

New Progress on Water!

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Recommended with a Commentary by Stephen Berry, University of Chicago

Water, among all the small molecules, has been one of the greatest, perhaps even the greatest, challenge to theorists. The first representation of a potential of interaction between water molecules was that of Bernal and Fowler in 1933, and there have been innumerable attempts to find a better description since then. An ideal theoretical model would describe the properties of dimers and small clusters of water molecules and of bulk liquid water, and would also describe the freezing, melting and vaporization processes. A still more challenging goal would be finding a model that described the interaction of water molecules with other species, e.g. metal and insulator surfaces, ions and molecules that act as nucleation centers in the atmosphere, and biomolecular surfaces. Just simulating the freezing process illustrates the difficulties of dealing with water; this was done successfully in 2002¹

There are many approaches to creating an effective model, from empirical representations based on known properties such as molecular size, dipole moment and polarizability, to fully *ab initio* representations derived by solving the Schrödinger equation for interacting molecules and constructing a potential from those *ab initio* results. A review² describes the vast effort that has gone to try to address this problem. Recently, two approaches have made major steps, bringing us very close to accurate modeling of the properties of water, both in clusters and in bulk. One is the use of quantum calculations to fit a very powerful, adaptive model potential, by Fanourgakis et al., an approach that has succeeded in demonstrating the importance of quantum effects, notably zero-point energies and amplitudes of vibrations, as well as reproducing the experimental heat of vaporization within approximately 1 kcal/mole. These simulations were able to show how dimer and cluster formation affect bond angles and, fairly well, bond lengths as well. Then the most recent advance appeared by Bukowski et al., in which the authors derived quantum levels of the dimer, including tunneling splittings, and second virial coefficients of bulk water. This model used an almost completely *ab initio* approach, apart from requiring the monomers to be rigid, and including a polarizability center close to each oxygen atom. The results for the vibration-rotation levels of the dimer are in quite good agreement with the experimental figures, including the tunneling splittings. The second virial coefficient and radial distribution functions were evaluated from simulations of 256 and 512 water molecules confined to a box to make the density 1g/cm³. The model is already being extended to allow for flexibility in the monomer.

1. M. Matsumoto, S. Saito and I. Ohmine, *Nature* **416**, 409-413 (2002).
2. B. Guillot, *J. Molec. Liq.* **101**, 219-260 (2002).