

Polarisable Water Modelling using Quantum Drude Oscillators: Summary

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1 What is my project about and why it is important?

Earlier last year, EPSRC identified understanding the physics of life as being one of the four grand challenges of physics, with both a high economical (through biomimicking technologies) and societal impact (through health and personalised medicine) [4].

One of the keys to this area of research is water. It acts as both a solvent for biological matter, as a catalyst for chemical reactions and as an active biomolecule, making it a crucial element in supporting life [2, 3]. Therefore, understanding the properties of water and how its condensed phase properties emerge is an important first step towards the detailed understanding of biology.

Computer simulations play an important role in this process. They allow us to perform experiments that would either be too costly or physically impossible to do in a laboratory. Simulations also give us a degree of control that no current experimental probe can, allowing us to see individual microstates of the system rather than just statistical averages as well as to change the physics in controlled ways to understand how properties emerge.

However, simulations are only as good as the model behind them. In the case of water, no model has yet managed to reproduce all the properties of even the liquid phase [5]. We have recently proposed a novel model of water [6, 7] based on a Quantum Drude Oscillator (QDO) model of electronic response.

A QDO is a simple model of an atom, where a light negative charged particle is bound harmonically to a heavy positive nucleus. Despite its simplicity, this model can reproduce the electronic response of atoms and simple molecules to external fields. The charge, spring constant and reduced mass of the QDO can then be adjusted such that this response matches that of the molecule of interest. Despite its richness, a QDO is sufficiently simple to be efficiently simulated.

In collaboration with the National Physical Laboratory and IBM Watson Research, we have recently proposed [6, 7] using QDOs to create a transferable model for water called QDO-water. The aim of this model is to start with a reasonable physical description of a water molecule and have the properties of the condensed phase emerge naturally. Recent results show that the model does indeed produce a physical liquid and liquid–vapour interface, the latter being my original contribution.

The plan for my PhD is to both use the model to investigate the properties of water in both its liquid and solid form and contribute to the development of the model and its simulation methods.

2 How does it fit into the wider context?

The creation of a transferable computational model for water is a grand challenge of physics. The simplest such models are constructed from point charges connected by rigid bonds in a fixed geometry. The geometry and the charges are parametrised to reproduce a mixture of condensed phase properties and represent a mean field description of the electrostatics of a molecule in a certain environment. Dispersion interactions, arising due to quantum correlations of the electrostatic moments of electrons (the leading order of which being the van der Waals interaction) are included using empirical potentials such as the 6–12 Lennard–Jones potential. Similarly, short range repulsion arising due to electron exchange is treated in an empirical way.

However, these static models do not take into account the fact that the electrostatics of any molecule changes with changing environment. In order to account for these changes, polarisable models have been developed. However, they are usually limited to dipole polarisation, even if higher order polarisations are important to the physics of condensed phases [1].

Alternative approaches to simulating the physics of the condensed phases of water have been *ab initio* simulations, using mainly Density Functional Theory (DFT). The main issue with these simulations is the fact that they are computationally inefficient when compared with classical models and, if not corrected for the effects of dispersion interactions overstructure liquid water, although they are powerful and allow chemical reactions to be examined. Adding accurate dispersion interactions to DFT is currently an active area of research, as is the generation of general improved functionals.

QDO-water sits somewhere in the middle of the *ab initio* to classical spectrum. The model itself is a simplified quantum mechanical system, yet the method of simulation is classical molecular dynamics. This is achieved by using Path Integral Molecular Dynamics

(specialised for QDOs), which essentially transforms the quantum mechanical electron of a QDO to a chain of classical point particles (or ‘beads’), connected by harmonic springs. This combination of quantum description and classical simulation results in a model that both accurately reproduces the long range interactions between water molecules and yet is efficient to simulate.

QDO-water fits well with the current approaches to modelling water. Parametrising the models from either the properties of a single molecule or energies of clusters with less than 50 molecules is a popular approach at the moment. However, we believe QDO water to have a unique position in the spectrum of water models due to its unique construction.

3 What have I done so far?

My project so far has been the study of the liquid–vapour interface of QDO-water. This simple system provides a benchmark for testing the model’s behaviour in heterogeneous environments. The results presented in this report were computed using Mark I QDO-water, which was the initial iteration of the model. We have recently parametrised Mark II QDO-water, which has an improved performance in reproducing the thermodynamics of the liquid. By the time I will publish these conclusions, I will update them using Mark II.

The main finding of the study was that the surface of the liquid shows a more open structure than the bulk. What I mean by this is that the average distance between nearest neighbours is *longer* at the surface than in the bulk liquid by around 2%. This result has been reproduced by *ab initio* calculations, but QDO water is the first semiclassical model that predicts such a large surface relaxation. This effect is linked with a more open hydrogen bond at the surface, with a larger accessible bonded distance and larger bond angles.

Finally, there is a preferential orientation of the water molecules. Figure 1 shows the three different ways the hydrogen bonded network can be broken at the surface. Our results show that the AA and D orientations of water molecules are preferred, with the DD orientation being suppressed. This preferential alignment causes the surface to be negative, since the oxygen atom is locally negative. I postulate that this preferential reorientation is due to the asymmetry between the hydrogen bonds on the acceptor and donor sides of the molecule. This intuition is supported by the fact that the hydrogen bonds on the oxygen side (acceptor bonds) have a larger angular extent than those on the hydrogen side (donor bonds). To further support this intuition, Figure 2 shows the average position of the oxygen atoms of molecules hydrogen bonded with a given molecule in the bulk liquid.

