

## Isochoric Differential Scattering Functions in Liquid Water: The Fifth Neighbor as a Network Defect

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We show that isochoric differential x-ray experiments of Bosio, Chen, and Teixeira are consistent with the possibility that water molecules can exist in distinct configurations characterized by either four or five neighbors in the first coordination shell. Associated with the molecules with five neighbors are defects in the tetrahedral bond network ("bifurcated bonds") which offer paths with low energy barriers between different network configurations and in turn enable the fast restructuring of the network with thermal energies  $kT$  much smaller than the hydrogen-bond energy.

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Recently, Bosio, Chen, and Teixeira<sup>1</sup> made accurate measurements of the oxygen radial distribution function for two different temperatures  $T_1$  and  $T_2$  chosen such that the density  $\rho$  of water is the same for both temperatures; this is possible due to the existence of a maximum in the function  $\rho(T)$ . By subtracting the respective radial distribution functions, they obtained *isochoric temperature differential functions* displaying the remarkable property that only the heights of the peaks and valleys (but not their positions) depend on temperature [Fig. 1(a)]. Their finding can be interpreted in a first approximation by assuming that there are two species,  $A$  and  $B$ —present with *temperature-dependent* concentrations  $x_A(T)$  and  $x_B(T)$ , respectively ( $x_A + x_B = 1$ )—such that the total radial distribution function  $g_T$  is related to the radial distribution functions  $g_A$  and  $g_B$  of species  $A$  and  $B$  by

$$g_T(r, T) = x_A(T)g_A(r) + x_B(T)g_B(r). \quad (1)$$

Then the isochoric temperature differential function is given by

$$g_T(r, T_2) - g_T(r, T_1) = [x_B(T_2) - x_B(T_1)][g_B(r) - g_A(r)]. \quad (2)$$

By using Eq. (2), we can interpret the change shown in Fig. 1(a) on increasing the  $T_2 - T_1$  range as an effect of the decreasing concentration of the  $B$  species on cooling.

It would be desirable if we could associate the two species  $A$  and  $B$  with specific structures in the hydrogen-bonded (HB) network. An important clue is provided by the fact that there are, on average, more than four water molecules in the first coordination shell; specifically, the integral over the first peak of the oxygen distribution function demonstrates that the coordination number is about 4.5.<sup>2</sup> This fact is sometimes interpreted to mean that the tetrahedral network cannot be perfect but must contain defects of some sort. The presence of these defects (caused by "extra molecules" in the first coordina-

tion shell) is potentially of considerable importance to the *dynamic* properties of water.<sup>3</sup>

Here we analyze a molecular-dynamics (MD) simulation of liquid water in order to identify and characterize the defects in the HB network. We study a system composed of 216 water molecules which interact via the ST2 potential.<sup>4</sup> The density is 1.0 g/cm<sup>3</sup> and the average temperature is 273 K. A 100-ps time series of configurations<sup>3</sup> is the basis of the following results, which we confirm by also analyzing analogous MD simu-

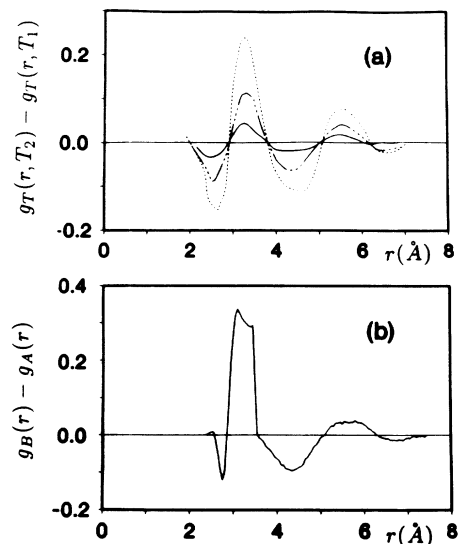


FIG. 1. (a) Isochoric differential x-ray-scattering data of Bosio, Chen, and Teixeira (Ref. 1) for the function  $g_T(r, T_2) - g_T(r, T_1)$ , which is the left-hand side of Eq. (2). The solid line is for the pair  $T_1 = 40^\circ\text{C}$ ,  $T_2 = -11^\circ\text{C}$ ; the dot-dashed line is for the pair  $T_1 = 23.5^\circ\text{C}$ ,  $T_2 = 0.2^\circ\text{C}$ ; and the dotted line is for the pair  $T_1 = 15.5^\circ\text{C}$ ,  $T_2 = 7.1^\circ\text{C}$ . (b) Dependence on  $r$  of the function  $g_B(r) - g_A(r)$ , which is the right-hand side of Eq. (2). Here we identify species  $A$  with the four-bonded molecules and species  $B$  with the molecules having five or more bonds.

