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## Bridge over troubled water: the apparent discrepancy between simulated and experimental non-ambient water structure

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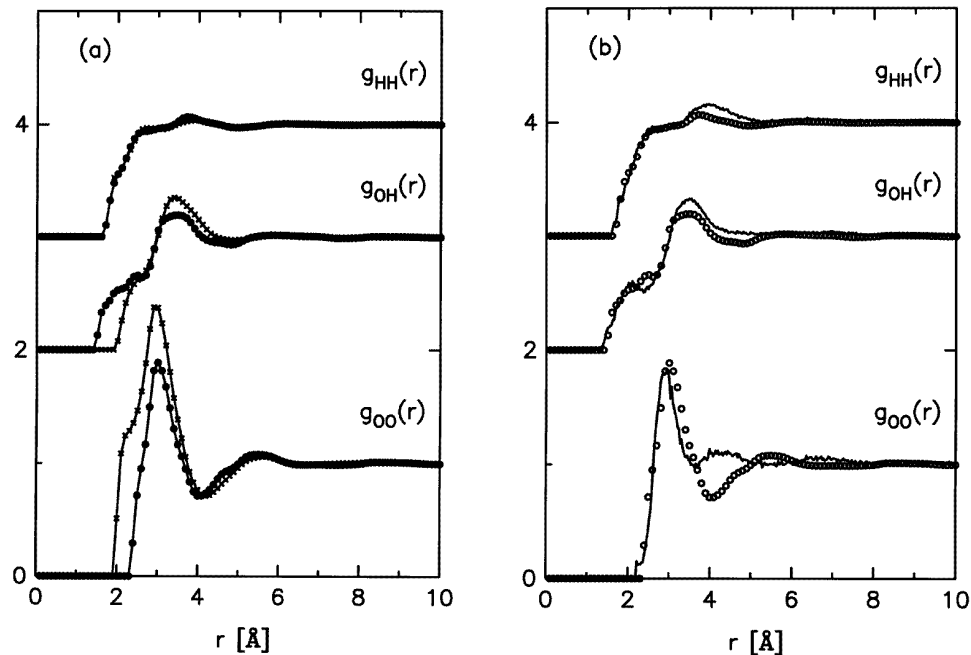
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**Abstract.** Recent neutron diffraction experiments, which exploit hydrogen isotope substitution techniques to extract the HH, OH and OO site–site radial distribution functions for water, indicate that as the temperature of water is raised above the critical point, the hydrogen-bonding network, as measured by the height of the first peak in the OH distribution function, collapses. Several computer simulations, however, dispute the accuracy of the experimentally determined distribution functions: they show that the measured data cannot be obtained from any physical arrangement of water molecules. By applying additional constraints on the small-radius behaviour of the radial distribution functions, and by repeating some of the experiments under different experimental conditions, the accuracy of the extracted radial distribution functions has now been improved. The new distribution functions, while not qualitatively different from what has already been published, satisfy the fundamental objection to the previous results, namely they can be simulated with physical assemblies of water molecules. These simulated distributions of molecules indicate a weak degree of hydrogen bonding in water at 673 K which is greatly reduced compared to that in the hydrogen-bond network of ambient water. The analysis is supported by a new computer simulation of water structure using an ‘empirical’ water interaction potential, which contains none of the long-range features of traditional charge models, such as SPC/E. This short-range potential is able to reproduce most features of the experimental data to good accuracy, even under supercritical conditions.

At about the time when Simon and Garfunkel first sang their famous song, Barker and Watts (1969), and Rahman and Stillinger (1971), had begun to calculate the properties of water using an assumed intermolecular potential energy function with the (then) novel technique of computer simulation. The water potential, involving as it did long-range charge interactions, was too complex to be tackled by standard liquid-state theory (Hansen and McDonald 1986), and the main ideas about water structure had been based on disordered crystalline models of the liquid (Narten and Levy 1969). Now it became possible to generate a wide range of three-dimensional configurations of water molecules for which positional correlations disappeared after the relatively short distance of 8 Å or so, a view which was in contrast to the ‘static’ picture generated by quasi-crystalline models of water structure.

