

## Structure of supercooled and glassy water under pressure

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We use molecular-dynamics simulations to study the effect of temperature and pressure on the local structure of liquid water in parallel with neutron-scattering experiments. We find, in agreement with experimental results, that the simulated liquid structure at high pressure is nearly independent of temperature, and remarkably similar to the known structure of the high-density amorphous ice. Further, at low pressure, the liquid structure appears to approach the experimentally measured structure of low-density amorphous ice as temperature decreases. These results are consistent with the postulated continuity between the liquid and glassy phases of H<sub>2</sub>O. [S1063-651X(99)10007-2]

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The structure of liquid water has been well-studied at ambient pressure by a variety of experimental and simulation techniques. It has been recognized that each water molecule is typically hydrogen bonded to four neighboring molecules in a tetrahedral arrangement, leading to an open bond network that can account for a variety of the known anomalies of water [1,2]. More recently, the effect of pressure on both the structure and the hydrogen bond network of liquid water has been studied experimentally [3,4] and by simulations using a variety of potentials, including the ST2 potential [5,6], the MCY potential [7], the TIP4P potential [6,8–10], and the SPC/E potential [11]. Furthermore, understanding the effects of pressure may be useful in elucidating the puzzling behavior of liquid water [12,13].

In particular, three competing “scenarios” have been hy-

pothesized to explain the anomalous properties of water: (i) the existence of a spinodal bounding the stability of the liquid in the superheated, stretched, and supercooled states [14]; (ii) the existence of a liquid-liquid transition line between two liquid phases differing in density [6,10,15–17]; (iii) a singularity-free scenario in which the anomalies are related to the presence of low-density and low-entropy structural heterogeneities [18].

Here, we present molecular-dynamics (MD) simulations (Table I) of a comparatively large system of 8000 molecules [23,24] interacting via the extended simple point charge (SPC/E) pair potential [25]. We find remarkable agreement with neutron-scattering studies of the effect of pressure on the structure of liquid D<sub>2</sub>O [4], indicating that the SPC/E potential reproduces many structural changes in the liquid

