PhD Thesis Summary

Systematic development of a transferable water potential for molecular simulations

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Budapest, 2014

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Introduction

Besides water is the most ubiquitous matter on the Earth, it is an interesting liquid in itself. Compared to a simple analogous molecule (like methane) it has more than 60 anomalous properties. Water is the most common solvent, and this is medium of the biochemical processes and reactions. So is it not surprising that up till now more than a hundred classical models have been suggested for the water molecule.

The increase of the computational power in the last 10-15 years gives the opportunity to replace the widely used nonpolarizable models by polarizable one, which could provide better performance in diverse environments. This process is still goes on, but the overall quality of polarizable models we found in the literature is still far behind the best nonpolarizbale water model (TIP4P/2005). The main goal of my PhD work was to test the existing polarizable models, and develop a new model for water, which corrects the errors of the TIP4P/2005 caused by the lack of polarizability, but, at the same time preserve the good prediction of that model for condensed phase properties.

Based on earlier experience in the new water model the point charges have been replaced by Gaussian charge distributions. Gaussian charge distributions are not part of the simulation canon, therefore an important part of my PhD work was to develop numerical methods and algorithms to handle Gaussian charge distributions in order to determine properties in different parts of the phase diagram. All programs including the molecular dynamics code used to produce the results presented in this thesis were written by me.

Results

Developments in simulation technology

- In molecular dynamics simulations the electrostatic interactions need a special treatment because of their long-range nature. There are two widely used methods: the reaction field, which is an approximate method, and the exact Ewald summation. I derived expressions of the Ewald summation for the electrostatic energy, force and pressure tensor for the case of Gaussian charge distributions and molecular systems.

- The most efficient implementation of the Ewald summation uses Fast Fourier Transform based Particle Mesh Ewald (PME) algorithm to calculate the reciprocal part quantities. Originally the PME was developed for point charges, and cannot be extended to Gaussian charge distributions. Therefore I suggested a modified direct space energy expression, thus the PME can be used in the reciproc space without any modification. It is easy to install this method to existing program packages, which makes them suitable to handle point charges and Gaussian charge distributions together.

- I derived theoretically and verified by test simulations that the pressure tensor of polarizable models can be calculated by the same expression as the pressure tensor of nonpolarizable ones provided the induced dipoles are in their equilibrium position.

Development of water models

- The gas-phase trimer of SPC type water models has qualitatively erroneous geometric structure. I showed that the main reason of this is that the negative charge is placed on the oxygen. I also showed the traces of this erroneous geometry are noticeable in liquid phase too.

- I developed a method to predict the density of the high pressure ice VII accurately. In this method the van der Waals interactions between two water molecules ware calculated by a linear combination of two potentials. The linear

combination coefficients depend on the attractive or repulsive forces acting on the molecule. This linear combination coefficient can be interpreted as a size of the molecule.

- I suggested three water models (named as Bkd1-3) which have the experimental gas phase geometry, use Gaussian charge distributions and Buckingham potential, and the polarization was expressed by charge-on-spring method using one polarizable charge. I tested extensively the BKd and the recently developed COS and SWM4 models by determining the ambient properties, the density-temperature function, the solid-liquid and vapor-liquid equilibrium properties and the densities of different ice phases. It turned out that the BKd models are explicit progress compared to the COS and SWM4 models, mainly in phase equilibrium properties. In gas phase thanks to the polarizability the BKd models are superior to the TIP4P/2005, which is the best nonpolarizable water model at present, but their condensed phase properties in overall do not reach the quality of the TIP4P/2005.

- I draw some important conclusion about the parametrization of the water models. The dielectric constant and the density-temperature function should be fitted directly, otherwise the match of these properties is accidental. The low temperature part of the density-temperature function is related to the freezing temperature, and the slope of the high temperature region of this functions correlates with vapor-liquid equilibrium properties. Therefore the fit of the density-temperature function guarantees that these phase equilibrium properties will also be accurate. To get better freezing point the enthalpy difference between the water and ice Ih should be fitted at 273 K.

- Based on earlier experiences with BKd models I developed the BK3 water model. The main innovation of this model is that all three charges take part in the polarization, not just the negative one. The polarizability is divided between the charges proportionally to their magnitudes, the van der Waals interactions are described by Buckingham potential. The BK3 is a relatively simple and elegant

model, which uses the experimentally derived properties of the water monomer. The bond length is 0.975 Å, the average bond length in condensed phases are around this value, the polarizability and dipole- and quadrupole moments of the nonpolarized molecule are in the best possible match with the experimental gas phase values. The model was fitted primarily to the density-temperature function of water.

- I examined in detail the properties of the BK3 model in terms of temperature and density. I calculated the vapor-liquid coexistence curve and the melting point, and some anomalous properties of the water. Compared to the TIP4P/2005 the BK3 is much better in those properties, where the polarizability plays an important role (dielectric constant, vapor pressure, vaporization enthalpy, gas phase properties), meanwhile it predicts the other (mainly condensed phase related) properties at least as accurately as the TIP4P/2005. The BK3 model describes quantitatively numerous anomalous properties of the water: the density maximum and its shift to lower temperatures at higher pressures, the compressibility minimum, the densities of different ice phases and the increase of the diffusion constant with increasing pressure at low temperature. Qualitatively predicts the decrease of the viscosity with increasing pressure at low temperature. To our knowledge presently the BK3 is the best classical polarizable model of the water molecule.