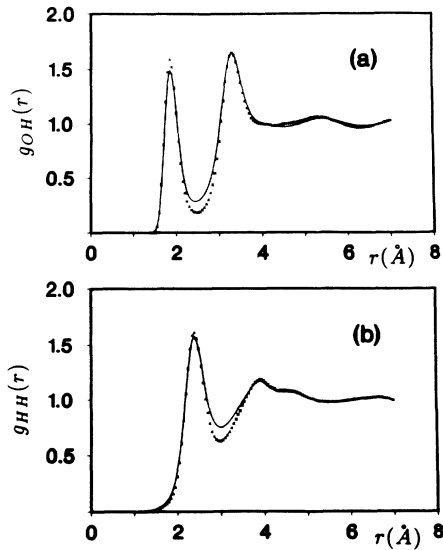


FIG. 2. (a) OH radial distribution function for the total  $g_T(r, T)$  (solid line) and the radial distribution function for the four-coordinated molecules  $g_A(r)$  (points). (b) Same as (a) for the HH radial distribution function.

lations of molecules interacting via the SPC (Ref. 5) and TIP4P (Ref. 6) potentials.

Figure 1(b) shows  $g_B(r) - g_A(r)$  of Eq. (2), calculated from the MD simulation. Here species  $A$  refers to the four-bonded molecules and species  $B$  refers to the molecules with five (or more) bonds.<sup>7</sup> We see that the calculations [in Fig. 1(b)] are similar in their  $r$  dependence to the experimental data [in Fig. 1(a)], providing support for this identification.

Figures 2(a) and 2(b) show the OH and HH radial distribution functions, respectively, for the total and for the four-bonded component. We note that—in comparison to the total function—there is, for the four-bonded component, an increase in the OH radial distribution function at about 1.9 and a deeper minimum between 2.3 and 2.6 Å. Again, by identifying the five-bonded component as the defect population that increases with  $T$ , we find agreement with the experimentally observed temperature dependence in the neutron data.<sup>8</sup>

A consequence of a fifth bonded molecule in the first coordination shell is that a proton is shared by two different oxygen atoms (Fig. 3). From the MD data we separate<sup>9</sup> the *linear* bonds (LBs, for which each proton is bonded to only one oxygen atom) from the *bifurcated* bonds<sup>10,11</sup> (BBs, for which a hydrogen atom is bonded to two oxygen atoms). We observe that the four-bonded molecules are linked to the bond network only through four LBs, while the five- (or more) bonded molecules are linked to the network with both LBs and BBs.

Figure 4(a) shows the distribution of the  $H_1-O_1-O_2$  angle  $\theta_H$  and Fig. 4(b) shows the distribution of  $R_{OH}$  for both the LB and BB populations. The areas under each

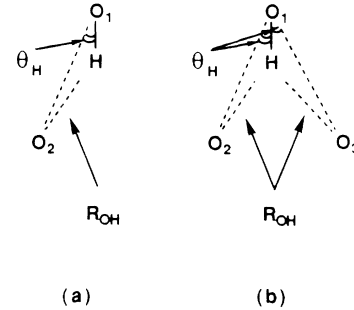


FIG. 3. Schematic representations of (a) LBs and (b) BBs, also illustrating the notation  $\theta_H$  and  $R_{OH}$ .

curve are proportional to the number of bonds for each type. While the LB distribution is unimodal, the BB distribution displays two broad peaks. By analyzing the two values with which each proton contributes to the BB distribution, we find that each BB is composed of one almost linear bond (whose properties do differ slightly from the LB set), shared with one more “bent” bond. To better characterize the geometry of the BB, we study the distribution of the  $O_2-O_1-O_3$  angle, where  $O_1$  is the proton donor and  $O_2$  and  $O_3$  are the acceptors. We find that the  $O_2-O_1-O_3$  distribution peaks at about  $50^\circ$ , an angle much smaller than the tetrahedral angle  $109.5^\circ$ .<sup>10,11</sup>

We also analyze the geometric distribution for bonds living longer than some selected time (as in Ref. 12). We find that while the shape of the LB distribution is

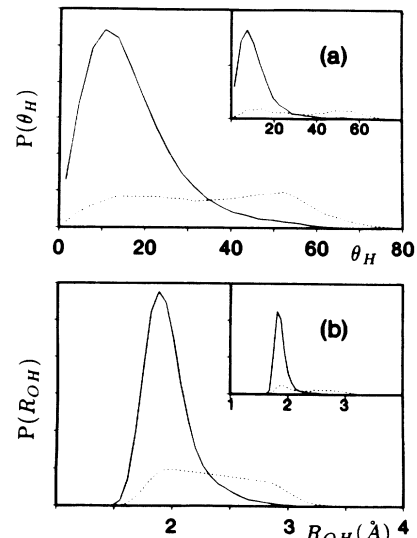


FIG. 4. (a) Distribution function for the  $H_1-O_1-O_2$  angle  $\theta_H$  for the LBs (solid line) and BBs (dashed line). (b) Same as (a) for the  $R_{OH}$  distribution function. Note that each BB contributes with two different values to the distribution. Insets: The analogous plot for the “inherent” or quenched configurations.

