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The Water Molecule and its Interactions:
the Interaction between Theory, Modelling, and Experiment

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Abstract

Understanding the behaviour of water at the molecular level requires a quantitative understanding of the water molecule and its interactions. Although many current empirical potential functions are able to reproduce some of the known behaviour, our understanding of the water molecule and its interactions is not yet sufficient for our modelling to reproduce much of the subtleness of the water molecule's behaviour in both the pure liquid and in solution. Some recent experimental and theoretical developments are discussed that may lead to an improvement in our understanding of the water molecule and its interactions in a range of environments and over a range of experimental conditions.

1. INTRODUCTION.

Towards the end of the 1960s, a conference on liquids was held at the University of East Anglia, Norwich, UK. At that meeting, which I attended as a recently appointed young lecturer, I witnessed one of the first presentations on computer simulation of water, given by John Barker. It was at the time an ambitious thing to try to do. For his water model, Barker chose to use one of three water models that had been proposed some 20 years earlier by John Rowlinson [1,2]. The elements of the potential used were a spherical repulsion (proportional to r^{-12}, where r is the separation between molecular centres), a spherical dispersion (r^{-6}), an averaged dispersion term also varying as r^{-6}, while the electrostatics was handled by a positive charge on the hydrogens and negative charges close to the oxygen. The appropriate parameters were fitted to experimental data, namely the second virial coefficient, and the structure and lattice energy of ice. In the particular Rowlinson potential used by Barker, the negative charge was split above and below the molecular plane at the oxygen centre (see figure 1(a)), recognising the importance of the quadrupole moment of the molecule.

While Rowlinson's potential as used by Barker might be regarded as the forerunner of more recently-developed four-point-charge models such as BNS [3] and ST2 [4], it was not the first attempt to quantitatively specify a water model. Bernal and Fowler in 1933 [5] had proposed two models. Focussing on the second of these, which they used to estimate a number of properties to compare with experiment, they again used spherically symmetric repulsion and dispersion terms with the same radial dependence as Rowlinson. They also considered it necessary to include an induction term to take account of polarisability in an average way, their model molecule having a dipole moment some 7% greater than that of an

isolated molecule. Rather than separate the negative charge as Rowlinson had done, they preferred to use only a single charge. Rather than place this on the oxygen - which would have given an excessively high dipole moment some three times the isolated molecule value - they chose to shift it towards the hydrogens along the HOH angle bisector (figure 1(b)). The Bernal/Fowler model might be considered as the forerunner of subsequent three-point-charge models such as SPC [6], and the TIPS series [7]. It is interesting to note that, in fitting the various parameters, several later three-point-charge models also place the negative charge in a similar position to that of the Bernal/Fowler model. In fact, the TIPS2 potential places the negative charges (0.535e cf. 0.49e for Bernal/Fowler) at precisely the same position.
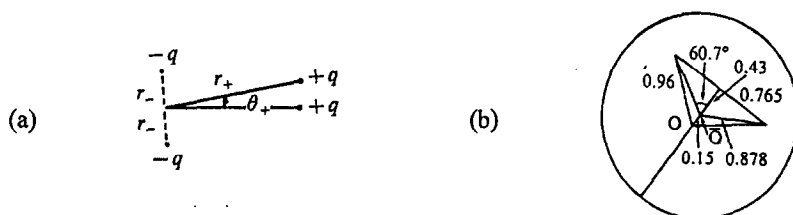

Figure 1. Rowlinson (a) and Bernal (b) models for the water molecule.

In the thirty years or so since the Norwich meeting, a major industry has developed to try to reproduce with empirical models the quantitative behaviour of water. In this keynote lecture, I want to look at how we have approached this problem, and look forward to the future possibilities. In trying to develop an 'empirical' model of the water molecule, we might consider two aspects. First, we need to choose a *good model form*. For example, how many charges do we need, and in what kind of locations are we going to place them? How do we deal with repulsion, dispersion, and induction? Secondly, we need an *effective parametrisation* of this form. This leads us to consider such aspects as the quality of the data we use in fitting the relevant parameters, the amount of data needed and available (from experiment and/or theory), and the quality of the fit we obtain.

2. WATER MODEL FORM.

I want to consider four particular aspects of forms used for water molecule potentials. These aspects are not exhaustive, but are relevant to a range of models that have been used. To focus the discussion, at the risk of being provocative, I present these aspects in terms of four 'myths' that seem to have grown up around the water molecule and its interactions.

Myth 1: the water molecule is tetrahedral.

