Computer simulation study of water using a fluctuating charge model

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Abstract. Hydrogen bonding in small water clusters is studied through computer simulation methods using a sophisticated, empirical model of interaction developed by Rick *et al* (S W Rick, S J Stuart and B J Berne 1994 *J. Chem. Phys.* **101** 6141) and others. The model allows for the charges on the interacting sites to fluctuate as a function of time, depending on their local environment. The charge flow is driven by the difference in the electronegativity of the atoms within the water molecule, thus effectively mimicking the effects of polarization of the charge density. The potential model is thus transferable across all phases of water. Using this model, we have obtained the minimum energy structures of water clusters up to a size of ten. The cluster structures agree well with experimental data. In addition, we are able to distinctly identify the hydrogens that form hydrogen bonds based on their charges alone, a feature that is not possible in simulations using fixed charge models. We have also studied the structure of liquid water at ambient conditions using this fluctuating charge model.

Keywords. Water; clusters; fluctuating charge; electronegativity.

1. Introduction

Ever since the pioneering work of Stillinger and Rahman [1] over three decades ago, the study of water through computer simulation methods has attracted considerable attention. Simulation methods offer an unique perspective to the study of liquids, in terms of the richness in microscopic details that they offer, both in structure as well as in dynamics. Such detailed information is often difficult to obtain through experimental techniques. On the other hand, analytical work on the study of a liquid like water, with subtle hydrogen bonding interactions, is intractable. Computer simulation methods are thus able to complement various experimental data on liquid water and aqueous solutions.

Traditionally, such simulation methods have employed a molecular model for liquid water, in which the bonds within molecules are assumed to be immutable. The models differ only in the way the water molecules interact with each other. In such models, hydrogen bonding between molecules is constructed to arise out of ionic interactions. Needless to say, the size of the interaction sites also plays a crucial, but often forgotten role, in such intermolecular bonding. Typically, such interaction models take experimental data on the structure of water molecules in its gas phase as the starting point. The interaction sites on such a molecule can be the atom positions (oxygen and hydrogens) themselves. One such model is the simple point charge (SPC) model for

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water[2]. One can then do a high quality quantum chemical calculation to obtain partial charges on the interaction sites. The partial charges have to yield the correct dipole moment of an isolated water molecule. It is usually found that an interaction model constructed so as to match experimental data on the gas phase of water, performs poorly for properties of the condensed state. This problem is particularly acute for a liquid like water, as the electronic charge distribution on the interaction sites is highly polarizable. The effective dipole moment of a water molecule in the liquid state is around 2·5 D, as opposed to a value of 1·85 D in the gas phase. Failure to take this into account results in much larger transport coefficients for the simulated liquid water. One way of handling this increase in the dipole moment in the condensed phase is to increase the charges on the interaction sites in the simulated model. For the SPC model, this yields the highly popular, extended simple charge model (SPCE) of water[3]. The SPCE model is able to provide a much better agreement with experimental data on the oxygen–oxygen pair correlation function. It also performs reasonably well in reproducing the dynamics of water. In particular, the single particle and collective relaxation times obtained using this model are in rough agreement with experiment. Yet, in all these quantities, the results obtained from simulations are quantitatively 15 to 20% away from experiments[4]. Typically, the simulated diffusion constants are larger, and relaxation times smaller than the experimental values. A drawback of these models is that the charges on the interaction sites of a molecule are fixed during the course of the simulation. The charges are thus unresponsive to the varied environment that they see. These charges are only mean, or effective charges, and as highlighted above, are not transferable across the different phases of water. Correcting this lacunae in these models will enable one to study accurately not only the properties of liquid water in bulk, but also water in anisotropic, and inhomogeneous environments, such as liquid interfaces, macromolecular solutions, water in biological systems.

Polarization of the charge distribution (induction effect) can also be treated using fixed gas phase charges and including point polarizabilites. A variety of dipole polarizable models to study liquid water have been introduced[5,6]. The fluctuating charge model (fluc-q), where the charges are allowed to fluctuate, depending on their local environment, encompasses polarizabilities in all charge moments unlike these models. Further, the fluc-q model is less time-consuming to run.

The fluctuating charge model of water was first proposed by Rick *et al*[7,8]. Here we outline their formalism and apply the model to a study of small water clusters and bulk water.