Although these early computer models of water were tested against the available x-ray and neutron total diffraction pattern data from water, it was more than a decade later before the first attempts to measure the individual site–site pair correlation functions of water, using three neutron diffraction experiments with different hydrogen isotope substitutions, could

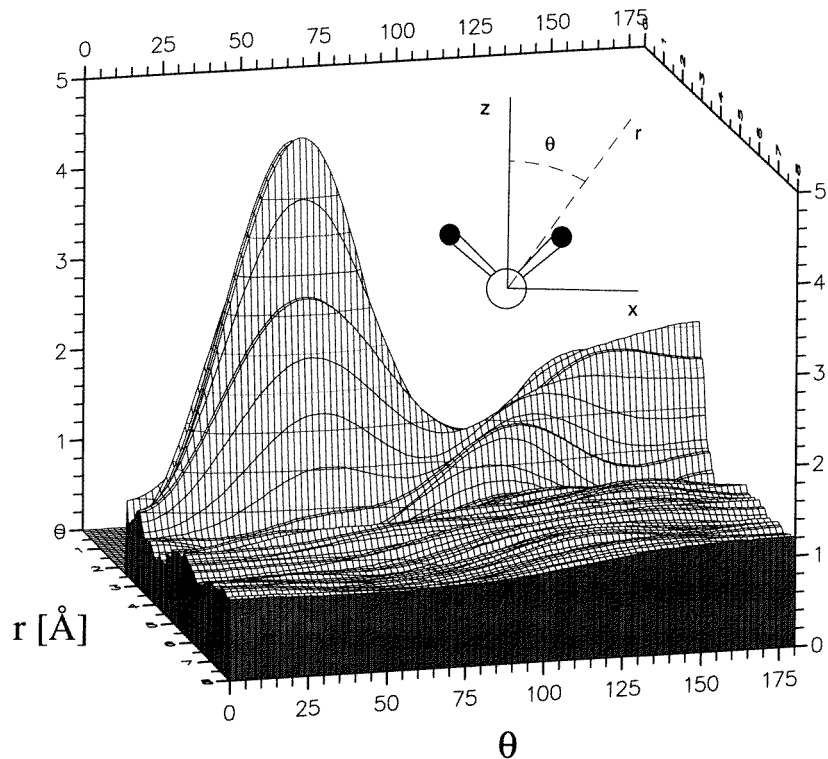
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**Figure 1.** (a) Comparison of the old (crosses) and new (circles) versions of the measured HH, OH and OO pair correlation functions for water at 673 K and at a density of 0.022 molecules per  $\text{\AA}^3$ . (b) The new version of the correlation functions (circles) compared with the result of the empirical potential Monte Carlo simulation using a potential derived from the ambient water diffraction data (line).

be compared with the simulations (Narten *et al* 1982, Soper and Silver 1982, Soper and Phillips 1986). There was far from perfect agreement between the different experimental results. Nonetheless the search for an improved water potential persisted (Berendsen *et al* 1987, Watanabe and Klein 1989), and to some extent was influenced by the new diffraction data. These new effective potentials were subsequently used to predict the structure and thermodynamics of water under non-ambient conditions (see, for example, Kalinichev 1991, Cummings *et al* 1991, Brodholt and Wood 1993, Guissani and Guillot 1993) and were shown to give a sensible description of the thermodynamic properties of water near the critical point (Guissani and Guillot 1993). The appropriate experimental information on the site–site correlation functions for water under non-ambient conditions appeared shortly after (Postorino *et al* 1993, Tromp *et al* 1994, Postorino *et al* 1994), not, however, without some controversy (Löffler *et al* 1994, Chialvo and Cummings 1994, Gorbaty and Kalinichev 1995, Jedlovszky and Vallauri 1996).