In my case, this myth was implanted at school, where I was told there was a positive charge on the hydrogen atoms, and separated negative charges places in tetrahedral locations 'behind' the oxygens. This geometry was inherent in the early BNS model, as well as the ST2

potential developed from it. It is however not the geometry of the three-point-charge models which are perhaps most frequently used, so in effect this myth has been dispelled in actual potential functions used, though we often hear of the water molecule's geometry being tetrahedral. It is perhaps instructive to see how this idea might have arisen from a confusion between the geometry *of the molecule itself* and the geometries *of the structures in which the molecule participates*. In the case of water, it is natural to refer to the crystalline ice Ih phase, where the molecules are clearly arranged in a tetrahedral local geometry. However, this does not automatically mean that the *geometry of the molecule itself* must be tetrahedral: Bernal certainly did not fall into this trap, producing a trigonal water molecule model that reproduced many of the properties of both ice and water [5]. It is also now generally recognised that the use of tetrahedral water models produces a simulated water that is too structured [8].
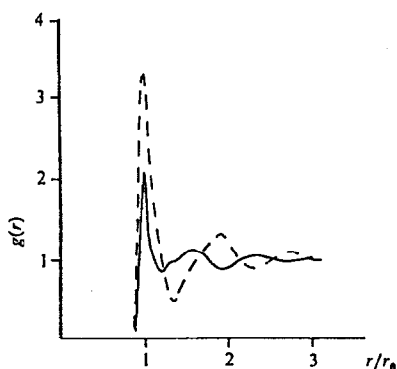

Figure 2. Water-like and simple-liquid like pair correlation functions.

To what extent can the structure of *liquid water itself* be characterised as tetrahedral, and how does the structure of simulated water depend on the degree of tetrahedrality *of the molecule*? Figure 2 compares the pair correlation functions of a simple liquid and a water-like liquid. The point on which to focus for this discussion is the position of the second peak, which for water occurs at lower r than for the simple liquid. Because the distance at which this peak appears is centred on one which can be calculated by assuming a local tetrahedral intermolecular geometry for first neighbours, it is often referred to as the tetrahedral peak. We should note however that the peak is broad, and covers a range of other possible intermolecular geometries, including a trigonal one (120° is not very different from 109.5°). As has been discussed elsewhere [8], transitions from simple-liquid-like to water-like pair correlation functions can be followed as the nature of the molecular model is changed. These studies show that the so-called tetrahedral peak can indeed be induced by increasing the degree of tetrahedrality of the water molecule model, as in the work of Ben Naim [9]. But molecular tetrahedrality is not a necessary condition: other work increasing the degree of *trigonality* of the molecule gives similar results [10]. And it is such trigonal geometry of the electron distribution which high quality quantum mechanical calculations on the water molecule indeed predict [8,11,12].

The electrostatics of the water molecule therefore is not tetrahedral, nor are the lone pairs usefully considered as separated - rather, there is a single lobe of negative charge which might more accurately be thought of as trigonally disposed with respect to the hydrogens. Four-point-charge models of water tend to give water structures which are too structured. And tetrahedrality of the water molecule model is not needed to reproduce the qualitative features of water-like pair correlation functions.

Myth 2: the water molecule's repulsive core is spherical.

In the absence of evidence to the contrary, it is reasonable to assume - as did both Bernal and Rowlinson - that the intermolecular repulsion between water molecules can be handled through a spherically symmetrical term. This assumption has subsequently been made in nearly all the more recent empirical potentials. An interesting exception is MCY [13], which places repulsive terms on the hydrogens, a point which may be responsible for its relative success [8].

There is, however, good evidence to the contrary. Since the advent of high resolution neutron diffraction on high quality crystals containing water, experimental evidence has accumulated to suggest that the water molecule's 'van der Waals radius' is better represented in terms of a small, but significant, degree of non-sphericity [14-16] as indicated in figure 3. In fact, a strong case can be made for such non-sphericity explaining a range of features observed in water-containing systems [16]. In addition to enabling us to rationalise water molecule orientations in (ordered and disordered) crystalline hydrates, we can also explain aspects of the complexity of the ice phase diagram, hydrogen disorder in high pressure ice phases (see also ref. 17), trigonal water geometry that tends to be observed for short hydrogen bonds, and even the local tetrahedrality frequently observed in water-containing systems [16]. Nor is the only evidence experimental. As our computational abilities have improved, so also has the quality of quantum mechanical calculations on the water molecule itself. For example, calculations by Hermansson [18] show a degree of non-sphericity in the electron distribution that is very similar to that deduced from the experimental crystallographic results.
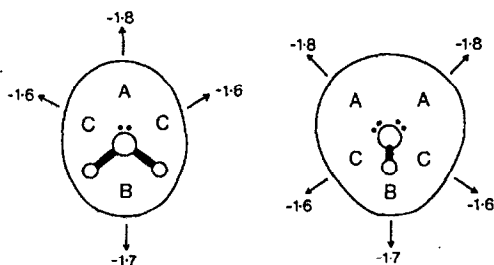

Figure 3. Regions of differing van der Waals radius (in Å) around a water oxygen.