2. Simulation details

The charges on any site fluctuate due to a difference between the site's instantaneous electronegativity value and the value in its vicinity. This difference is the driving force for the change in the charge on that site. Density functional theoretical methods have shown that the chemical potential of an atom is the negative of the Mulliken electronegativity. Thus, the charges in a many-atom system will vary to keep the chemical potential the same at every site. This principle, called electronegativity equalization, was first proposed by Sanderson[9] and has been applied to understand the structure of several molecular systems. In the following, we briefly describe the mechanism of charge dynamics. Interested readers are recommended to read the original article of Rick *et al*[7].

If E is the ground state energy of an atom, then the Mulliken electronegativity (c_i) is the negative of the chemical potential (m) and is defined as [10]

$$m = \frac{\partial E}{\partial N} = -c_i = -e\frac{\partial E}{\partial Q_i},$$ (1)

where N is the number of electrons in the system (treated as a continuous variable), Q is the charge on the atom and e is the elementary charge. Q is related to N by $Q = -e(N-Z)$, where Z is the atomic number of the atom. Also, we define electronegativity per unit electron $\tilde{c}$ as

$$\tilde{c} = c/e.$$ (2)

The energy of creating a partial charge Q_A in an isolated atom can be expanded as a Taylor series in charges, up to second order as

$$E(Q_A) = E_A(0) + \tilde{c}_A^0 Q_A + \tfrac{1}{2}J_{AA}^0 Q_A^2,$$ (3)

where $\tilde{c}_A^0$ is the Mulliken electronegativity per electronic charge, and J_{AA}^0 is twice the hardness of the electronegativity of the isolated atom. Hence, the energy of the system with N_{molec} molecules each containing N_{atoms} is [10]

$$U[(Q),(\mathbf{r}) = \sum_{i=1}^{N_{molec}} \sum_{a=1}^{N_{atom}} [E_a(0) + \tilde{c}_a^0 Q_{ia} + \tfrac{1}{2}J_{aa}^0 Q_{ia}^2] +$$

$$\sum_{ia<jb} J_{ab}(r_{iajb})Q_{ia}Q_{jb} + \sum_{ia<jb} V(r_{ia\,jb}),$$ (4)

where $E_a(0)$ is the ground state energy of atom a, r_{iajb} is the distance, $J_{ab}(r_{iajb})$ is the Coulomb interaction and $V(r_{iajb})$ is any non-Coulombic interaction between ia and jb, such as the Lennard–Jones interaction. Here i and j are molecular indices, while a and b denote atom indices within a given molecule. The electronegativity per unit charge of atom A is

$$\tilde{c}_A = (\partial U / \partial Q_A).$$ (5)

The electronegativity equalization principle states that equilibrium site charges are those that make the site electronegativities equal. This is equivalent to minimization of energy, subject to charge neutrality constraint. In this work, we consider each molecule to be neutral, i.e., there is no intermolecular charge transfer. Thus, for all i,

$$\sum_{a=1}^{N_{atom}} Q_{ia} = 0.$$ (6)

Now treating the charges as independent variables, and using the method of undetermined multipliers, we get the Lagrangian as,

$$L = \sum_{i=1}^{N_{\text{molec}}} \sum_{a=1}^{N_{\text{atom}}} \tfrac{1}{2} m_{a} \dot{r}_{ia}^{2} + \sum_{i=1}^{N_{\text{molec}}} \sum_{a=1}^{N_{\text{atom}}} \tfrac{1}{2} M_{Q} \dot{Q}_{ia}^{2} - U[(Q),(\mathbf{r})] - \sum_{i=1}^{N_{\text{molec}}} \mathbf{l}_{i} \sum_{a=1}^{N_{\text{atom}}} Q_{ia} ,$$

(7)

where m_{a} is the mass of the atom a, and M_{Q} is a fictitious charge "mass" which has units of $time^{2}/charge^{2}$ and the $\mathbf{l}$ are the Lagrange multipliers. The nuclear degrees of freedom evolve according to Newton's equation

$$m_{a} \ddot{r}_{ia} = -\frac{\partial U[(Q),(\mathbf{r})]}{\partial r_{ia}},$$

(8)

and the charges evolve in time according to

$$M_{Q} \ddot{Q}_{ia} = -\frac{\partial U[(Q),(\mathbf{r})]}{\partial Q_{ia}} - \mathbf{l}_{i} = -\tilde{c}_{ia} - \mathbf{l}_{i},$$