The dissertation based on the following publications

P. T. Kiss, A. Baranyai
Sources of the deficiencies in the popular SPC/E and TIP3P models of water.
Journal of Chemical Physics, **134** 054106 (2011)

P. T. Kiss, A. Baranyai
Transferable model of water with variable molecular size.
Journal of Chemical Physics, **134**, 214111 (2011)

A. Baranyai, P. T. Kiss
Polarizable model of water with field-dependent polarization.
Journal of Chemical Physics, **135**, 234110 (2011)

P. T. Kiss, A. Baranyai
On the pressure calculation for polarizable models in computer simulation.
Journal of Chemical Physics, **136**, 104109 (2012)

P. T. Kiss, A. Baranyai
Density maximum and polarizable models of water.
Journal of Chemical Physics, **137**, 084506 (2012)

P. T. Kiss, P. Bertsyk, A. Baranyai
Testing recent charge-on-spring type polarizable water models. I. Melting temperature and ice properties.
Journal of Chemical Physics, **137**, 194102 (2012)

P. T. Kiss, A. Baranyai
Testing the recent charge-on-spring type polarizable water models. II. Vapor-liquid equilibrium.
Journal of Chemical Physics, **137**, 194103 (2012)

P. T Kiss, A. Baranyai
A systematic development of a polarizable potential of water.
Journal of Chemical Physics, **138**, 204507 (2013)

P. T. Kiss, A. Baranyai,

Anomalous properties of water predicted by the BK3 model.

Journal of Chemical Physics, **140**, 154505 (2014)

Publications connected to the topic of the thesis

P. T. Kiss, A. Baranyai

Clusters of classical water models.

Journal of Chemical Physics, **131**, 204310 (2009)

A. Baranyai, P. T. Kiss

A transferable classical potential for the water molecule.

Journal of Chemical Physics, **133**, 144109. (2010)

P. T. Kiss, M. Darvas, A. Baranyai, P. Jedlovszky

Surface properties of the polarizable Baranyai-Kiss water model.

Journal of Chemical Physics, **136**, 114706 (2012)

Other publications

T. Turanyi, T. Nagy, I. G. Zsely, M. Cserhati, T. Varga, B. T. Szabo,

I. Sedyo, P. T. Kiss, A. Zempleni, H. J. Curran

Determination of rate parameters based on both direct and indirect measurements.

International Journal of Chemical Kinetics, **44**, 284 (2012)

A. R. Imre, A. Baranyai, U. K. Deiters, P. T. Kiss, T. Kraska, S. E. Quinones Cisneros

Estimation of the thermodynamic limit of overheating for bulk water from interfacial properties.

International Journal of Thermophysics, **34**, 2053 (2013)

P. T. Kiss, A. Baranyai

A new polarizable force field for alkali and halide ions

Journal of Chemical Physics, **141**, 114501 (2014)

Lectures

A. Baranyai, P. T. Kiss, *A transferable model of water*, 32nd International Conference on Solution Chemistry, La Grande Motte, France, 2011

A. Baranyai, P. T. Kiss, *A transferable model for water*
8th Liquid Matter Conference, Vienna, Ausria, 2011

A. Baranyai, P. T. Kiss, *A transferable classical polarizable model for the water molecule*, 22nd V.M. Goldschmidt Conference, Montreal, Canada, 2012

P. T. Kiss, A. Baranyai, *From high pressure ice to gas clusters of water*, European Molecular Liquids Group Annual Meeting, Eger, Hungary, 2012

P. T. Kiss, A. Baranyai, *Polarizable, transferable potentials for water and alkali- and halide ions*, Molecular Liquids Group Annual Meeting, Lille, France, 2013

P. T. Kiss, *Handling of the Gaussian charge distributions in computer simulations*, Central European Statistical Mechanics Mini-meeting, Budapest, Hungary, 2014

Posters

A. Baranyai, P. T. Kiss, *A transferable classical potential for the water molecule*, 8th Liblice Conference, Brno, Czech Republic, 2010

P. T. Kiss, A. Baranyai, *Clusters of classical water models,* 8th Liblice Conference, Brno, Czech Republic, 2010

P. T. Kiss, A. Baranyai, *Liquid-vapor equilibrium properties of a water model with nonlinear polarization*, 8th Liquid Matter Conference, Vienna, Austria, 2011

P. T. Kiss, András Baranyai, *A systematic development of a polarizable potential of water*, 9th Liquid Matter Conference, Lisbon, Portugal, 2014

P. T. Kiss, András Baranyai, *A new polarizable force field for alkali and halide ions*, 9th Liquid Matter Conference, Lisbon, Portugal, 2014