As experiment suggests, and theory confirms, that the water molecule's effective van der Waals radius is not spherical, it would seem sensible to try to include this non-sphericity in empirical models. Yet nearly all empirical models still assume a spherical repulsion,

forcing all the directionality of the water-water interaction into the electrostatics. This may not be the most effective way of handling the directionality [8].

Myth 3: the water-water hydrogen bond is essentially electrostatic.

Although the possibility of significant charge transfer in hydrogen bonding was raised when water simulations began, it was generally accepted that - in the case of water at least - any such charge transfer was small enough to be neglected. Such an assumption was backed up by quantum mechanical calculations which, as they improved, seemed to show the degree of charge transfer reducing. This consensus has been recently challenged, again both experimentally and theoretically.

Recent experimental work has exploited third generation synchrotron sources to measure the Compton scattering in ice. Work at the ESRF Grenoble by Platzman and colleagues [19] has measured Compton profile anisotropies that are sensitive to the phase of the electronic wave function, and hence to the degree of covalency of the hydrogen bond. Their results on ice disagree with a purely electrostatic model for the water-water hydrogen bond.

Although one might perhaps argue that the degree of charge transfer obtained in ice at low temperature might be greater than that in water at room temperature (where the oxygen-oxygen hydrogen bond is some 3-4% longer), recent *ab initio* molecular dynamics calculations also suggests electronic shifts in the liquid phase that could be envisaged as a charge transfer process [20]. Thus, it seems that the previous consensus that an empirical model of the water molecule could reasonably ignore charge transfer may be beginning to fall apart. The degree to which charge transfer needs to be incorporated into a viable model - and the means whereby it could be modelled - remain questions to be further investigated.

Myth 4: water-water interactions are essentially pair-additive.

Returning to the Norwich conference, after John Barker's talk, a question was raised concerning the validity of using a pair-additive water model. After all, Bernal had realised in the 1930s that induction effects were likely to be significant, and subsequent measurements of the dipole polarisability of water showed it to be sufficiently large that, even in pure water under ambient conditions, local enhancements of the dipole moments of individual water molecules would be expected. Similar objections raised subsequently to other pair-additive models were countered by arguments that such effects could be taken account of in an average way by the water molecule model having a higher dipole moment than the isolated molecule. In the earliest days of water simulations, we should also remember that the computational resources needed for non-pair-additivity to be incorporated explicitly were just not available.

In recent years, as computational resources have increased, the development of non-pair-additive potentials has turned into something of an industry. We should, however, remember that early attempts were made 20 to 30 years ago, initially by the Birkbeck [21-24] and Groningen [25] teams, and subsequently by Campbell and Mezei [26] and Stillinger and David [27]. The earliest attempts were made by including dipole polarisability on a 'base' model of point charges or a multipole moment expansion. Although these models explored many of the problems of obtaining and using polarisable models, they were only partially successful in obtaining good structural results.

More recent attempts to develop polarisable models are exampled by the work of Brodholt et al [28], Chialvo and Cummings [29], and Dang and Chang [30]. All these models again add dipole polarisability to a point charge 'base' form, with parameters fitted to reproduce a range of experimental data such as ambient pressure and energy, or dipole and quadrupole moments. Although this is still a very active field, and new results are to be expected in the near future, the results so far indicate that, although all the three examples given above capture the main features of water structure, none improves significantly on the original 'base' TIP4P or SPC models. None do particularly well in reproducing the equation of state, failing to reproduce well the density change as temperature increases. The dielectric constant for the Brodholt *et al* model is too high by a factor of two.

Thus, while polarisable models show improvement in the description of some water properties, their overall performance is disappointing, being unable to describe simultaneously the thermodynamics, structure, and dielectric behaviour of real water. It is unclear whether this failure is a result of the inadequacy of the models, their parametrisation, or both.

That an effective model should be able to deal with non-pair additive effects is underlined by the *ab initio* molecular dynamics calculations of water mentioned above with respect to charge transfer [20]. These show a distribution in water molecule dipole moment ranging from about 2 to just over 4 Debye, with an average value of 2.95D that is considerably higher than was expected. All water molecules are clearly not equal, and with dipole moment enhancements of this magnitude and variability, we should be encouraged to incorporate polarisability effects in any empirical model that attempts to reproduce water away from ambient conditions, and in any kind of solution.

