Supplementary Material to
Computational Assessment of the Entropy of Solvation of Small-Sized Hydrophobic Entities

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I Structural Analysis of AMOEBA Based MD Simulations of Liquid Water with Special Emphasis on Hydrogen Bond Networks

Important insight into the H-Bond mediated behaviour of intermolecular relationships between individual water molecules in bulk water has been gained from X-ray absorption spectroscopy as well as X-ray Raman scattering [40]. It is important to demonstrate that the applied model description of the liquid state of water does cover most of the specific intermolecular interactions observed in these experiments. This is especially important with respect to maintainance of the Hydrogen Bond (HB) network in liquid water, since this latter is a crucial determinant in LCW theory.

The three central *Radial Distribution Functions* (RDF) for the description of bulk water have been derived from the $\lambda = 0.5$ simulations, which are quasi-unperturbed. Corresponding plots for T=300 K and T=370 K are shown in Figures A – F.

In general we notice rather close agreement with the RDFs reported in the original AMOEBA paper (see [21] Figures 5 – 7). This is somewhat surprising, considering the limited amount of structural data available to this present study.

The $g_{OO}(r)$ shows the characteristic immediate neighborhood peak at 2.9 Å. A second, diminishing peak is very broadly distributed around 4.6 Å but hard to distinguish from the baseline. The second peak in the $g_{OH}(r)$ is attributed to pairs of water molecules directly associated via HBs. This second peak appears at 1.9 Å in the present data with a width of $\pm$ 0.55 Å. The $g_{HH}(r)$ exhibits a characteristic second peak at 2.5 Å. It is interesting to note that present data RDFs match the MP2 results of the QM/MM study by Xenides et al [41] rather well. In order to investigate the actual HB mediated coordination in greater detail we followed the procedure outlined in [41]. A HB is thus characterized to

1. occur between a pair of water molecules where the O – O distance is less than 3.5 Å,

2. involve a not covalently bond H which falls into the domain of the second peak of the $g_{OH}(r)$ (1.9 $\pm$ 0.55 Å),

3. exhibit an HB angle (O...H-O) greater than 100 degree.

Following along this lines we get an average number of established HBs of 1.6 and a frequency of tetrahedrally HB-connected coordination of only about 2 % at 300 K. This seems to be re-confirming the previous findings of Wernet et al [40] of predominantly 2 HBs in bulk water (against the conventional view of 4 HBs in tetrahedral coordination) as well as of Xenides et al [41] that the tetrahedral coordination is rather the exception than the rule.

Significant changes in going from 300 K to 370 K are the entire loss of the second, very broad shoulder around 4.6 Å in the $g_{OO}(r)$, the decrease of the average number of HBs to 1.4 and the general loss of tetrahedrally HB-mediated coordinations.

References

[21] P. Ren, J. W. Ponder, *J. Phys. Chem. B*, 2003, **107**, 5933.

[40] Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L.Å. Näslund, T.K. Hirsch, L. Ojamäe, P. Glatzel, L.G.M. Pettersson, A. Nilsson, *Science*, 2004, **304**, 995.

[41] D. Xenides, B.R. Randolf, B.M. Rode, *J. Chem. Phys.*, 2005, **122**, 174506.