(9)

where $\mathbf{l}_{i}$ is the Lagrange multiplier for the charge neutrality constraint. As the total charge on the ith molecule is a constant of motion, therefore for all i

$$\sum_{a=1}^{N_{\text{atom}}} \ddot{Q}_{ia} = 0.$$

(10)

Solving for $\mathbf{l}_{\text{i}}$ we get,

$$\mathbf{l}_{i} = -\frac{1}{N_{\text{atom}}} \sum_{a=1}^{N_{\text{atom}}} \tilde{c}_{ia} ,$$

(11)

where $\mathbf{l}_{i}$ is the negative of the average electronegativity on molecule i. Substituting, we get the equation of motion of charge as

$$M_{Q} \ddot{Q}_{ia} = -\frac{1}{N_{\text{atom}}} \sum_{b=1}^{N_{\text{atom}}} (\tilde{c}_{ia} - \tilde{c}_{ib}).$$

(12)

The force on the charge is simply the difference between average electronegativity on the molecule and the instantaneous electronegativity at a particular atomic site. For example, if the site electronegativity is greater than the average, then the force acts to decrease the charge until the electronegativities are all equal and vice versa. For the constraint chosen here, that of each molecule being neutral, there is no intermolecular charge transfer. We can, of course, choose a more liberal constraint that only the full system need be charge

neutral. Intermolecular charge transfer will occur in that case. The Lennard–Jones interaction between oxygen sites is given by

$$U_{LJ}(r) = 4e\left[\left(\frac{s}{r}\right)^{12} - \left(\frac{s}{r}\right)^{6}\right].\tag{13}$$

Since we are defining the energies relative to the isolated gas-phase energy, the gas-phase energy E_{gp} needs to be subtracted. For an isolated gas-phase water molecule, the charge constraint gives $Q_O = -2Q_H$, and thus we get the charge which minimizes the energy as

$$Q_H^{gp} = \frac{-(\tilde{c}_O^0 - \tilde{c}_H^0)}{2J_{OO}^0 + J_{OO}^0 - 4J_{OH}(r_{OH}) + J_{HH}(r_{HH})},\tag{14}$$

and the gas phase energy as

$$E_{gp} = \frac{-(\tilde{c}_O^0 - \tilde{c}_H^0)^2}{2J_{OO}^0 + J_{HH}^0 - 4J_{OH}(r_{OH}) + J_{HH}(r_{HH})}.\tag{15}$$

The total energy for N_{molec} molecules is then a sum of the Lennard–Jones part, the intermolecular Coulombic part, an intramolecular self-energy and the gas phase energy correction, along with periodic system using Ewald sum, and is given by

$$E = \sum_{i=1}^{N_{molec}} \sum_{j<i} \left\{ 4e\left[\left(\frac{s}{r_{iO,jO}}\right)^{12} - \left(\frac{s}{r_{iO,jO}}\right)^{6}\right] + \sum_{a=1}^{3}\sum_{b=1}^{3} Q_{ia}Q_{jb}\,erfc(\boldsymbol{k} r_{iajb})/r_{iajb} \right\}$$

$$+ \frac{1}{2}\frac{4p}{L^3}\sum_{G\neq 0}\frac{1}{G^2}e^{-G^2/4k^2}\left|\sum_i\sum_a Q_{ia}e^{iG.r_{ia\,jb}}\right|^2$$

$$+ \sum_{i=1}^{N_{molec}}\sum_{a=1}^{3}\left\{\tilde{c}_a^0 Q_{ia} + \frac{1}{2}\sum_{b=1}^{3} Q_{ia}Q_{jb}[J_{ab}(r_{iajb}) - erf(\boldsymbol{k} r_{iajb})/r_{iajb}\right\}$$

$$- N_{molec}E_{gp},\tag{16}$$

where $\boldsymbol{k}$ is a screening parameter, G is a reciprocal lattice vector of the periodic simulation cells, $erf(x)$ is the error function, $erfc(x)$ is the complementry error function, and L is the side length of the primary simulation box.

