

Unpredicted density dependence of hydrogen bonding in water found by neutron diffraction

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The oxygen-hydrogen pair correlation functions for water are determined at five density states along the $T=573$ K isotherm, using the hydrogen isotope substitution technique in a neutron-diffraction experiment. The results are sufficiently accurate to reveal significant discrepancies with computer simulations of water, which use the traditional site-site charge interactions to generate hydrogen bonds. They imply that these models of the interatomic potential overemphasize the strength of the hydrogen bonding interaction in water. [S0163-1829(96)08541-4]

The phenomenon of hydrogen bonding plays a fundamental role in the structure, function and properties of many liquids of chemical and biological importance. The interaction manifests itself as a pronounced, directional correlation between specific sites on neighboring molecules. It also produces a highly characteristic vibrational density of states in hydrogen bonded molecules, and dramatically affects the thermodynamic properties of a fluid compared to what they would be if the molecules interacted simply by van der Waals interactions.¹

Arguments have persisted over many decades over the true cause of the hydrogen bond interaction. Conventional analyses, particularly with regard to understanding the solid forms of water,² treat the hydrogen bond as if it were a weakly covalent effect associated with the so-called "lone pair" electrons on a hydrogen-accepting site: hence the use of the term "bond." Moreover, simple "sticky hard sphere" (that is short-range) models of the hydrogen bond are able to reproduce the essential features of the atom-atom correlation functions of water under ambient conditions and successfully describe the solvation of simple ions in solution.³ Yet computer simulations of liquid water and other hydrogen bonded liquids reproduce both thermodynamic and structural properties with some success⁴ using an empirical intermolecular potential energy function which consists of long-range Coulomb's law interactions between a few strategically placed charges on the molecules, plus weak attractive dispersion and short-range repulsive forces.⁵ The hydrogen bond interaction appears as the strong attractive interaction between a positively charged site (usually a hydrogen atom) on one molecule and a negatively charged site, usually close to an oxygen atom, on another. This kind of potential model predicts that hydrogen bonding in water is retained even at temperatures and pressures well above the critical point,^{6,7} a feature which is not unexpected, given that the intermolecular interactions are being modelled by static electrical charges.

However, recent neutron-diffraction experiments on superheated water^{8,9} have cast doubt on these charge models for the water potential. They suggest that as the critical temperature of water is approached the hydrogen bond interaction, as manifested by the height and position of the first

peak near 1.9 \AA in the OH site-site distribution function, diminishes more rapidly than predicted by computer simulation with simple charge models, and has apparently mostly disappeared above the critical temperature at moderate densities. Other experimental data suggest that the same peak is density dependent¹⁰ at a given temperature, and more so than is seen in the simulations. To investigate this density dependence in more detail we have enhanced the range of densities at 573 K for which neutron data on water exist by repeating the water experiment at four additional densities and under different experimental conditions to the earlier results. These data are combined with a method of analyzing the neutron experiment which serves to circumvent some of the systematic artifacts which have been postulated.^{7,11,12} A full account of this work is being published elsewhere;¹³ here we highlight the principle conclusion, that is density dependent effects on the hydrogen bonding in water are certainly discernible in the neutron experiment. It is worth pointing out that although the structure of superheated water has been investigated in several previous diffraction experiments, both x ray^{14,15} and neutron,⁸⁻¹⁰ the present data represent an in-depth study of the site-site radial distribution functions for water for a range of densities at *fixed* temperature.

The essence of the neutron-diffraction experiment on water is to exploit the very large change in coherent neutron-scattering length between the hydrogen and deuterium isotopes to separate the individual hydrogen-hydrogen, oxygen-hydrogen, and oxygen-oxygen partial structure factors, (S_{HH} , S_{OH} , S_{OO}), from diffraction data on light water, heavy water, and at least one mixture of the two.⁹ These in turn are related by Fourier transform to the corresponding site-site pair correlation functions $g_{HH}(r)$, $g_{OH}(r)$, $g_{OO}(r)$. Of these the OH function is of considerable interest because it measures the degree of correlation between oxygen on one molecule and hydrogen on another, and is therefore a direct indication of the degree of hydrogen bonding in water. For this reason, only the OH radial distribution function is discussed here, while the full set of distribution functions from both the present experiment and from the reanalyzed old data are described in Ref. 13.

