Final report of project K84382

Our model of water created by the support of the K67783 project was the best *polarizable* model in the literature[1]. The reason that our model was better than other polarizable models was that we used Gaussian charge distributions instead of point charges and exponential repulsion instead of the $r^{-12}$ repulsion. For polarization we opted for the charge-on-spring (COS) method instead of the polarizable point dipole because of simpler numerical handling. However, there were simultaneous efforts in the literature to reparametrize existing nonpolarizable models. The most successful of them is the TIP4P/2005 model[2] which used information obtained from the determination of the complete phase diagram of water[3]. While TIP4P/2005, being nonpolarizable, was unable to be consistent in the vapor-liquid regime and entirely useless in the gas phase (gas clusters, second virial coefficient), it produced good estimates for many density related properties all over the phase diagram. In this respect, polarizable models, including ours, were inferior. The major aim of the K84382 project was to create a transferable model for water which can be used all over the phase diagram. To achieve this goal we carried out extensive calculations in order to understand the relationship between parameters and property predictions.

If water is used as a solvent its relative permittivity must match the experimental value. The relative permittivity correlates with the size of the dipole moments of the constituent particles. However, it is also a function of the microscopic structure in a less obvious way. Most models both polarizable and nonpolarizable predict the relative permittivity inaccurately. We attempted to achieve this by two ways. First, we introduced field-dependent polarization[4]. (It has been shown by density functional calculations that if the charge distribution of the molecule is described by point charges the actual polarization is smaller than the experimental gas-phase value.) Since then this approach has been used by other authors as well. Second, as an alternative, we considered the repulsive part varying in terms of the net force acting on the molecule. This way we could grasp the density variation and the relative permittivity simultaneously[9]. The variable molecular size concept was already used for accurate prediction of the density of ices[5].

The pressure is a relatively sensitive property of the system. Small variations of repulsive wings can introduce huge changes in the pressure. The pressure is calculated using a virial formula for additive pairwise interactions. It has been discussed[6] that this formula cannot be used for polarizable potentials under periodic boundaries because polarizable potentials are not pairwise additive. We carried out demonstrative calculations to show that provided the induced dipole is accurately estimated, there is no difference between the formula used for nonpolarizable and polarizable models[7].

From the point of view of model creation the most crucial property of water is its temperature-density diagram. At ambient pressure the density of water has a maximum at 4C° between -40C° and 100C°. It became obvious for us that there is a strong correlation between the accuracy of the high-temperature part estimation of the curve and the quality of properties in the critical region. Since most of the polarizable models did not fit the temperature-density diagram, their estimate of the high-temperature part of the curve was accidental, although, in principle, the models possess the ability to fit this part of the curve. As for the low-density part of the curve, polarizable models were unable to estimate the low temperature and the high temperature part of this curve simultaneously. The low temperature part of the curve is related to the freezing properties of water. We determined this curve for several existing COS polarizable models and compared them to nonpolarizable ones from the literature. With the exception of the TIP4P/2005 and another newly parametrized nonpolarizable model, the TIP4P-EW[8] none of the existing models predicted this curve accurately[9].

Continuing the test of COS molecular models, we determined the melting temperature and densities of several ice polymorphs[10]. These calculations used sophisticated numerical methods. It turned out that previous COS models performed poorly, their best result was 215K. The estimate for our previous model [5] was 233K. We also determined vapor-liquid density curves in terms of the temperature[11]. We found similar results as for the melting temperature. The best result was 581K instead of the experimental 647K. Our model [5] produced 634K. The studied COS models were suggested by the GROMOS and the CHARMM group.

The most important results of project K84382 is the creation of the polarizable water model BK3[12]. There are four criteria for a good classical model: the gas phase model should be as close to

the experimental as possible; the physical principles describing the response of the molecule to the impact of the surrounding should be simple and reasonable; the numerical realization should be computationally economic; and most importantly, the experimental properties should be predicted with acceptable accuracy.