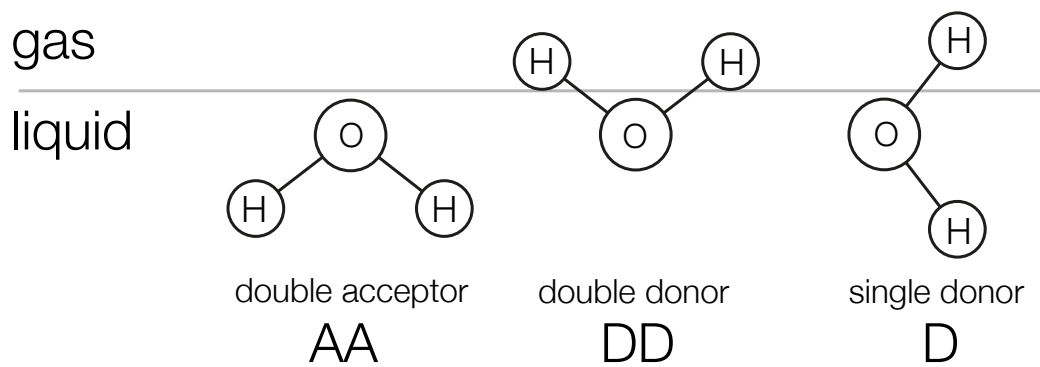


Figure 1: The three different species of broken hydrogen bonds.

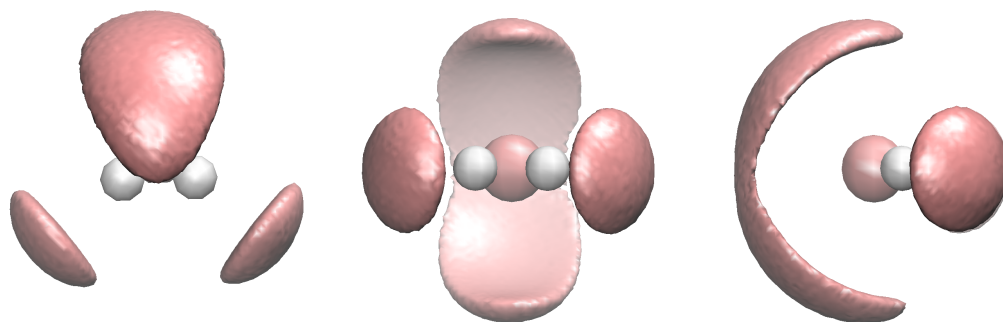


Figure 2: A density isosurface of the hydrogen bonded neighbours of a molecule in the bulk region of the lamella. Oxygen atoms are represented in pink.

4 What am I going to do next year?

First, I plan on updating the surface results using Mark II QDO-water. Afterwards, ices are a logical next step in pushing the transferability of the model further. Ice II is a simple test case since it is a proton ordered ice, meaning that both the oxygen and hydrogen atoms have well defined lattice sites. It also occurs at relatively low pressures and relatively high temperatures and therefore should be easy to sample. The next part of my project will focus on predicting the equilibrium properties of Ice II and comparing them with experiment.

Also, keeping in line with the current trend in developing water models, it would be interesting to compare the energies of clusters of a few water molecules between *ab initio* calculations and QDO-water. This calculation will show if QDO-water adapts correctly to the various instantaneous environments a water molecule may be in.

The team I'm working with has also been joined by a summer student, who will be working on optimising the method of calculating heat capacity for collections of interacting QDOs, extending part of my MPhys work. I am working closely with her and plan on then using her results to analyse the behaviour of the heat capacity and its anomaly at close to freezing point (whereby the heat capacity increases on cooling).

Finally, after looking at the liquid–vapour interface and ices, I plan on looking into more detail at the structure of the liquid phase itself. Recent experiments have been interpreted to suggest that the ambient temperature liquid might be a mixture of low density and high density local structures. However, these experiments have also been interpreted as revealing an asymmetry in the hydrogen bond. QDO-water would be a good test platform to compare these hypotheses.

On the theoretical side, a project I will embark on is creating a DFT for QDOs. This might shed some light into the quantum mechanical origins of dispersion interactions and provide another efficient method for simulating the interactions between QDOs.

5 Key outputs this year

5.1 Publications

1. Jones, A., *Cipcigan, F.*, Sokhan, V. P., Crain, J. and Martyna, G. J. Electronically Coarse-Grained Model for Water. *Physical Review Letters* 110, 227801 (2013).

2. A. P. Jones, J. Crain, *F. S. Cipcigan*, V. P. Sokhan, M. Modani, and G. J. Martyna, Electronically coarse-grained molecular dynamics using quantum Drude oscillators, Submitted to Molecular Physics, 2013.

5.2 Awards

1. Best talk at Ecole de Physique les Houhces: Water at Interfaces
2. First prize, Present Around the World South East Scotland (presentation skills competition)
3. Second prize, Teamwork Prize and Audience Award at EngineeringYES entrepreneurship training course and competition (as the team leader)
4. Romanian Ambassador’s diploma for my undergraduate research

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