunately, work is already in progress in that direction (Bellissent-Funel et al., 1997). Second, and for the same reason, it would be desirable to develop alternative experimental methods to determine microstructure, to avoid the use of isotope substitution and its troublesome inelasticity corrections. Third, we need alternative or complementary molecular-based methods to efficiently check the reliability of the experimental structural results, before they are used in model pa-

rametrization. Again, very new developments on the reverse Monte Carlo method are aimed toward that goal (Pusztai and McGreevy, 1997; Tóth and Baranyai, 1997).

Conclusions

In summary, the constructive interplay between molecular-based simulations and neutron scattering experiments on supercritical water has resulted in a thorough reexamination of both techniques. Better models for simulating water and better techniques for processing raw scattering data have resulted. Important implications have also resulted for studies of ambient water.

Molecular simulation has played an indispensable and unprecedented role in these developments. This unexpected outcome is an indication of the increasing reliability of the intermolecular potential models and the accuracy of the simulation results, made possible by high performance workstations and massively parallel supercomputers. The substantial agreement between models and experiments that has resulted from this interplay gives us greater confidence now in our abilities to measure and predict the microstructural properties of water at all conditions.

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Dedication

We are very pleased and honored to have the opportunity to dedicate this paper to Professor John M. Prausnitz on the occasion of his 70th birthday. Over many decades of distinguished scientific and engineering research, John foresaw long before others the role molecular-level modeling would play in chemical engineering. Today it is assumed in almost every subfield of chemical engineering (including reaction engineering, separations, transport phenomena, bioengineering, and thermodynamics) that a molecular-level understanding of the phenomena involved is essential to fully appreciate the potential of the related processes and the issues involved in their scale-up. Much of this current appreciation for the molecular-level perspective is a result of John's efforts, not only to show by his own research that molecular-level understanding has practical implications, but to evangelize the field to this new paradigm. In the work we present in this paper, we describe a situation in which molecular theory has led to new understanding of molecular-based experiment (neutron scattering) on a system of perennial interest (water). One of the first papers one of us (PTC) published on the subject of water concerned the phase envelope of water and was published jointly with John (*J. Chem. Phys.* **1991**, *93*, 7355–7359). In fact, this paper established the critical point of SPC water, which then permitted us to study supercritical water (as modeled by SPC), and in many ways finally led to the interplay between theory and experiment described in

this paper. We trust that John enjoys the overview we have presented in this paper, and the unusual story of theory resulting in new insights into experiment.

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