Note that unlike a simulation with fixed charge model, in the fluc-q model, there is an intramolecular interaction term, through the Coulomb integral. This term acts only on all pairs within a molecule, and is the overlap integral between Slater orbitals centred on each atomic site[7,10]. For a geometrically rigid model such as SPC, the integral turns out to

be just a number. The coulomb integral term smoothly changes to the standard $1/r$ form for site interactions across molecules.

The fictitious mass of the charge has to be chosen with care. It has to be small enough, so that the charges rapidly follow the nuclear motion, and are effectively on the Born–Oppenheimer adiabatic surface. On the other hand, a very small charge mass necessitates the use of a very small timestep of integration, which is not good for practically studying long trajectories. A balance has to be struck between these two opposing criteria. Reasonable values of the charge mass are given in the original paper of Rick *et al*[7]. In this spirit, the fluc-q model is essentially similar to the Car–Parrinello molecular dynamics method[11], where the electronic degrees of freedom are kept cold to start with, and are allowed to evolve using fictitious dynamics, but always on the Born–Oppenheimer surface. The separation in temperature allows no thermal coupling between the nuclear and charge (or electronic) degrees of freedom. It is thus important that one starts with the minimum energy configuration for the charges, given a nuclear configuration. The fictitious dynamics, then takes care that the charges stay "near the ground state" throughout the trajectory. This is ensured by a proper choice of the charge mass, as provided in the paper by Rick *et al*[7].

The Ewald summation method[12] used to handle the long range part of the ionic interactions is identical to the one used in the fixed charge model. In the fixed charge model, the self-energy term is a constant throughout the simulation, and needs to be calculated only once, at the start of the run. However, this term, in the fluc-q method, contributes to a non-zero force on the charges and thus must be evaluated at every timestep. In addition, if the real space part of the potential energy is shifted at the interaction cutoff, we can obtain a better value for the conservation of total energy. In the case of constant charges, this shift is independent of time, and is only a function of the cutoff distance and interaction parameters. However, in the fluctuating charge model, this term, being dependent on the interacting charges, has to be calculated within the force subroutine itself, for each pair, and during every time step. It also contributes to a non-zero force on the charges.

We have carried out simulations to determine minimum energy structures of small water clusters having up to 10 water molecules. Our aim has been to study the nature of hydrogen bonding in these systems, and the evolution of the cluster to the bulk liquid structure. All simulation parameters are the same as given in Rick *et al*[7], and are thus not provided here. Our results are for the fluctuating charge model for SPC water (SPC-FQ). We were able to convincingly reproduce the results of Rick and co-workers on the monomer and the dimer.

The initial configurations of higher n-mers were chosen from minimum energy structures of preceding water clusters. To obtain minimum energy clusters, we have followed a protocol of initially performing molecular dynamics (MD) runs at a constant temperature of 50 K, for a long time. This effectively samples a wide array of configurations, at the end of which we obtain a structure that is closer to the minimum energy. We then perform a energy minimization run, by the steepest descent method to reach the nearest minimum. For every nuclear configuration, the instantaneous charge configuration was obtained by minimizing the energy with respect to variation in charges alone. Although we cannot guarantee that the minima obtained here are the global minima for the clusters, there is a good agreement with structures reported here with those published in the literature for water clusters obtained with other potential models.

During the MD runs, as well as during minimization, we used the SHAKE and RATTLE methods [13] to satisfy the constraint that the water molecules are rigid.

We have also performed MD calculations of 256 water molecules in bulk at a temperature of 298 K and a density of 1·01 g/cm^3. The initial configuration of the system was chosen from a large sample of well-equilibrated water. The 256 molecule system was later equilibrated for about 15 ps. The temperature of the system was maintained by coupling the atomic momenta to a Nosé–Hoover thermostat [14,15]. The charge momenta were left unthermostated, with an initial temperature of 1 K, where it remained for the entire trajectory of 20 ps. The equations of motion were integrated with a timestep of 1·0 fs. Ewald summation method was used to handle the long range interactions, with a real space cutoff of 9·775 Å. Atomic configurations were stored at regular intervals from which the oxygen-oxygen and oxygen-hydrogen pair correlation functions were calculated. The correctness of the MD code [16] was tested, as usual, first by debugging the forces on the charges numerically, using a difference scheme. This provides an internal consistency check which is crucial in debugging. Later, we monitored the conserved energy as a function of time, and the standard deviation in that quantity was found to be less than one part in 10^4. In our case, the conserved energy is different from the standard conserved quantity for NVT ensemble [13], with an additional term corresponding to the kinetic energy of the charges, i.e., $\frac{1}{2}M_Q\dot{Q}^2$.