A well-known source of systematic error in this experiment is the fact that the neutron has a similar mass to the proton or deuteron, and so induces a substantial nuclear recoil. The recoil in turn causes a significant distortion to the scattered neutron pattern which can be estimated only approximately for light atoms. The distortion largely cancels if only the HH function is needed,¹⁶ but must be accounted for if the OH or OO functions are required.¹⁰ The correction is minimized by performing the experiment at low scattering angles ($2\theta \leq 20^\circ$) and using the high flux of neutrons at epithermal energies that is available at a pulsed neutron source.¹⁷ The size and shape of the correction is still affected by a number of factors, particularly the derivatives of the incident neutron spectrum as a function of neutron energy, the detector efficiency, and the van Hove dynamic scattering law.¹⁸ In the present experiment the incident neutron spectrum was obtained from a water neutron moderator at 300 K as opposed to the previous data, which were measured using a liquid methane moderator at 109 K. The water moderator shifts the position of the Maxwellian part of the neutron spectrum to larger energies and reduces its amplitude, with a corresponding reduction in the size of the recoil correction.

A second distinct feature of the experiment is that the data were analyzed in a different way. It has been pointed out¹¹ that residual systematic errors arising from the recoil distortion in one or more of the measured differential scattering cross sections can affect the shape of the OH and OO pair correlation functions in opposite ways. In this procedure the interference differential cross section of each sample i , $F_i(Q)$, was represented as the usual combination of the partial structure factors plus a background contribution, $T_i(Q)$:

$$F_i(Q) = a_{i1}S_{OO}(Q) + a_{i2}S_{OH}(Q) + a_{i3}S_{HH}(Q) + T_i(Q). \quad (1)$$

The a_{ij} 's are the weightings of the individual structure factors in the neutron experiment. $T_i(Q)$ was estimated from the requirement that the calculated radial distribution functions must be everywhere zero or positive definite. The same distribution functions are expected to be identically zero below a certain minimum radius value, and on integrating must satisfy the compressibility equation.¹⁹ Any residual Q dependence required to fit the measured data is then treated as the background function. Applying this procedure to both new and old experimental data resulted in a considerable degree of quantitative overlap¹³ between the site-site correlation functions derived from two data sets measured at the same thermodynamic state point but with different incident neutron spectra, even though the nuclear recoil corrections in the two cases were substantially different.

Figure 1 shows the oxygen-hydrogen radial distribution function, $g_{OH}(r)$, as derived from the neutron data in the present experiment, as a function of decreasing density at 573 K, and compares these functions with the same function in ambient water,²⁰ and the earlier measurement¹⁰ at 573 K at a density of 0.0309 molecules/ \AA^3 . The pronounced peaks centered near ~ 1.9 and ~ 3.3 \AA in ambient water contain direct information on the degree of short-range molecular association. The presence of these peaks is traditionally regarded as the signature of the hydrogen bond and they will

