

## Origin of Temperature and Pressure Effects on the Radial Distribution Function of Water

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(Received 25 November 1998)

No previous concept has explained all the intricate structural features of liquid water which occur in the radial distribution function (RDF) as a function of temperature and pressure. Using an outer-structure two-state model, successful in explaining all the anomalies of water, the RDF and its sensitivity to temperature and pressure can be reproduced. The crossings of these RDF's at specific distances confirm the precise two-state nature of this important liquid.

PACS numbers: 61.20.Gy, 61.90.+d

Water is a substance that holds special prominence, not so much as a result of its sheer abundance but rather, because of its necessity to life. Much is already known experimentally about the odd behavior of this substance compared with other liquids. An understanding of *all* these properties now appears possible if one considers *explicit outer bonding contributions* from nonhydrogen-bonded neighbors [1,2]. This concept is used here to interpret both the temperature and pressure dependence of the liquid-state oxygen-oxygen O···O radial distribution function (RDF) as well as the associated isochoric temperature differential (ITD) results [3].

The relative structural integrity of the inner intermolecular bonding characteristics in the liquid state of water is suggested by the high boiling point of this material compared with other substances having similar molecular weights. Our earlier papers [1,2] suggested that bonding characteristics in this inner nearest-neighbor region as well as those in the *outer* next-nearest-neighbor regions of this liquid are topologically related to the structures found in normal ice *Ih* and its denser polymorphs, ice II, etc. This approach is directly related to one suggested by Kamb [4], but, before our own work, the consequences of this idea for the liquid water problem had never been actively pursued. The occurrence of this explicit type of structure in the liquid and the transformation with increasing temperature or pressure through hydrogen-bond bending of the open 4.5 Å *Ih*-type O···O outer structure to a more dense II-type outer structure near 3.4 Å have now been beautifully confirmed by x-ray diffraction studies [3,5]. These outer structural characteristics in the liquid are dynamically interconverting on picosecond time scales and, on average, extend no farther than about 7–8 Å from any reference molecule, so, as expected for a liquid, long-range order would be missing.

The *Ih*-type tetrahedral molecular arrangement is very important to the current concepts of local structure in liquid water [6]. This arrangement is verified by the presence of two prominent maxima in the liquid-state O···O RDF [7], corresponding to two coordinating spheres around a refer-

ence molecule. The first coordination shell corresponds to the peak near 2.8 Å and arises from the correlation between the reference molecule and four other hydrogen-bonded molecules occupying the vertices of a *regular* tetrahedron. This 2.8 Å O···O structure is common to all of the ice forms [2] and would therefore not be expected to vary appreciably if indeed the liquid depends on *T, P*-dependent transformation related to bonding characteristics in the various polymorphs. The second prominent coordination sphere is evidenced by the O···O peak near 4.5 Å, and corresponds to the distance between molecules residing at the vertices of the regular tetrahedron.

Experimental evidence for explicit structural changes in the liquid under pressure may be found from diffraction studies. Bellissent-Funel and Bosio [8] concluded from their neutron studies of D<sub>2</sub>O that the number of hydrogen bonds does not change substantially with pressure (little change in the 2.8 Å structure). Rather, the O···O···O angles are modified (bent bonds). More directly, Okhulkov, Demianets, and Gorbaty [5] have found from x-ray studies a substantial increase in the O···O correlation near 3.3 Å with increasing pressure. Concomitantly, the 4.5 Å structure was seen to diminish.

Additional striking experimental evidence for these structural changes comes from temperature studies. In 1983, Bosio, Chen, and Teixeira [3] introduced a new approach for studying the subtle differences in the temperature-dependent O···O pair correlation functions (PCF) of water, with  $G(r) = 4\pi r^2 \rho_0 g(r)$ , where  $G(r)$  is the RDF,  $g(r)$  is the PCF, and  $\rho_0$  is the density. By taking two PCF's at a common isochore across the temperature-dependent density curve of D<sub>2</sub>O and subtracting one from the other, they obtained a very interesting result. Clearly demonstrated in their experiments was that there are at least two types of O···O outer neighbor shells (shells at a distance greater than 2.8 Å) involved in the temperature-dependent structural changes of liquid water. One is the 4.5 Å peak described above. The other is near 3.4 Å and increases in intensity with increasing temperature differential, at the expense of the

4.5 Å peak. This is exactly the same trend as that found from the pressure experiments [5], as will be illustrated more fully below. These changes in intensity correspond to an increase in the amount of dense structure present in the liquid, replacing the open structure. They lead straightforwardly to the increased density with increasing temperature, and to the density maximum at 4 °C (H<sub>2</sub>O) [2,9]. Also, from their results, Bosio, Chen, and Teixeira [3] recognized that the first coordination shell at 2.8 Å is less strongly affected by temperature than outer neighbor shells. One of their most important conclusions was that variations in O···O···O correlations are central to their experimental findings and that these variations must be related to the origin of the thermal anomalies of water.