3. Results and discussion

Our primary interest in this work has been to study the nature of hydrogen bond in small water clusters. A key feature of the fluc-q model as opposed to fixed charge model is that the former captures the essence of charge transfer during bond formation, at least qualitatively. In the fixed charge model, for small clusters, even though only one of the hydrogens may participate in hydrogen bond formation, the other hydrogen too will retain its charge, and for all practical purposes, be identical in nature to the one that forms the hydrogen bond. This is physically unappealing, and a drawback of the rigid charge model. The fluc-q model allows the charge to change dynamically depending on the site's local environment. Thus, in the specific case of small clusters, the charges on the hydrogen atoms in a given water molecule, need not be identical. This indeed turns out to be the case. We clearly see a transfer of charge within the molecule with the hydrogen forming the intermolecular hydrogen bond possessing a larger positive charge than the hydrogen that does not form the bond.

Minimum energy configurations for water clusters for sizes ranging up to 10 water molecules are shown in figure 1. Essential data on the geometry of the clusters are also provided, along with values of site charges. The oxygen-oxygen distance in the dimer is around 2·94 Å, and the oxygen atoms carry a charge of –0·7403*e*, while the hydrogen atom that is involved in the H-bond has a charge of 0·4251*e*. These charges must be compared with the bare charges of the SPC model, which are –0·82*e* and 0·41*e* respectively. We also note that the charge on the oxygen atoms increases in magnitude as the size of the cluster increases. It is also clearly seen that the hydrogen atoms participating in hydrogen bonds have a different charge than the ones that do not form hydrogen bonds. The configuration that we have obtained for the pentamer is a regular pentagon, while others [17] have reported a puckered, postal envelope like structure. Similarly, for the hexamer, we obtain the "open book" structure, while others have predicted the cage or the prism to be of lower energy [18]. Specifically, for the hexamer, we

(a)

