

Supporting Material for: “Pressure and Salt Effects in Simulated Water: Two Sides of the Same Coin?”

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In Figures 1-4 we show the oxygen oxygen radial distribution functions (RDFs) $g_{OO}(r)$ obtained for correlations including all water molecules. The $g_{OO}(r)$ have been recently suggested to be the most sensitive RDF to detailed changes of the water structure in the medium and longer range [1]. Figures 1-2 focus on the observed pressure and salt effect on the location and height of the first to maxima, whereas Figures 3-4 depict the long range behavior up to 1.2 nm.

The water-water correlations change significantly with increasing salt concentration, as well as with pressure. In particular we see for both scenarios, adding salt, as well as increasing pressure, that the first peak in the RDF weakens, and the second peak, which is traditionally regarded as the signature of tetrahedral bonding in water moves markedly inwards. In pure water it has been shown experimentally, that this peak moves to shorter distances upon application of an external pressure [2], which is also revealed by the TIP4P-Ew model here (see Figures 1, and 3). This is indicative of a distorted, but not necessarily broken, hydrogen bond network, and eventually at the highest pressures causes the collapse of the second neighboring shell into the first one [2]. In addition, the second maximum of the RDFs is found to be much more pronounced at 230 K compared to 300 K, which is in line with observation of a more ordered tetrahedral network at lower temperatures [3]. Finally, we would like to point out that our salt concentration and pressure dependent results are in good agreement with the recent neutron scattering experiments on aqueous salt solutions by Mancinelli et al. [1]. The inward shift of the second peak, at low, but as well at high temperatures (300 K), suggest that the water structure is changed due to the presence of the ions in a similar fashion as due to pressure. Since for 300 K only a minor structural influence has been obtained for “free water”, the changing RDFs, as shown here, have to be largely attributed to the changing water structure in the first and second hydration shell of the ions.

References

- [1] R. Mancinelli, A. Botti, F. Bruni, M. A. Ricci, and A. K. Soper. Perturbation of water structure due to monovalent ions in solution. *Phys. Chem. Chem. Phys.*, 9:2959–2967, 2007.
- [2] A. K. Soper and M. A. Ricci. Structures of high-density and low-density water. *Phys. Rev. Lett.*, 84:2881–2884, 2000.
- [3] D. Paschek and A. Geiger. Simulation study on the diffusive motion in deeply supercooled water. *J. Phys. Chem. B*, 103:4139–4146, 1999.

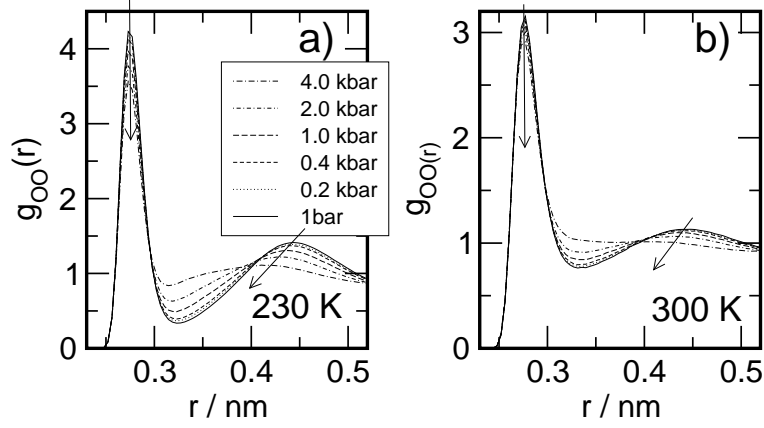


Figure 1: Oxygen-oxygen radial distribution functions for pure TIP4P-Ew model water (obtained from the MD simulations) as a function of pressure. a) $T = 230$ K. b) $T = 300$ K. The arrows indicate the position and shift of the first and second maximum as pressure increases.