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Figure A: Radial Distribution Function for the O - O distance in liquid water at 300 K as derived form AMOEBA MD/FEP simulations.
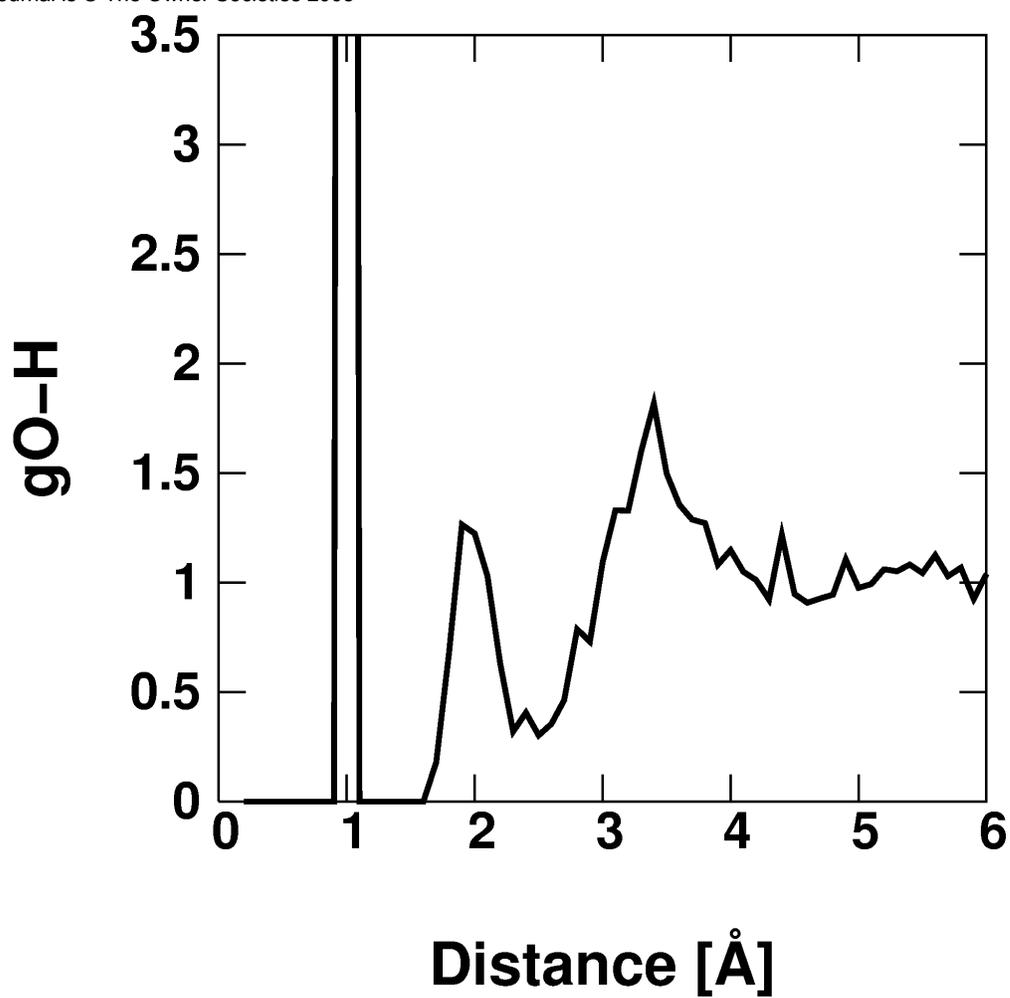