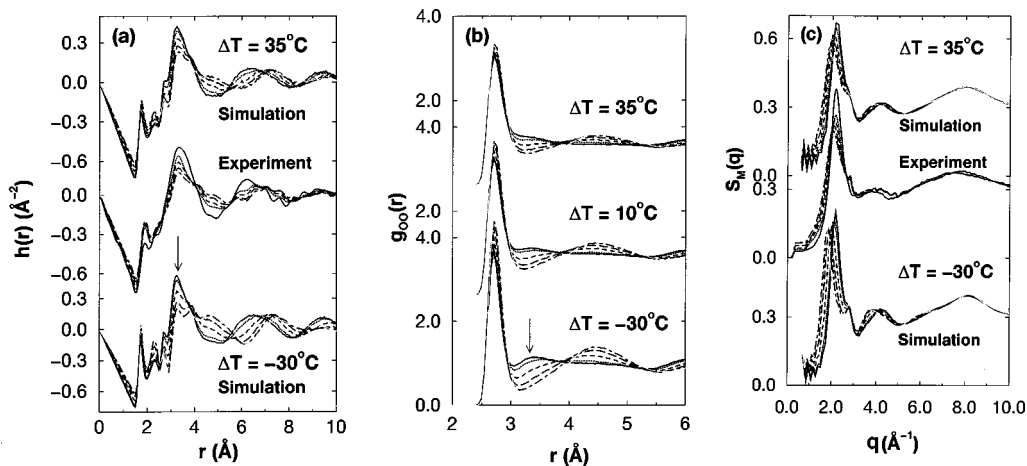


FIG. 1. Pair correlation function  $h(r)$  for two of five temperatures studied (Table I). The curves can be identified as follows (reading from top to bottom at the location of the arrow):  $P = 600$  MPa, 465 MPa, 260 MPa, 100 MPa, 0.1 MPa, and  $-200$  MPa. Pressures are the same for the experiments and simulations, with the exception that no experiment was possible at  $P = -200$  MPa. Note the pronounced increase in the  $3.3$  Å peak (arrow) when pressure is increased. To facilitate comparison with experiments, the simulation temperature is reported relative to the  $T_{MD}$  of the SPC/E potential at atmospheric pressure. Similarly, the experimental data are reported relative to the  $T_{MD}$  of D<sub>2</sub>O at atmospheric pressure. The behavior of the simulated  $h(r)$  strongly resembles the experimental results. (b) The pair correlation function  $g_{OO}(r)$  for three of five temperatures studied (Table I). Note the pronounced increase in the  $3.3$  Å peak (arrow) when pressure is increased. The curves may be identified as in (a). (c) The molecular structure factor  $S_M(q)$ , calculated from the Fourier transform of  $h(r)$  [(a)]. Looking at the first peak in  $S_M(q)$ , the curves are identified as described in (a). Note the shift in the first peak when pressure is increased.

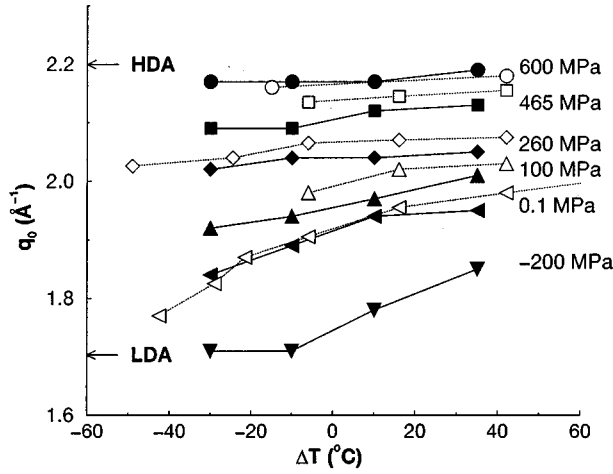


FIG. 2. The value  $q_0$  of the first peak of the structure factor from Fig. 1(c). At low  $T$ , both the simulated (filled symbols) and experimental (open symbols) values of  $q_0$  tend toward the values for the two amorphous forms of water, HDA and LDA.

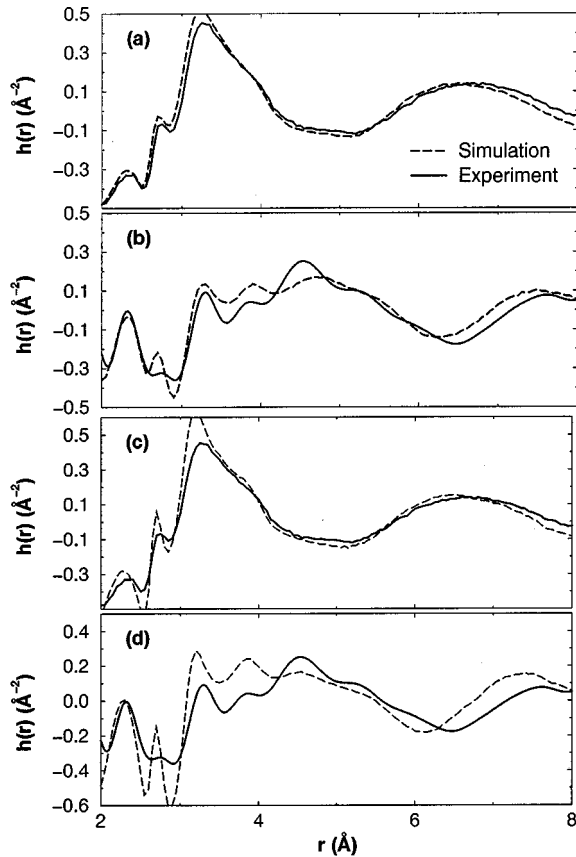


FIG. 3. (a) Comparison of the structure of the supercooled liquid at  $\Delta T = -30^\circ\text{C}$  and  $P = 600\text{ MPa}$  with the experimentally measured structure of HDA solid water from Ref. [32]. (b) Comparison of the supercooled liquid structure at  $\Delta T = -30^\circ\text{C}$  and  $P = -200\text{ MPa}$  with LDA solid water [32]. (c) Comparison of the structure of the glassy simulation at  $\Delta T = -145^\circ\text{C}$  and  $P = 600\text{ MPa}$  with the experimentally measured structure of HDA solid water from Ref. [32]. (d) Comparison of the glassy simulation at  $\Delta T = -145^\circ\text{C}$  and atmospheric pressure [35] with LDA solid water [32].