(b)
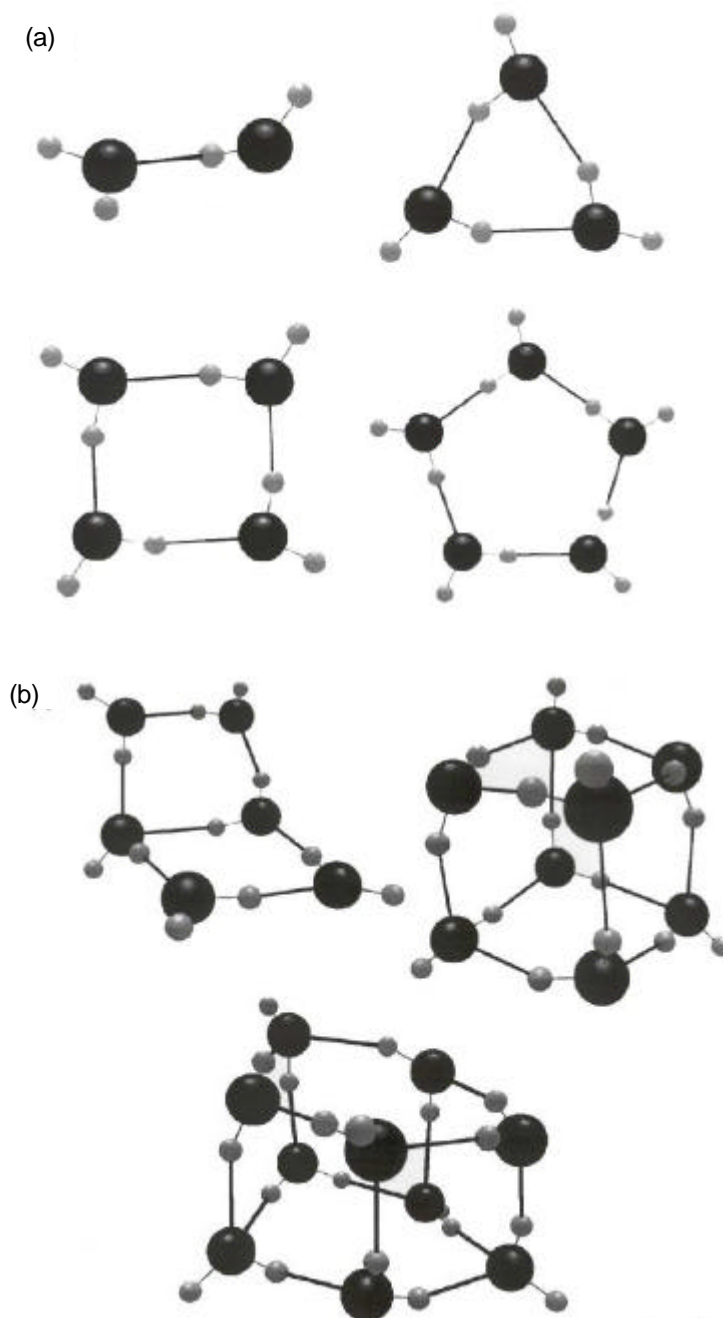
Figure 1. (**a**) Minimum energy structures for dimer, trimer, tetramer, and pentamer water clusters. Dark sphere denotes a oxygen atom and grey sphere represents hydrogen atom. Intermolecular hydrogen bonds are represented by dark lines and intramolecular O–H bonds are represented by light lines. The pentamer forms a regular pentagonal structure which is different from the structure reported in the literature [17]. (**b**) Minimum energy structures for hexamer, octamer, and decamer water clusters.
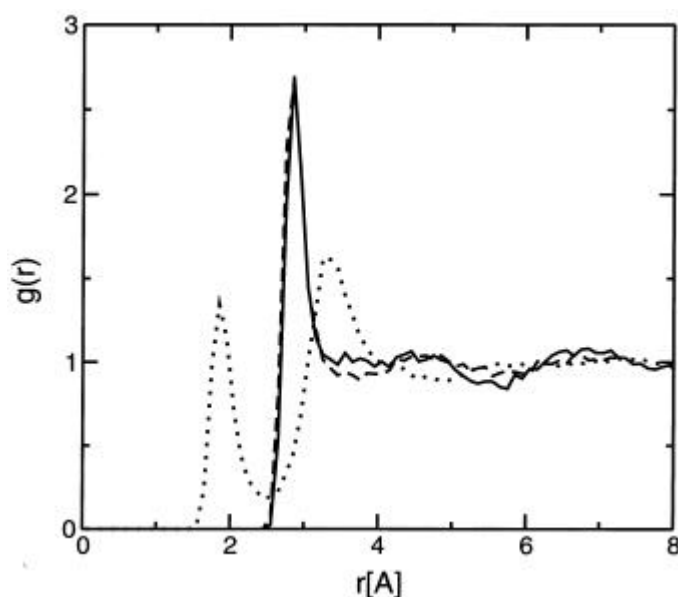
Figure 2. Pair correlation functions, $g(r)$, of oxygen–oxygen (solid line) and oxygen–hydrogen (dotted line) pairs in bulk water for the SPC-FQ model, compared with the oxygen–oxygen (dashed line) function for the SPC model.

Table 1. Potential energy, E, and average charge on oxygen, as a function of number of water molecules in the cluster, n.

n	E (kJ/mol)	Q_O (e)
2	−9·20	−0·747
3	−17·73	−0·823
4	−25·81	−0·917
5	−29·46	−0·973
6	−28·86	−0·950
8	−30·82	−0·948
10	−33·03	−0·979
256 (bulk)	−40·74	−1·016

have calculated the energy for the cage structure, within the fluc-q model, and we have found it to be higher than the "open book" structure. Clusters up to the pentamer form cyclic structures, in which the charges on all oxygen atoms are identical. Clusters beyond the hexamer form three dimensional structures, with the octamer forming a cube-like structure, while the decamer forms a pentagonal biprism structure. These minimum energy structures obtained are in good agreement with configurations published by others using different potential models[19].