3. WATER MODEL PARAMETRISATION.

As stated in the introduction, even if we had a 'good' model form, we need to parametrise it effectively. This raises questions such as the quality and amount of the (experimental and/or theoretical) data we use in fitting the relevant parameters, and the quality of the fit we obtain.

Even assuming that the data available are of adequate quality (though I am not clear how adequate quality in this context can be specified - within 5%? 10%? of the 'actual' values?), we still have a formidable problem of parametrisation. Consider for example a pair-additive model. For this, we have to specify 'with sufficient accuracy' a six-dimensional energy surface (five angular variables, one distance variable). Assuming it is adequate to specify potential energy every 5° in angle, and every 0.1Å in distance (is this sufficient?), then we need ~10^9 data points for a full parametrisation. Although we may be able to argue on physical grounds that all regions of the surface do not need to be so closely specified, we still have a formidable problem in obtaining sufficient data of sufficient quality to be confident we have enough for an adequate parametrisation of our functional form. And once we extend our horizons to non-pair-additive models, the problems are compounded by the increased dimensionality of the energy surface. Is it a realistic expectation to be able to obtain 'adequate' data to facilitate such parametrisations - even assuming our model form itself is good enough?

The dangers in parametrisation can be illustrated by work of Bounds with the MCY potential. Simulations using the MCY potential that was parametrised using 66 points on the energy surface gave quite good-looking water pair correlation functions [13]. Bounds then

reparametrised the potential *using the same model form and the same data points for the parametrisation*, the resulting goodness of fit of the reparametrised model being an improvement on the original [31]. When the reparametrised potential was run for liquid water, the pair correlation functions obtained were not only quantitatively different: the new - and better parametrised - potential failed even to give a water-like oxygen-oxygen pair correlation function. In addition to underlining the problems of parametrisation, this exercise also shows how sensitive the simulated structure of water-like liquids can be to the model used. Inspection of some of the energy surface sections of the two parametrisations show only small differences (see figure 25 of ref. 8). Yet the liquid structures for the two potentials are qualitatively different.

4. POSSIBLE WAYS FORWARD.

Recent experimental and theoretical developments suggest ways in which our understanding of the water molecule and its interactions might be advanced. Two possible ways forward are discussed briefly.

On the experimental side, it is now possible to take high quality experimental structural data on liquids such as water, using isotope substitution methods to obtain structural information at the partial structure factor and partial pair correlation function level. Coupling these data with recent developments in computational techniques that assist us in interpreting the data, we can begin to use experimental data on real systems to give us information that might help us to improve our empirical potentials.

With respect to water, the neutron data gives us three partial structure factors $S_{HH}(Q)$, $S_{OH}(Q)$, $S_{OO}(Q)$ which relate through Fourier transforms to the partial pair correlation functions $g_{HH}(r)$, $g_{OH}(r)$, $g_{OO}(r)$, where Q is the normal scattering vector whose magnitude is $4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ the neutron wavelength. Using the recently developed Empirical Potential Structure Refinement technique developed by Soper [32], we can interrogate the structure factor data to give information on the potential functions. In this method, a set of experimentally determined radial distribution function data $g^D_{\alpha\beta}(r)$ is used to constrain a Monte Carlo simulation. The method is based on the development of a potential of mean force $\psi_{\alpha\beta}(r) = -kT \ln g_{\alpha\beta}(r)$ between atoms α and β. Starting from a model fluid with the correct temperature and density, and using assumed potentials $U^O_{\alpha\beta}(r)$ between sites α and β, an estimate of the pair distribution function $g_{\alpha\beta}(r)$ can be made. A new potential energy function $U^N_{\alpha\beta}(r)$ is then estimated from:

$$U^N_{\alpha\beta}(r) = U^O_{\alpha\beta}(r) + (\psi^D_{\alpha\beta}(r) - \psi_{\alpha\beta}(r))$$
$$= U^O_{\alpha\beta}(r) + kT[\ln (g_{\alpha\beta}(r)/ g^D_{\alpha\beta}(r)].$$

This new potential is then fed back into the simulation, and particles within the simulation box moved. This process continues until such time as

$$U^N_{\alpha\beta}(r) \cong U^O_{\alpha\beta}(r)$$

and hence

$$g_{\alpha\beta}(r) \cong g^D_{\alpha\beta}(r).$$

In other words, the simulated data now shows good agreement with that measured experimentally. The Monte Carlo process is then continued, and various partial distribution functions are extracted. These can include the full set of interatomic partial pair distribution functions.