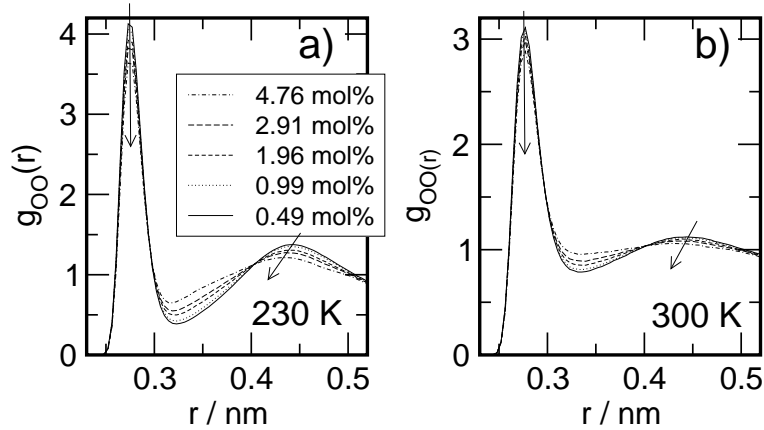


Figure 2: Oxygen-oxygen radial distribution functions for aqueous TIP4P-Ew (NaCl) salt solutions as a function of salt concentration. a) $T = 230$ K. b) $T = 300$ K. The arrows indicate the position and shift of the first and second maximum as the salt concentration increases.

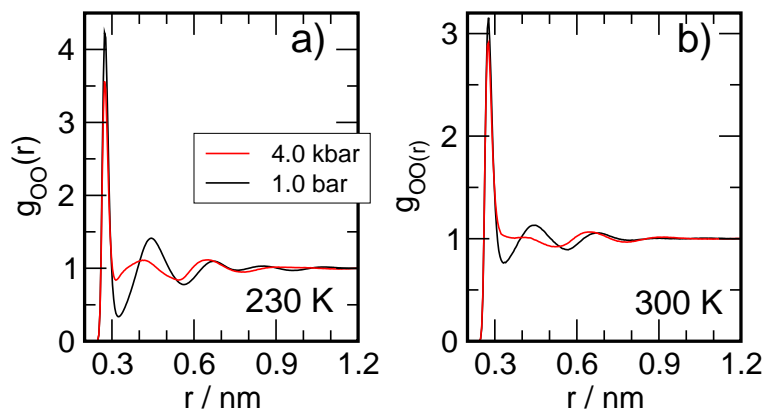


Figure 3: Oxygen-oxygen radial distribution functions for pure TIP4P-Ew model water (obtained from the MD simulations) as a function of pressure. a) $T=230$ K. b) $T=300$ K.

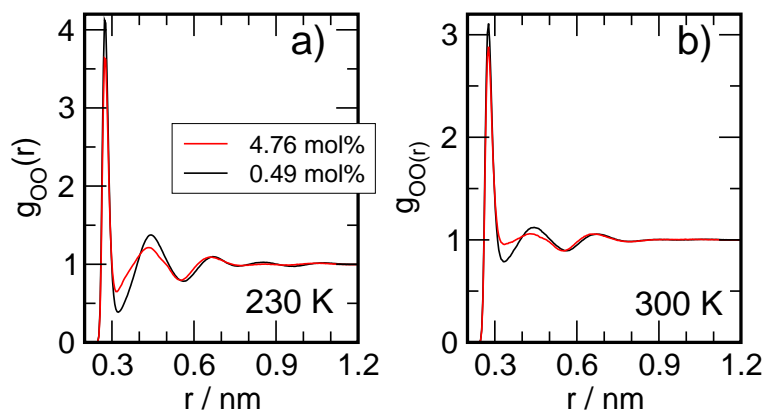


Figure 4: Oxygen-oxygen radial distribution functions for aqueous TIP4P-Ew (NaCl) salt solutions as a function of salt concentration. a) $T=230$ K. b) $T=300$ K.