The most significant discrepancy between the experiments and computer simulation was the apparent disappearance of the first intermolecular peak at  $r \approx 1.9$  Å in the oxygen–hydrogen (OH) radial distribution function as water was taken above its critical point. Löffler *et al* (1994) pointed out that the same data showed an unphysical extra intensity on the low-radius side of the main oxygen–oxygen (OO) radial distribution peak, and surmised that a systematic effect had somehow biased the OO and OH experimental distribution functions in opposite ways in this region. In addition Jedlovszky and Vallauri (1996) showed by reverse Monte Carlo simulation that all three site–site radial distribution functions could not



**Figure 2.** Spatial distribution of water about water, as defined by Svishchev and Kusalik (1993). The inset shows the geometry of the problem. The plane of the central water molecule coincides with the  $z$ - $x$  plane of the coordinate system, and the spatial density of the surrounding molecules is shown as a function of  $\theta$  and the radial distance  $r$  in this same plane. Note that the pronounced peak at  $\theta = 55^\circ$  corresponds to hydrogen bonding to a central water molecule. In ambient water this same peak is approximately three times higher than the one shown here, which combined with the lower density at 673 K, implies that the number of hydrogen-bonded water molecules around a central molecule in supercritical water is less than one quarter of the number under ambient conditions.

simultaneously be generated from a single three-dimensional distribution of water molecules.

The most likely candidate as a source of systematic bias in the neutron experiment is the inelasticity correction. If only the hydrogen-hydrogen (HH) pair correlation function is to be determined, then inelasticity effects should cancel to a good approximation (Soper and Silver 1982, Soper and Phillips 1986), but if the OH or OO terms are also needed, then some estimate of the inelasticity effect is required and a rigorous way of obtaining this has not yet been achieved (Zetterstrom *et al* 1996). Since these effects become progressively larger as the temperature of water is raised it is increasingly possible that the neutron OO and OH correlation functions will contain residual inelastic effects as the temperature is raised.

A new analysis of all the available high-temperature-high-pressure data on water was recently undertaken (Soper *et al* 1996). By applying realistic constraints on the low- $r$  behaviour of the correlation functions much of the systematic error was removed from the extracted site-site correlation functions. It was shown that these new radial distribution

functions did not suffer from the flaws of the earlier data, and that they could be generated from physical distributions of water molecules. Nonetheless the overall conclusion did not change appreciably, namely the first OH peak becomes indistinct and merges with the second peak above the critical point. In addition there appeared to be a small but significant movement of the first OH peak position with density at 573 K. For completeness the new versions of these radial distribution functions are compared with the old versions at 673 K in figure 1.

In parallel with the revised data analysis procedures an extension of the RMC procedure (called the 'empirical potential Monte Carlo' (EPMC) procedure; Soper 1996a) has been devised which generates a set of effective site-site potential energy functions for water. Because they are based on the radial distribution function the EPMC potentials for ambient water have a range of not more than about 8 Å (Soper 1996b). It is interesting to note that these empirical potentials generate a remarkably good fit to the data of figure 1 (Soper 1996b). The agreement with the HH and OH functions for both state points is particularly good, while the agreement with the OO function is less good, especially at 673 K. It is clear however that the first OH peak at both state points is significantly weaker in both the experiment and in the EPMC simulation than in the simulations with assumed potential functions such as SPC (Löffler *et al* 1994). Chialvo and Cummings (1994) in fact argue that the height of the first peak in the OH pair distribution function is not sufficient by itself to establish the degree of hydrogen bonding in the liquid. Instead it is necessary to apply orientational and energy constraints as well.

To address this issue the distributions of water molecules that were obtained from fits of the revised data of figure 1 were used to generate the spatial distribution function (Svishchev and Kusalik 1993) of water molecules about a central molecule at 673 K. The result is shown in figure 2, where it is seen that in the direction of the hydrogen bond,  $\theta = 55^\circ$ , there is indeed a lobe of density. The height of this lobe, however, bearing in mind the lower molecular number density at this temperature, corresponds to a reduction by a factor of  $\sim 4$  in the number of neighbouring water molecules involved in hydrogen bonding compared to that for ambient water.

In conclusion, it is possible to generate the revised site-site correlation functions for supercritical water from physical distributions of water molecules. In this case computer simulation has enabled an assessment to be made of both the accuracy of what is measured and what is implied by an assumed intermolecular potential. Because of the importance of establishing an accurate water potential suitable for a range of state conditions, I would hope that in the future the disparate diffraction and simulation communities can work more closely together, and, perhaps using computer simulation as a tool, form a *Bridge Over Troubled Water*.

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