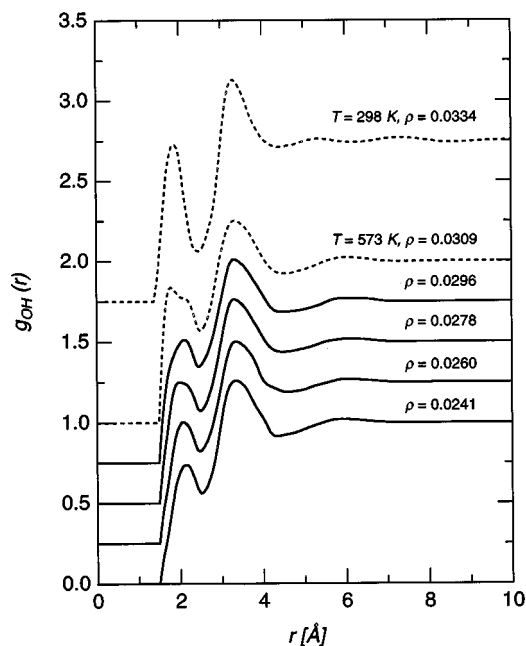


FIG. 1. The $g_{OH}(r)$ functions of water obtained at five density states on the isotherm at $T = 573$ K, compared with the same function for water at ambient conditions: the density decreases from top to bottom and the different curves have been shifted by an arbitrary quantity. Units of ρ are molecules/ \AA^3 . The experiments on ambient water (Ref. 20) and superheated water at $\rho = 0.0309$ molecules/ \AA^3 (Ref. 10), reported as dashed lines, have been performed with different experimental conditions.

be called the H-bond peaks accordingly. The H-bond peaks are well resolved and sharp in the case of water at ambient conditions, indicating a strong directionality in the hydrogen bonding of room temperature water.²⁰ With increasing temperatures the first peak moves to a larger distance than in ambient water (see Fig. 1) and broadens, while the number of molecules engaged in the hydrogen bonding decreases.^{10,13}

The experimental results confirm that clear and systematic changes show up in the local hydrogen bonding with increasing temperature and decreasing density. In order to demonstrate this point more clearly Fig. 2 shows the centroid of the first H-bond peak in $g_{OH}(r)$ as a function of density, as obtained by fitting a Gaussian plus a background to this peak. The first H-bond peak is centered at ~ 1.85 \AA for the ambient liquid and moves to ~ 2.15 \AA for the saturated liquid at 573 K, while at the highest density investigated ($\rho = 0.0309$ molecules/ \AA^3) it shows a broader, possibly double, structure. The peak shift is accompanied by a decrease in the slope of the $g_{OH}(r)$ function at short distances with decreasing densities. Also shown in this figure is the position of the peak as estimated by computer simulation of TIP4P (Ref. 5) water on a supercritical isotherm:⁷ clearly the shift in position of the peak is not accurately reproduced by the simulation.

The observed shift of the hydrogen bond peak towards larger distances compared to ambient conditions suggests the presence of highly distorted and possibly bifurcated hydrogen-bonds for these lower density and higher temperature states. This inference is also supported by the shape of the $g_{OO}(r)$ functions, which show a structure around 4 \AA .¹³

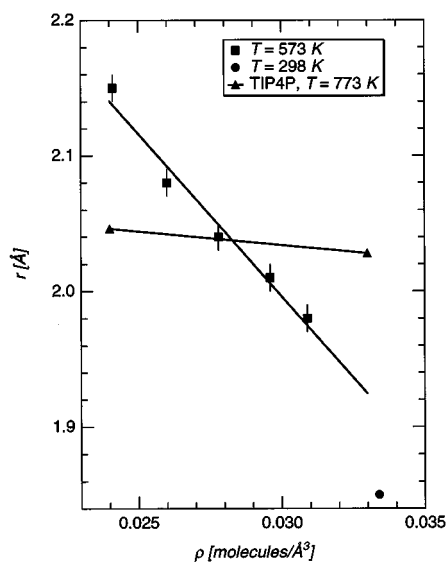


FIG. 2. Position of the centroid of the first H-bond peak as a function of density (squares). The circle indicates the peak position at ambient conditions. The triangles are the result of a simulation of TIP4P water at $T=773$ K. (Ref. 7). Solid lines are guides for the eye.

