Thermodynamics of water clusters calculated ab initio

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Water clusters play an important role in many areas of science, including atmospheric chemistry, environmental sciences, or biophysics and biochemistry.[1] Therefore, they have attracted great attention of both experimentalists and theoreticians in the past as well as at present. The geometric structure of water clusters is of principal importance for the chemical physics and physical chemistry community as it influences the role water complexes in many physical and chemical processes. While there is quite an extensive literature on the zero-temperature structure of pure water clusters[2], much less effort has so far been devoted to theoretical investigation of temperature-induced structural changes in these clusters, mainly because of huge computational demands symptomatic for such studies. Whenever water clusters have been a subject of thermodynamic simulations, mostly focused on structural transformations of these systems with changing temperature, simple and computationally cheap empirical interaction models have been used (despite the fact that they were adjusted to bulk properties of water, which, nevertheless, shows rather different behavior as compared to what is observed in clusters and nanodroplets). See, e.g., Fig. 1 where curves of the heat capacity of water tetramer are depicted as obtained for two such empirical potentials (TIP4P[3] and TIP5P[4]) together with a curve calculated for an empirical potential (TIP6P[5]) re-adjusted using DFT calculations. Note that DFT methods, often being questioned in connection of their reliability, perform quite well for hydrogen-bonded water networks provided proper exchange-correlation functionals are used. In this case, an MP2 level of theory can be reached.[6]

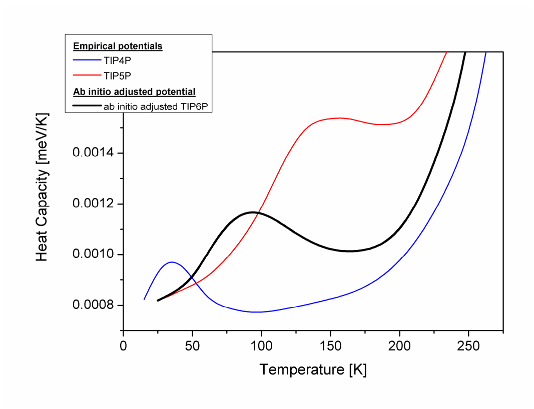

Figure 1
Constant-volume heat capacity of pure water tetramer, $(H_2O)_4$, calculated for two empirical, bulk-adjusted potentials (TIP4P and TIP5P) and a potential fitted on data obtained at the DFT (B97R+aug-cc-pVTZ) level of theory. Local maxima correspond to a solid-to-liquid phase transition in the cluster as predicted by the three models used.

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[1] R. Ludwig, Angew. Chem. Int. Ed. 40 (2001) 1808.

[2] B. Bandow and B. Hartke, J. Phys. Chem. A 110 (2006) 5809; D. Wales et al. *Cambridge Cluster Database*.

[3] W. L. Jorgensen et al. J. Chem. Phys. 79 (1983) 926.

[4] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. 112 (2000) 8910.

[5] H. Nada and J. P. J. M. van der Eerden, J. Chem. Phys. 118 (2003) 7401.

[6] F. S. Sousa et al. J. Chem. Phys. A 111 (2007) 10439.

Recent investigations of zero-temperature structures of small and medium-sized water clusters showed that at least MP2 level of theory and aug-cc-pVDZ basis sets are required for obtaining realistic results concerning water clusters binding energies and equilibrium structures.[7] Such calculations are, however, too demanding for thermodynamic simulations, in particular in regions of structural transformations, where a lot of (dozens of millions) sample geometries have to be generated, either by Monte Carlo or molecular dynamics methods, to reach convergence and avoid unphysical correlations. One possible way for overcoming these technical limitations within the Monte Carlo approach is the Boltzmann-weighting (BW) technology[8], which first employs a simple, computationally cheap interaction potential (guiding potential) for sampling the configuration space of the system under study and only then more sophisticated quantum chemistry calculations are used to refine the simple-potential data and to reach the required level of theory. The necessary condition for an acceptable rate of convergence of the BW approach is that the simple potential and quantum chemistry data do not differ much from each other for a pre-generated set of samples. *For this reason we have used guiding potentials re-parametrized for each cluster size using quantum chemistry data obtained at the same level theory as proposed for the BW refinement.*

Another problem emerging in relation to the BW approach is that only several thousands of sample configurations are manageable by quantum chemistry methods while much more are usually required for Monte Carlo chains to converge. *To escape from this trap due to the technical limitations of present computational resources, we have combined the BW approach with recently proposed multiple-histogram (MH) methodology [9] and computationally efficient parallel-tempering (PT) method [10]*. The PT method considerably accelerates the convergence of thermodynamic data by mixing information reached at various temperatures, the MH scheme assembles the information collected at various temperatures in a unified form of density of states and re-uses the collected information in a new set of calculations performed at newly selected temperatures that are need for further analysis. The MH approach reduces the number of sample configurations per a temperature point saving thus computer time considerably.

The novel methodology for thermodynamic simulations combining high level of electronic structure calculations with the Monte Carlo approach has been applied to the pilot system of pure water tetramer, $(H_2O)_4$. Results are shown in Figure 2.

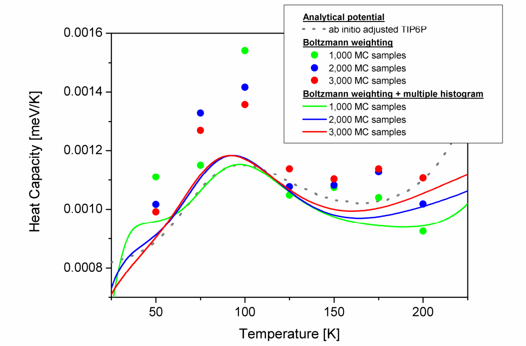

Figure 2
Constant-volume heat capacity of pure water tetramer, $(H_2O)_4$, calculated using BW Monte Carlo (points) and BW & MH Monte Carlo simulations (full lines) for various simulation lengths. The same level of theory is used as in Figure 1. Compare the rates of convergence for BW and BW+MH methodology. Note also that a simple TIP6P potential performs well if re-parametrized using quantum chemistry (here DFT) data.

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[7] See, e.g., G. S. Fanourgakis et al. J. Chem. Phys. 121 (2004) 2655.

[8] See, e.g., M. P. Allen and P. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, Oxford 1987.

[9] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. 61 (1988) 2635.

[10] R. H. Swendsen and J.-S. Wang, Phys. Rev. Lett. 57 (1986) 2607; see also D. J. Earl and M. W. Deem, PCCP 7 (2005) 3910.