Figure B: Radial Distribution Function for the O - H distance in liquid water at 300 K as derived form AMOEBA MD/FEP simulations.
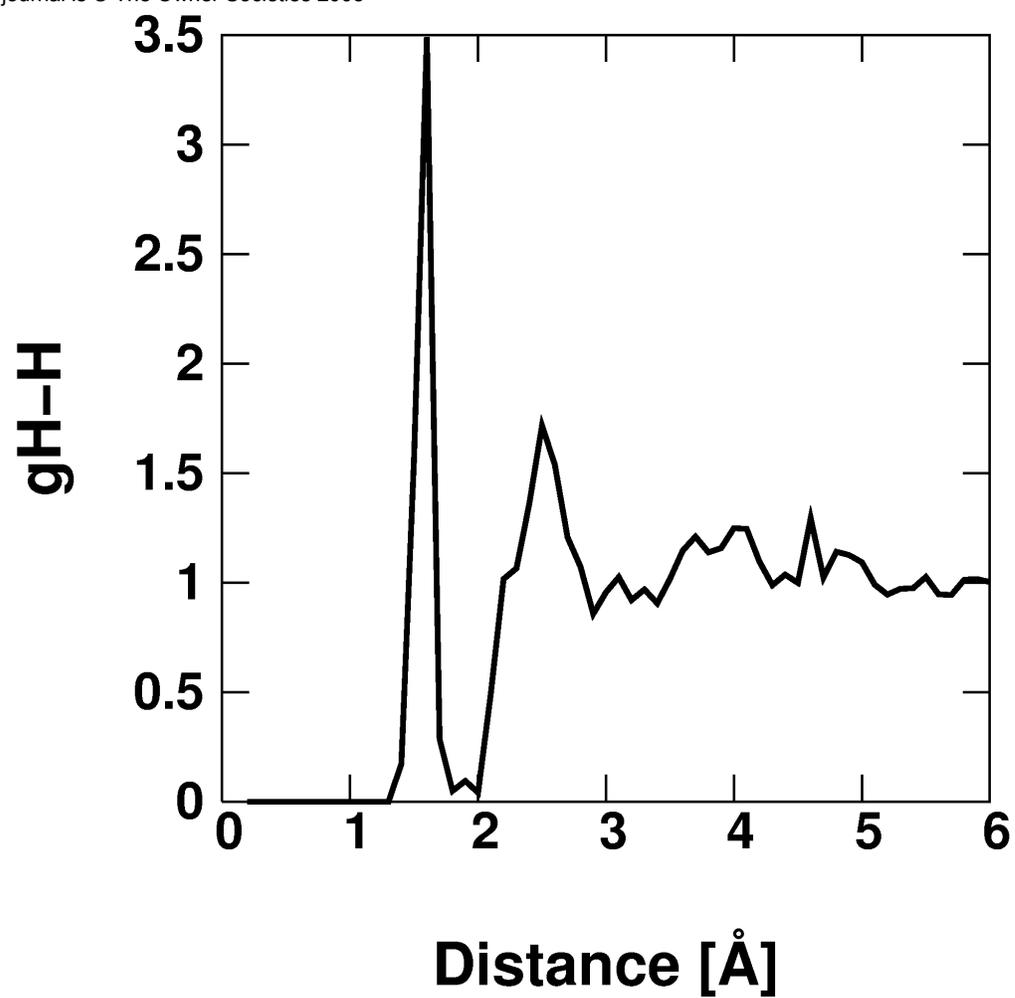
Figure C: Radial Distribution Function for the H - H distance in liquid water at 300 K as derived form AMOEBA MD/FEP simulations.