The centerpiece of the outer structure concept used here to create the RDF's therefore comes from recognizing contributions, not only from tetrahedrally bound inner neighbors, as has been done in the liquid water problem for a very long time, but also those from second neighbors, whose distance from the reference molecule varies through the bending [4,10,11], not the breaking, of hydrogen bonds. If indeed the liquid state of water can be considered to be comprised of two dynamically interconverting mixed microdomains that possess, on average, bonding characteristics similar to those found in ice *Ih* and ice II, then a combination of these components should be capable of reproducing the main features of the liquid-state RDF as a function of  $T$  and  $P$ ,

$$G_{\text{liq}}(T, P) = f_{\text{I}}G_{\text{I}} + f_{\text{II}}G_{\text{II}}, \quad (1)$$

where  $f_{\text{I}}$  and  $f_{\text{II}}$  ( $f_{\text{I}} + f_{\text{II}} = 1$  in a two-state model) are the  $T, P$ -dependent fractional contributions of *Ih*-type and II-type bonding, which can be determined from the analysis of the density [2] of the liquid, and  $G_{\text{I}}$  and  $G_{\text{II}}$  represent the  $r$ -dependent RDF's of ice *Ih* and ice II [4]. Equation (1) then allows *composite* RDF's or PCF's representing the liquid to be constructed for a series of temperatures. Initially, it may be assumed that the  $T, P$  dependence of the functions  $G_{\text{I}}$  and  $G_{\text{II}}$  themselves is of a secondary importance. Because of this approximation (see below), the intent here is not to obtain perfect agreement with the experimental data but rather to show how the composite model is capable of capturing the interesting trends in the  $T, P$ -dependent RDF's and thus to provide an understanding of these trends.

When the resulting composite RDF from Eq. (1) is compared with the experimental x-ray data [7] at 20 °C, the main difference was found to be a greater distance in the composite between the two main peaks. Exact agreement would not be expected because of the omitted effects of thermal broadening and shifts in  $G_{\text{I}}$  and  $G_{\text{II}}$ , combined with experimental uncertainties in the diffraction studies. A more severe test of the composite lies in the ITD's, which must consider a range of temperatures. The composite ITD's compared with the experimental curves for D<sub>2</sub>O [3] are shown in Fig. 1.

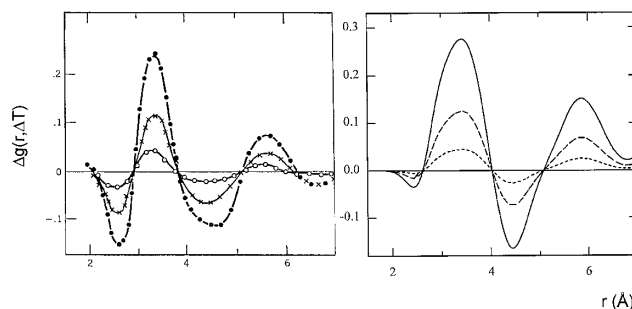


FIG. 1. Isochoric temperature differentials related to O···O pair correlation functions for D<sub>2</sub>O. Experimental results [3] on the left, ice-*Ih*/ice-II composite curves at the right. The isochoric temperature pairs, top to bottom near 3.4 Å, for both the experimental and composite curves are -11 °C/+40 °C, +0.2 °C/+23.5 °C, and +7.1 °C/+15.5 °C.

Considering that the ITD's are small differences between large quantities, the level of agreement between the calculated and experimental ITD's is very good. This confirms that their origin indeed arises from an increase with increasing temperature in the fraction of a dense II-type structure having non-nearest-neighbor distances near 3.4 Å, with a simultaneous decrease in the fraction of a non-nearest-neighbor open *Ih*-type structure near 4.5 Å. Again, the near equivalence of the first-neighbor O···O distances in all of the ice forms [2] causes the first peak in the ITD in a relative sense not to be so greatly affected by temperature when compared with its rather large PCF amplitude [7].

