**Accurate Prediction of the Thermodynamic Properties of Water from Molecular Dynamics**

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Water is arguably the most important molecule on Earth, with a near ubiquitous role in biological, chemical and industrial processes. Despite its molecular simplicity, accurately predicting its properties, which involves many known examples of anomalous behavior, has been surprisingly difficult. Historically, attempts to predict its behavior were confined largely to either empirical correlations or equation of state modelling [1], [2]. More recently, molecular simulation [3] has become the method of choice because of the nexus between underlying intermolecular interactions and observable macroscopic properties. An accurate intermolecular potential for the evaluation of inter-particle forces or energies is the key to reliable predictions. Many alternative intermolecular potentials for water [4] have been proposed, although the basis of the underlying model is often largely semi-empirical. The most widely used models are rigid and variants of either the four-site transferable interaction potential (TIP4P) or the three-site simple point charge (SPC, SPC/E) models. These types of potentials are computationally easy to implement and in many cases they have provided worthwhile predictions. Comparisons with experimental data are often focused at relatively low temperatures and pressures, with a temperature of 25 ºC and a pressure of 1 atmosphere being a popular choice. Polarization is a very important contribution to the intermolecular interaction in water that has been largely missing from many simple potentials. Recent work [5], using an ab initio based potential (MCYna) strongly indicates that including polarization greatly improves the accuracy of predictions. In this work, we report molecular dynamics results for phase equilibria, thermodynamic properties and diffusion data for both water and aqueous mixtures using the MCYna potential, other alternative polarizable potentials, and traditional potentials such as TIP4P/2005, SPC and SPC/E. The comparison with experimental data covers a wide range of temperatures and pressures. It is demonstrated that, in many cases, including polarization in the MCYna potential results in almost perfect agreement with experiment and as such it is more accurate than can be obtained from conventional approaches. Importantly, the improvement gained in accuracy was achieved without resorting to fitting theory to experiment and as such the calculations represent genuine a priori predictions.

References

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