TABLE I. Summary of results from the 24 liquid and 2 glassy state points simulated. The liquid state points simulated at positive pressure correspond roughly to temperatures and pressures studied in the experiments of Ref. [4]. We equilibrate systems of 8000 molecules to a constant temperature and pressure by monitoring the evolution of the density and internal energy. We adjust the temperature and pressure via the methods of Berendsen [19] and we account for the long-range Coulomb interactions using the reaction field technique with a cutoff of 0.79 nm [20]. The equations of motion evolve by the SHAKE algorithm [21] with a time step of 1 fs. To facilitate comparison between simulations and experiments, we define  $\Delta T \equiv T - T_{\text{MD}}$ , the temperature relative to that of the 1 atm temperature of maximum density  $T_{\text{MD}}$  [22]. Thus we report the simulation temperature relative to  $T_{\text{MD}}^{\text{SPC/E}} \approx 245\text{ K}$ . Similarly, experimental temperatures reported relative to the 1 atm  $T_{\text{MD}}$  of  $\text{D}_2\text{O}$ , 284 K. All state points are liquid, except  $\Delta T = -145^\circ\text{C}$ , which is glassy.

$P$ (MPa)	$\Delta T$ ( $^\circ\text{C}$ )	$\rho$ (g/cm $^3$ )	$U$ (kJ/mol)	Equilibration time (ps)
600	35	$1.1930 \pm 0.0003$	-47.65	1100
	10	$1.2041 \pm 0.0004$	-49.02	1300
	-10	$1.2139 \pm 0.0005$	-50.22	2000
	-30	$1.2236 \pm 0.0003$	-51.43	3000
	-145	$1.250 \pm 0.008$	-55.3	4000
465	35	$1.1616 \pm 0.0004$	-47.61	1100
	10	$1.1723 \pm 0.0005$	-49.05	1300
	-10	$1.1803 \pm 0.0005$	-50.24	1800
260	-30	$1.1899 \pm 0.0004$	-51.49	2500
	35	$1.1060 \pm 0.0004$	-47.59	550
	10	$1.1145 \pm 0.0006$	-49.09	750
100	-10	$1.1201 \pm 0.0005$	-50.33	1500
	-30	$1.1224 \pm 0.0005$	-51.62	2100
	35	$1.0514 \pm 0.0004$	-47.51	600
0.1	10	$1.0570 \pm 0.0005$	-49.11	800
	-10	$1.0555 \pm 0.0003$	-50.48	1500
	-30	$1.0513 \pm 0.0006$	-51.85	2100
	-145	$1.022 \pm 0.009$	-56.1	4000
-200	35	$0.9064 \pm 0.0003$	-46.73	600
	10	$0.9212 \pm 0.0005$	-48.83	800
	-10	$0.9245 \pm 0.0003$	-50.59	1500
	-30	$0.9283 \pm 0.0004$	-52.12	3000

over a wide range of temperatures and pressures. By comparing the simulated pair correlation functions and structure factor with our experimental data, we find that the structure of the supercooled liquid at low pressure resembles the structure of low-density amorphous (LDA) ice. At high pressure, we find that the structure of the liquid appears independent of temperature and is nearly indistinguishable from that of high-density amorphous (HDA) ice. The combined results at high and low pressure appear consistent with continuity between the liquid and glassy states of water at all pressures.