It is accepted in the literature that this model is the best classical model of water. (See for instance the comprehensive site on water http://www1.lsbu.ac.uk/water/water_models.html). In terms of quality of predictions the only competitor is the IAMOEBA model, but this model has much more parameters and inconsistent because only the permanent charges polarizing the polarizable sites[13].

Our new model is rigid and contains three Gaussian charges. Contrary to other models (including our previous model [1]), all charges take part in the polarization of the molecule. They are connected by harmonic springs to their gas-phase positions: the negative charge to a prescribed point on the main axis of the molecule; the positive charges to the hydrogens. The dipole moment exactly, the quadrupole moment by a least mean square fit matches the gas-phase experimental value. The mechanical equilibrium between the electrostatic forces and the spring forces determines the polarization of the molecule which is established by iteration at every timestep. (For details, see Ref. 13.) The model gives excellent estimates at ambient conditions, very good critical behavior, cluster energies and geometries, second virial coefficient, temperature dependent viscosity, dielectric constant, self-diffusion and pair-correlation function, ice densities at very high pressures. Predicts the anomalous properties of water at least qualitatively correctly (temperature-density, temperature-self-diffusion, temperature-isotherm compressibility curves in terms of pressure, and temperature-viscosity curves at different pressures)[14]. Being rigid and classical there are two properties our model cannot mimic. It does not vibrate. It has been shown that classical vibrations would increase the cost of calculations considerably (short timesteps) and they do not affect the bulk properties of water with the exception of heat capacity and the presence of intra-molecular contribution of its vibrational spectrum in the bulk. In fact, to be correct, quantum vibrations are needed but their cost is two orders of magnitude slow down the code. The other property is dissociation of protons which is very rarely happens in bulk. (Only one in ten million molecules is dissociated at room temperature.) We know that excess proton can jump from one molecule to the other without substantial barrier. The driving force is the coordination of molecules. It prefers the low coordination of the host molecule. So, geometrical criteria and transformations can be built in but this could make the program cumbersome.

For a model using non-standard numerical tools (Gaussian charges instead of point charges; exponential repulsion instead of $r^{-12}$; charge-on-spring polarization) requires technological developments. Many authors use the freely accessible package of GROMACS. This package is able to simulate simple and complex systems using classical interaction models. We developed two speed-up techniques (particle-mesh for Gaussian Ewald, and Kolafa's method for faster iteration) and we made the last version of GROMACS capable to handle Gaussian charges, using our BK3 model as an example[15].

We developed a force field for the complete set of alkali halides to be consistent with BK3 water. We used the same approach: Gaussian charges and COS polarizability[16]. To obtain good results for semi-empirical potentials the force fields should be fitted consistently. With this paper we made the first step towards a new generation of force fields with larger accuracy than before.

In addition to the systematic result described above we were involved in two papers written in collaboration with other authors. In the first case we studied the surface properties of our earlier water model[17]. In the second case we supplied data for thermodynamic calculations[18].

This work formed the basis of the PhD dissertation of my student, Péter Kiss. His thesis of 120 pages contains a very detailed account of this systematic work and all the applied numerical techniques developed partly by us. Both of the opponents of his thesis said that the presented work could well be a basis of a Doctor of MTA title.

At the end of his dissertation we presented a table. This table was suggested by C. Vega who, with his coworkers, created the TIP4P/2005 nonpolarizable model. The table contains numerous measured properties of water and each model obtains points depending on how accurately the model predicts the experimental value. He used this to compare the existing nonpolarizable models. The maximum value of model qualification is 10. The TIP4P/2005 obtained 7.2 far more than the other nonpolarizable models. In fact, none of the polarizable models were able to reach this value. Our

model, the BK3 obtained by this evaluation method 8.5. I think that by classical models this is the largest possible value.

The importance of classical models is to provide more accurate description of simulations in material science, or, even more importantly describing solvation of biomolecules. In the not very far future accurate force fields can replace expensive experimental techniques in pharmaceutical research.

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