As the original potential function $U^O_{\alpha\beta}(r)$ has in effect been modified in order to obtain agreement between the experimental data and the simulation, we can now, under certain circumstances, interrogate the calculations to see how the experimental results are driving the perturbation of the starting potentials. For example, in the case of t-butanol [33], this approach has shown how the starting potentials overemphasise the hydrogen bonding between the alcohol OH groups. In the case of pure water, initial unpublished results of Soper, using the SPC/E potential [34] as the starting potential, suggest that the OH part of the potential needed to reproduce the experimental data is harder than SPC/E (perhaps relating to the potential's neglect of anisotropy of repulsion, as discussed above). There are also indications that the OO part of the SPC/E potential should be softened.

Although these techniques are still in their infancy, they promise much in terms of indicating how empirical potentials might be improved. A further possible way of making progress on the theory/modelling side is that of so-called *ab initio* computer simulation, made possible by both theoretical advances and major increases in available computational resources.

In 'conventional' computer simulations, we input the fundamental laws of statistical mechanics, together with an 'empirical' potential function model. After extensive computation, we output comprehensive information on the structure and properties of the ensemble of these model molecules over the thermodynamic conditions specified. In an *ab initio* simulation, we input also, in addition to the laws of statistical mechanics, and instead of a set of empirical potentials, the fundamental laws of quantum mechanics. Without having to invoke the adjustable parameters inherent in empirical potential functions, we now proceed to solve Newton's laws for ions in a potential that comes from solving the electronic structure each simulation step.

Ab initio is, however, perhaps a misleading term: the method is certainly not problem-free. The density functional methods involved were designed essentially for molecular structure, and extending them for intermolecular structure is not trivial. Different approaches - as in using empirical models - can lead to a range of predicted properties (e.g. structure, diffusion coefficient): how are we to make sensible choices between these different approaches?

Despite the problems, recent work using localised orbitals is promising. The standard implementation of density functional theory is the local density approximation (LDA) [35,36]. For our uses, the limitations of LDA in accurate prediction of relative energies are a problem, so there have been significant efforts to improve the evaluation of energies with non-local terms of the form of a gradient correction) [35,36]. As an example of recent work, Sprik et al [37] have performed *ab initio* molecular dynamics simulations of water at 300K using three different functionals resulting from different gradient corrections. In terms of predicted structure, all three functionals give partial pair correlation functions in reasonable agreement with experiment, though the range of partials obtained is no less than the range obtained using different empirical potentials (see figures 6 - 8 of ref. 37). Furthermore,

dynamical properties such as orientational relaxation times and diffusion coefficients for the three functionals differ by up to an order of magnitude. Nevertheless, bearing in mind that these methods are at a relatively early stage of development, the fact that functionals can be found which give good experimental agreement should be regarded as very promising. As both theory and computational techniques develop, it seems likely that these methods will become increasingly able to reproduce the structural and dynamical properties of water over a range of thermodynamic conditions without - as is necessary for empirical potentials - having to resort to doubtful assumptions regarding model force fields.

5. SUMMARY.

We conclude that the derivation and fitting of empirical models is not a straightforward procedure. Although few models now retain the molecular tetrahedrality that characterised some of the earliest potential functions used in computer simulations, there is evidence to suggest that assumptions concerning spherical repulsions and pair additivity may no longer be acceptable. The earlier consensus concerning treating the water-water hydrogen bond as essentially electrostatic may also need renegotiating. In devising empirical models for force fields, effective parametrisation is also not easy, a problem made very much more difficult in the much-increased dimensionality of the energy surface for non-pair additive potentials. Despite these problems, several empirical models do pretty well at fitting structure at ambient conditions. When extending these models to try to fit a range of experimental quantities simultaneously (e.g. dielectric constant, diffusion coefficient, structural changes with temperature and pressure), they are less successful.

Future prospects are positive on both the experimental and modelling/theory fronts. Experimentally, we can now, using neutron diffraction with isotope substitution together with recently developed modelling techniques, begin to think about 'refining' empirical models against the experimental data. For pure water, there are already some indications concerning the relative hardness of the various repulsive terms that could be explored in modified potentials. Theoretically, further progress should be expected in so-called *ab initio* modelling. Even here, however, the approach is not problem free.

Overall, we probably have a reasonable, semi-quantitative idea of the water molecule and its interactions under ambient conditions. But major progress - probably using *ab initio* methods - is needed before we can tackle with confidence calculations on pure water away from ambient conditions, and on aqueous solutions.

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