We analyze the structures found in our simulations by calculating the atomic radial distribution functions  $g_{\text{OO}}(r)$ ,  $g_{\text{OH}}(r)$ , and  $g_{\text{HH}}(r)$ . To compare the distribution functions

with neutron-scattering measurements, we form the weighted sum

$$h(r) \equiv 4\pi\rho r [w_1 g_{\text{OO}}(r) + w_2 g_{\text{OH}}(r) + w_3 g_{\text{HH}}(r) - 1], \quad (1)$$

where the weighting factors  $w_i$  are selected to coincide with experimental measurements of  $\text{D}_2\text{O}$  [26]. Experimentally,  $h(r)$  is obtained by Fourier transformation of the molecular structure factor. The dominant contributions to  $h(r)$  are the H-H and O-H (or D-D and O-D for  $\text{D}_2\text{O}$ ) spatial correlations, so  $h(r)$  includes relatively little contribution from oxygen-oxygen correlations. Figure 1(a) shows  $h(r)$  at two of the five temperatures simulated and also compares with experimental data. The peaks centered at 1.8 Å, 2.3 Å, and 2.8 Å correspond to the O-H, H-H, and O-O intermolecular distances in the hydrogen-bonded configuration, respectively. While the magnitudes of these peaks change slightly, their ubiquity demonstrates the stability of the first neighbor ordering, namely, that each molecule is typically surrounded by four molecules in a tetrahedral configuration.

We find that the peak at 3.3 Å of  $h(r)$  becomes more pronounced as  $P$  increases. Examination of the individual radial distribution functions shows that the increase at 3.3 Å can be attributed to changes in  $g_{\text{OH}}(r)$ . In addition,  $g_{\text{OO}}(r)$  shows a pronounced increase at 3.3 Å under pressure [Fig. 1(b)], but cannot account for the changes in  $h(r)$ , as the  $g_{\text{OO}}(r)$  weighting factor in Eq. (1) is small [3]. The growth at 3.3 Å in  $g_{\text{OO}}(r)$  indicates that the liquid locally has the structure of an interpenetrating tetrahedral network similar to ice VI and VII, the ice polymorphs close to the high-pressure liquid [27,28], and can also be associated with the formation of clusters with structure similar to HDA [29].

To directly compare with experimental measurements, we calculate the molecular structure factor  $S_M(q) = S_M^{\text{intra}}(q) + S_M^{\text{inter}}(q)$ , where  $S_M^{\text{intra}}(q)$  and  $S_M^{\text{inter}}(q)$  are the intramolecular and intermolecular contributions to  $S_M(q)$ , respectively. We calculate  $S_M^{\text{intra}}(q)$  explicitly, as described in Ref. [30], and Fourier transform  $h(r)$  to obtain  $S_M^{\text{inter}}(q)$ . We find striking

agreement between simulated and experimental values of  $S_M(q)$  [Fig. 1(c)]. In particular, the value  $q_0 = q_0(P, T)$  of the first peak of  $S_M(q)$  shifts to larger  $q$  values as  $P$  increases [Fig. 2]. We note the feature that as temperature is lowered (i) for  $P = 600$  MPa,  $q_0$  approaches the experimental  $q_0$  value of HDA ice ( $2.20 \text{ \AA}^{-1}$ ), (ii) for  $P = 0.1$  MPa and  $-200$  MPa,  $q_0$  approaches the experimental  $q_0$  value of LDA ice ( $1.69 \text{ \AA}^{-1}$ ). Indeed we find that the high-pressure liquid structure resembles that of HDA ice [Fig. 3(a)], and the low-pressure liquid structure that of LDA ice [Fig. 3(b)] [31].

We also study the structure of the glassy phase [33,34] and find that the structure of the simulated glasses strongly resembles the experimentally measured structure of HDA and LDA solid water [Figs. 3(c) and 3(d)], suggesting that the simulated glassy state points are the analogs of HDA and LDA solid water for SPC/E. Furthermore, by compression of the simulated LDA-like system, we are able to reversibly transform the structure to the HDA-like system, reminiscent of the experimentally observed reversible first-order transition of LDA to HDA under pressure [36].

The absence of a dramatic structural difference between the liquid and the glassy states is consistent with the postulated continuity between atmospheric pressure water and LDA ice [37], based on measurements of the free energy [16,38] and dielectric relaxation time [39] at 1 atm. Our results are also consistent with continuity between high-pressure liquid water and HDA ice [4,6], but thus far the glass transition of HDA has not been experimentally observed, due to the difficulties of studying supercooled water under pressure.

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