Bifurcated hydrogen bonds versus linear ones would imply longer hydrogen bond distances and shorter OO distances between second neighbors.²¹

In order to gain a better understanding of the implications of these data for the structure of nonambient water, empirical potential Monte Carlo simulations (EPMCS) (Ref. 22) of the measured site-site radial distribution functions at the two extreme densities at 573 K were performed and compared with the results of the same simulation for room temperature water.²² This simulation attempts to set up, by standard Monte Carlo methods, three-dimensional (3D) distributions of water molecules with the correct intramolecular structure, which reproduce the measured correlation functions. These distributions fulfill two important tasks: they verify that the radial distribution functions extracted from the neutron data are in fact physically reasonable, and they can then be used to calculate a variety of other structural quantities of interest, in this case the angular distribution of H bonds around an oxygen atom on a water molecule. Note that the simulation fits all three site-site pair correlation functions, HH, OH, and OO, and not just the OH function discussed here. Figure 3 shows the estimated distribution of angles between the OH bond on one molecule and the $O \cdots O$ vector between molecules separated by distances between 2.4 and 3.5 Å, and averaged over all directions of the $O \cdots O$ vector. The distributions are normalized to one water molecule at the origin. The angle, θ , is defined so that $\theta=0$ corresponds to the OH bond on one molecule pointing directly away from the oxygen of a neighboring molecule. Hence the sharp peak at $\cos\theta=-1$ and the distinct hump at $\cos\theta=0.2$ observed under ambient conditions are the signature for sharply defined collinear bonds. At 573 K the sharp peak at $\cos\theta=-1$ has broadened considerably and the second hump at $\cos\theta=0.2$ becomes almost flat at the lowest density. It will also be observed that if the hydrogen bond is defined to exist only

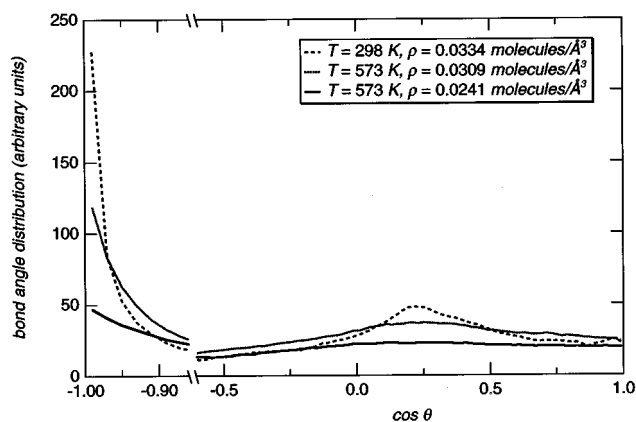


FIG. 3. $O \cdots O-H$ bond angle distribution for water at ambient conditions (dashed line), compared with those for superheated water at $T=573$ K and $\rho=0.0309$ molecules/Å³ (dotted line) and $\rho=0.0241$ molecules/Å³ (full line).

when $\cos\theta < -0.87$ (which corresponds to deviations from linearity by up to 30°) then the number of hydrogen bonded molecules, as indicated by the area under the peak at $\cos\theta=-1$, decreases rapidly with decreasing density. Therefore on both counts, i.e., the rapid broadening of the angular distributions and the consequent fall in number of hydrogen bonds with density, the present experimental data indicate a rapid decrease in hydrogen bonding in superheated water as the density falls.

The principle result of the present work is that the first peak in the OH radial distribution function for water changes position with density at constant temperature. This implies that the local minimum of the interatomic potential is changing markedly with density, an effect that can only occur if many-body interactions are an important component of the interatomic potential. In fact, even in a pairwise additive system small shifts in the near-neighbor peak of a liquid can occur at high densities, depending on the relative strengths of the attractive forces binding the molecules together and the repulsive forces which prevent molecular overlap. The point to be emphasized, however, is that this shift is not observed in the traditional water potentials which have been used almost ubiquitously to predict water and aqueous solution properties over a wide range of state conditions from supercooled to supercritical for the last 25 years or so. The fact that these potentials do not reproduce the observed peak movements suggests that they overemphasize both the strength of the attractive hydrogen bond interaction and the corresponding repulsive interaction preventing molecular overlap; changes in density at constant temperature do not then produce an observable peak shift with density change. Therefore, our data indicate that for accurate predictions of water and aqueous solution properties over a wide range of temperatures, densities, and pressures, such as are often required in a variety of applications in the chemical and geological sciences, existing potentials for water will need to be modified.

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