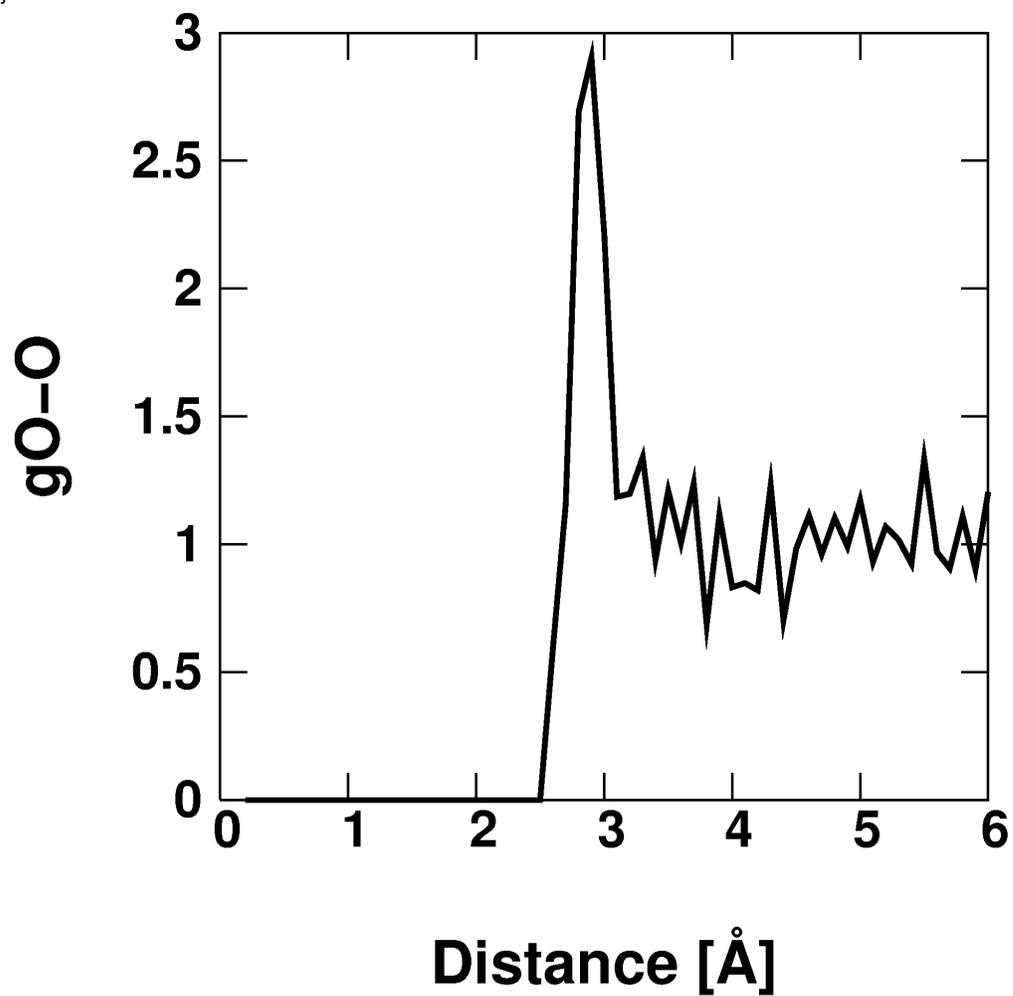
Figure D: Radial Distribution Function for the O - O distance in liquid water at 370 K as derived form AMOEBA MD/FEP simulations.
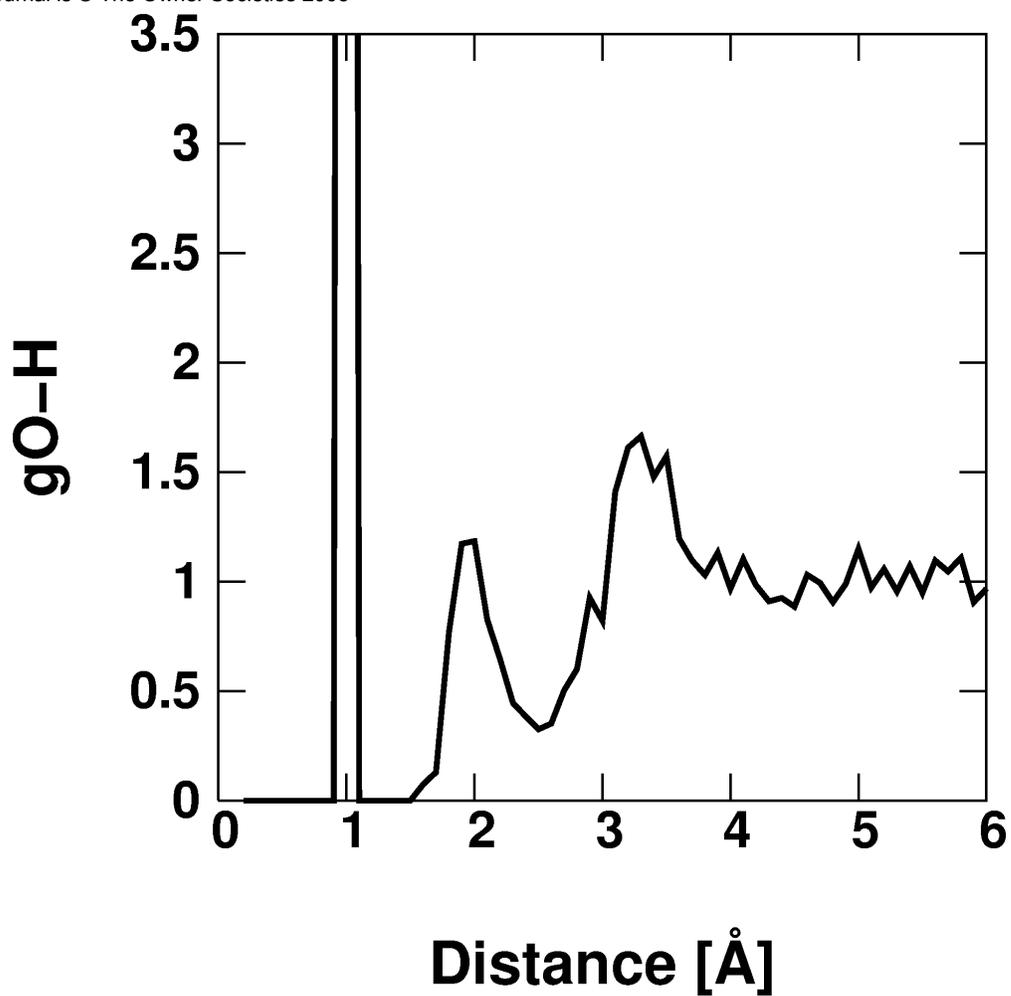
Figure E: Radial Distribution Function