approximately the same as the instantaneous configuration (Fig. 4), the BB distribution *rapidly* loses those bonds with larger  $\theta_H$  and longer  $R_{OH}$ —supporting the possibility that the BB may be a transition state between two different LB configurations. To confirm that this BB “transition state” is not just a thermal excitation but is actually a *local minimum* on the energy hypersurface, we study the “inherent” or quenched structure—which represents the structure of the liquid if there were no thermal excitations. We find, using the Stillinger-Weber method,<sup>13</sup> that both peaks of the BB configuration survive the quenching process (see insets of Fig. 4). Hence the BBs are not artifacts of the thermal motion, but are indeed locally stable states.<sup>13</sup> This survival of the BBs is in accord with the recent observation that even the quenched-structure trajectories yield fast fluctuations of the individual water-molecule energies.<sup>14</sup>

The distributions of the interaction energies (Fig. 5, and the inset for the inherent structure) suggests that the sum of the *two* interaction energies of a BB is roughly the energy of *one* LB. Thus the comparatively small value of  $kT$  may be sufficient to transform a LB into a BB. This possibility is also in agreement with Raman data showing that the positions of the OH bands have a frequency ratio corresponding to a 2:1 energy ratio.<sup>15</sup>

To see if the presence of a fifth molecule indeed “catalyzes the reorganization of the local network,” we compare the *shell-occupation-time correlation functions*<sup>16</sup> for the four- and five-bonded molecules.<sup>17</sup> We find evidence for preferential exchange of molecules near the five-or-more-bonded molecules, suggesting a higher mobility and a more rapid reshuffling of the network in the vicinity of the BBs. In this respect, the conversion among BBs and LBs may be one of the mechanisms on which the reorganization of the network is based.<sup>18</sup>

We also observe that other systems generically described as continuous tetrahedral random networks (e.g.,  $\text{SiO}_2$  and  $\text{BeF}_2$ ) are characterized by five-or-more-coordinated “defects” whose concentration decreases with temperature.<sup>19,20</sup> In these glass-forming systems, the elementary diffusion step that enables the network reorganization has been identified with the conversion of a four-coordinated atom to a five-coordinated atom and back (when the incoming and leaving atoms are different). In such systems, as well as in simulated liquid water,<sup>3</sup> the concentration of five-coordinated sites controls the system diffusivity.<sup>19,20</sup>

Thus we see that the BBs are a local energetically stable arrangement and—although each group of molecules is characterized by a continuum of possible energies—the *mean* energies of LB and BB arrangements are roughly the same. This fact, together with our finding on the quenched structure, supports the possibility that the BBs offer a path connecting different LB configurations through activation barriers lower than the energy needed to break a LB, and furnishes a structural

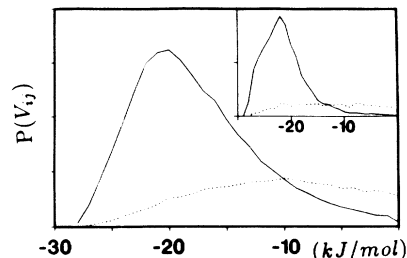


FIG. 5. Distribution function for the pair interaction energy  $V_{ij}$  for the LBs (solid line) and BBs (dashed line). Note that each BB contributes with two different values to the distribution. Inset: The analogous plot for the inherent or quenched configurations.

explanation of the low-energy-barrier flip-flop mechanism that characterizes the HB network reorganization.<sup>14</sup>

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<sup>7</sup>We define two water molecules to be “neighbors” if their O-O distance is less than the position of the first minimum in the O-O radial distribution function ( $R_{\min} = 3.5 \text{ \AA}$ ) (the results of this paper are not affected for a range of values  $R_{\min} = 3.2\text{--}3.5 \text{ \AA}$ ). Also, we define two neighbors to be “bonded” if their pair interaction energy is negative—with this definition, we find roughly 99.7% of the molecules have four or more intact bonds. We also find that Fig. 1(b) is unchanged if we identify species *A* as the four-coordinated molecules (instead of the molecules with four bonds). It is more than a mere semantic point if we use such a liberal definition of a bond, since the analysis of the quenched configurations confirms that the shape of the distribution of pairs with negative interaction energy does not change with the quenching process; hence what we term bonds are truly “legitimate bonds” (cf. inset of Fig. 5). Removing bonding ambiguities through quenching processes is discussed in T. A. Weber and F. H. Stillinger, *J. Chem. Phys.* **87**, 3252 (1987).

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<sup>9</sup>Given two neighboring molecules with negative pair interaction energy, we select the proton closest to the O-O connecting line. We associate this proton with the bond between the two water molecules. If the same proton is associated with two bonds, we say the proton is "bonded" to two oxygen atoms.

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<sup>17</sup>This function gives information on how long a molecule, which belongs to the first-neighbor shell ( $R_{OO} < 3.5 \text{ \AA}$ ) at time  $t=0$ , remains in the vicinity of the same molecule.

<sup>18</sup>It is worth noting that this picture could provide a microscopic (structural) explanation of the previously observed potential-energy correlation ("flip-flop mechanism") among neighboring molecules that characterizes the energy exchanges in water (Ref. 14).

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