Another interesting feature of the ITD curves is the observation that, regardless of which isochore is chosen, the ITD's intersect the zero differential at precisely the same  $r$  values. This is seen both in the experimental ITD's and in the ice-*Ih*/ice-II composite curves, though the crossings are at slightly different  $r$  values ( $\Delta r < 0.2$  Å) in the two cases. These intersections must therefore separate well-defined coordination shells for the liquid state of water, whose boundaries are not substantially disrupted by temperature increases. Furthermore, the precise intersections in the experimental curves provide strong support [12] for the two-state representation of liquid water over the full temperature range covered by the experiments, -11 to +40 °C.

Finally, the increased correlation near 5.6 Å in the experimental ITD curves is also interesting, since it is reproduced by the composites, though again shifted by about 0.2 Å. A likely source of this feature is that reference molecules at distances of 4.5 or 3.4 Å bring along with them more distant hydrogen-bonded molecules. Looking at distance maps of the O···O structure [4], one sees that in ice *Ih* there are no neighbors within 0.4 Å of the 5.8 Å ITD composite peak, while for ice II there are about ten. Thus, an increase in the II-type outer neighbor structure with increasing temperature would be expected to give rise to an increased correlation in the liquid near this 5.8 Å distance, as observed. This

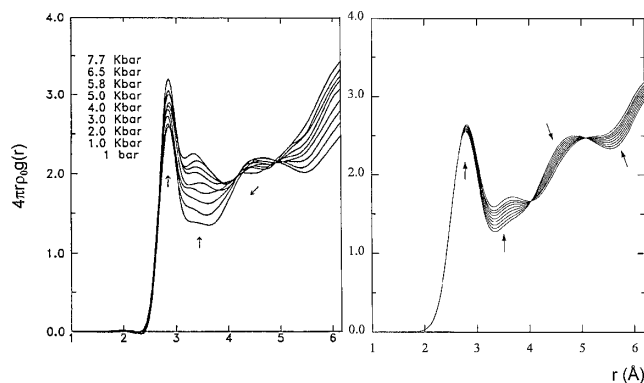


FIG. 2. Pressure effects on the radial distribution function of liquid  $\text{H}_2\text{O}$ . Experimental results [5] on the left, ice-Ih/ice-II composites on the right. In Ref. [5] the RDF was divided by  $r$  to obtain flatter curves. For both sets of data, the pressures label the curves top to bottom near  $3.3 \text{ \AA}$ , and the arrows indicate the direction of change with increasing pressure. The noticeable movement inward with the increasing pressure of the  $3.4 \text{ \AA}$  peak in the experimental curves is a result of compression of the entire material, not considered in the composite curves.

is further evidence for structural integrity in the liquid out to this relatively large  $\text{O}\cdots\text{O}$  separation for a wide temperature range, and for the transformation of the I-type structure to the II-type structure with increasing temperature.

In addition to the explicit change of structure with temperature and the resulting ITD's, pressure effects [5] on the RDF's can also be reproduced through differentiation of Eq. (1) with respect to pressure and the use of  $(\partial f_1/\partial P)_T$  values obtained from earlier isothermal compressibility analyses [13]. See Fig. 2 for a reproduction of this pressure dependence compared with the experimental data. One of the most remarkable things about the pressure effects, in both the experimental [5] and composite RDF's, is that all of the curves, from low to high pressure, cross at common  $r$  values, the most prominent crossings occurring near  $4.0$  and  $5.0 \text{ \AA}$ . By comparing with Fig. 1, these are seen to be close to two of the same  $r$  values marking zero differentials in the ITD curves. This means

that the positions of these intermediate regions between "inhabited shells" of liquid water do not vary substantially with either temperature or pressure changes, a feature which provides further strong experimental support for the two-state model of liquid water [12].

For support of this work, we thank the R. A. Welch Foundation (D-0005 and D-1094), the Petroleum Research Fund (ACS-PRF No. 32253-AC6), and private support from Dr. and Mrs. Jamine Lee and the Chemistry Support Fund at Texas Tech.

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