In table 1, we provide the potential energy and the average charge on the oxygen atom of these clusters. This gives us an indication of the spatial evolution of the structure of water towards its bulk. Such small water clusters are also found in supramolecular complexes, and stabilize them[20].
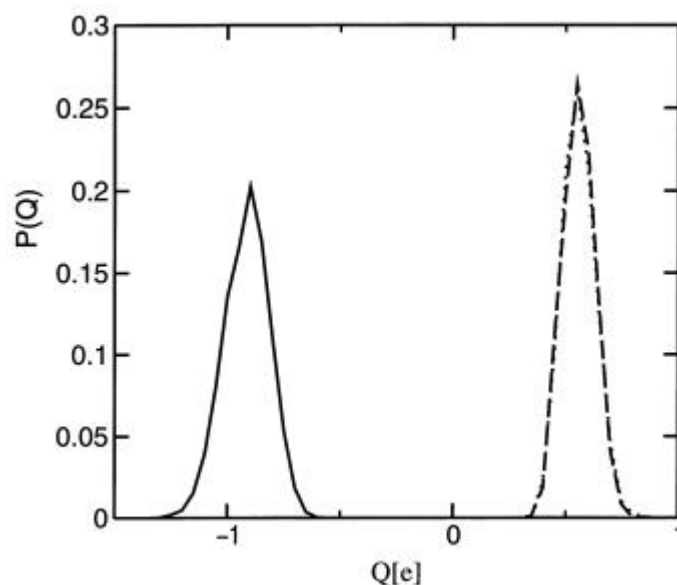
Figure 3. Probability distribution of oxygen and hydrogen charges, *Q*, in bulk water for the SPC-FQ model. The charge distributions on hydrogen atoms overlap. The original SPC model has fixed charges of -0.82 and $+0.41$ for the oxygen and hydrogen atoms respectively.

Figure 2 shows the pair correlation function of the oxygen atoms. The first peak is at 2·85 Å with the first coordination shell of oxygen, taken to be up to 3·3 Å consisting of about 4·4 water molecules, forming a neat tetrahedron. The pair correlation functions obtained here are in close agreement with the results of Rick *et al*[7] and the experimental work of Soper *et al*[21]. We also show the pair correlation function of intermolecular oxygen-hydrogen pairs in the same figure. The first coordination number here is around 3·95 at a distance of 2·55 Å with a sharp first peak at 1·85 Å.

We have also calculated the distribution of charges on oxygen and hydrogen in bulk liquid water. These are shown in figure 3. Note that the distribution is nearly identical for the hydrogen atoms, as, on average, both the hydrogen atoms will behave equivalently. The charge on the oxygen atoms in bulk water can be smoothly extrapolated from its values for small water clusters as the cluster size increases.

4. Conclusions

We have studied the formation of hydrogen bonds in small water clusters through a new potential model for water, i.e., the fluctuating charge model. In this model, the charges on sites are allowed to respond to their local environments, such that their site electronegativity matches the electronegativity of the neighbourhood. The flow of charge is driven by local differences in chemical potential. The dynamics of the charge is treated using an extended Lagrangian method, similar in spirit to the Car–Parrinello MD method[11]. In this specific work, we have studied the minimum energy structures of small water clusters, i.e., clusters containing up to ten water molecules. The fluc-q model effectively captures the essence of hydrogen bonding in these clusters, and is able to

differentiate, in terms of charge, the hydrogen atoms that form H-bonds versus the ones that do not. We have also calculated the molecular structure of bulk liquid water within the fluc-q model, and have found that it agrees quite well with experimental data.

We plan to test the collective properties of this model, like shear viscosity[4] and dielectric constant, and also its applicability at high pressures[22]. Another area of work is to study liquid–liquid and liquid–solid interfaces with water as one of the components. For example, at an air–water interface[23–26], the water molecules do not have their dipole moments randomly oriented, as in the bulk. The dipoles at the interface are oriented in the plane of the interface, giving rise to a small, but not inconsequential potential difference at the interface. Such a subtle anisotropy in the structure of water has to be necessarily studied using a potential model that is flexible in terms of allowing the site charges to vary. One can visualize the use of the fluc-q model in a variety of such interfaces, including the behaviour of water molecules near a micellar interface[27], bound water in proteins etc. The fluc-q model itself can be augmented by the variation of the size of the oxygen atoms depending on its instantaneous charge. It is not unreasonable to expect that as the negative charge on the oxygen atoms increase, the σ parameter of the Lennard–Jones potential to increase, effectively mimicking the increase in its ionic radius. We are currently working on developing this model in this direction.

Acknowledgements

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