for the O - H distance in liquid water at 370 K as derived form AMOEBA MD/FEP simulations.
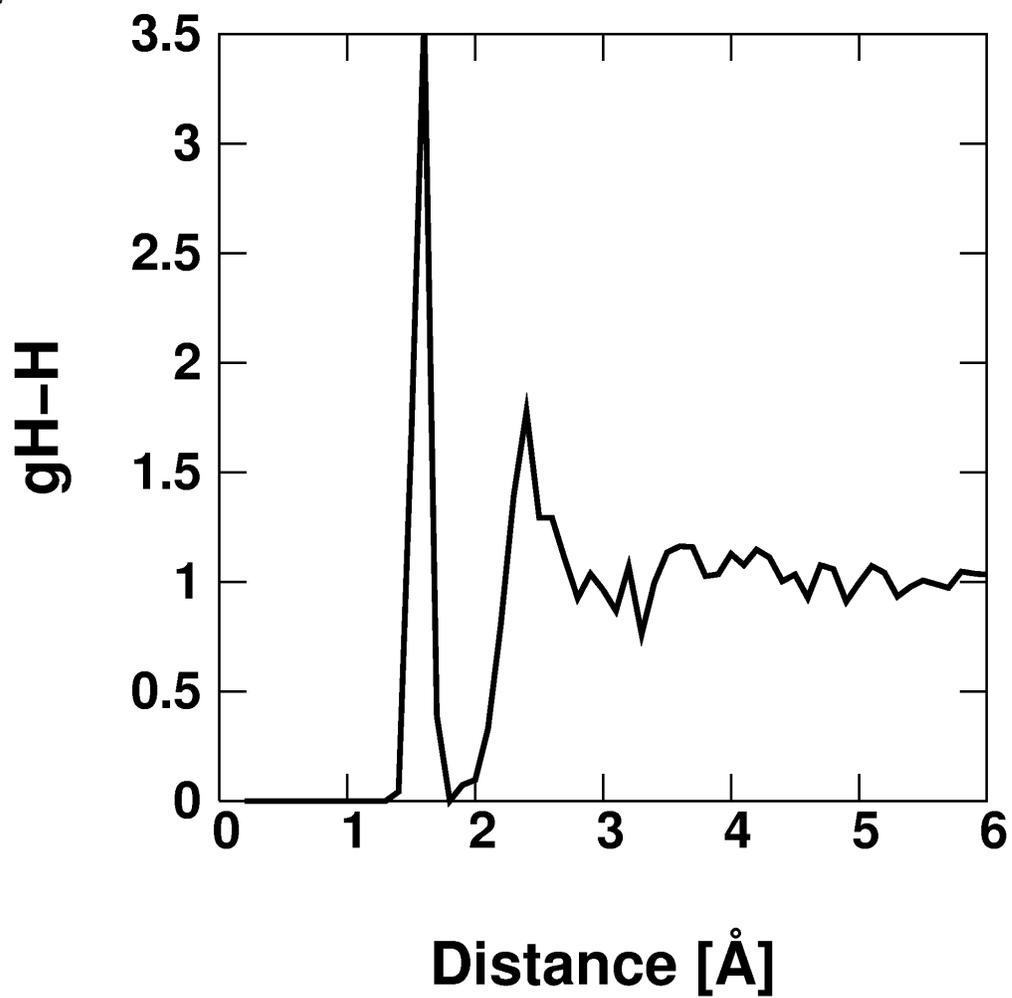
Figure F: Radial Distribution Function for the H - H distance in liquid water at 370 K as derived form AMOEBA MD/FEP simulations.