An asymmetric model for water structure

2005 J. Phys.: Condens. Matter 17 S3273

(http://iopscience.iop.org/0953-8984/17/45/012)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) S3273–S3282 doi:10.1088/0953-8984/17/45/012

An asymmetric model for water structure

A K Soper

ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

Received 18 October 2005
Published 28 October 2005

Abstract

Most classical computer simulations of water use an effective potential which reflects the local symmetry of the water molecule's nuclei. This in turn gives rise to a symmetric distribution of neighbouring molecules on average. Recent data from x-ray absorption spectroscopy however are interpreted as implying that there is local asymmetry in water structure with some strong and some weak hydrogen bonds. Here, existing neutron and x-ray diffraction data are interpreted with empirical potential structure refinement using an asymmetric water potential. It is found that quite accurate representations of the diffraction data are possible by this means. This does not prove that the asymmetric model is correct, nor that the symmetric model is incorrect, but that x-ray and neutron diffraction data on water are rather insensitive to these details of the water interaction potential.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Going back to earliest computer simulations of water [1], it has been built into virtually all computer models [2] that, on account of the symmetric nature of the water molecule, the electron distribution would be symmetric with respect to the H–O–H plane of the water molecule. This has been built into effective interaction potentials for water by assuming typically that the oxygen has a net excess of electron density associated with it while the two protons have a deficit of electron density, giving rise to an electric dipole moment vector which lies in a direction from the oxygen atom to a point midway between the two protons; figure 1(a). However, we also know that the electron distribution can be polarized by neighbouring molecules.

When a water molecule approaches others, the excess of electron density on the oxygen will be attractive to neighbouring protons, which have a deficit of electron density, and the phenomenon of 'hydrogen bonding' occurs, which in the case of water produces a network structure quite distinct from simple liquids like liquid methane or carbon tetrachloride. When such a hydrogen 'bond' is formed (there is still an active debate about the degree of covalency in this bond) [3] it can have the further effect of polarizing the water molecule, i.e. enhancing

0953-8984/05/453273+10$30.00

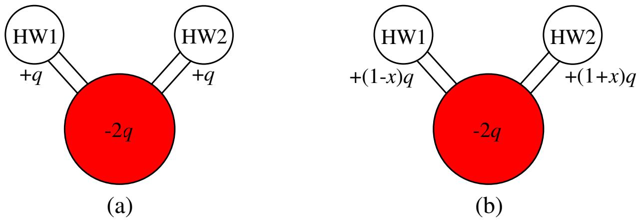

Figure 1. (a) Representation of a symmetric charge distribution on a water molecule. A single unit of positive charge, q, is placed on each proton, with corresponding negative charge, $-2q$, placed on the oxygen atom, preserving the nuclear symmetry. (b) Representation of the asymmetric charge distribution on a water molecule. An amount of charge, xq, where $-2q$ is the charge on the oxygen atom and $0 \leqslant x \leqslant 1$, is transferred from HW1 to HW2. This occurs because of the proximity of a neighbouring water molecule which forms an H bond with HW2.

the imbalance of charge density between oxygen and protons. Again virtually all computer simulations that model this polarization effect [4] assume that the polarization is symmetric between the two protons, i.e. a loss of electron density on one proton is mirrored by an exactly similar loss on the other. Hence the induced charge imbalance is assumed to remain symmetric. *Ab initio* simulations of liquid water, which attempt to model the electrons using a quantum mechanical representation, so far have not highlighted any failure of this underlying symmetry in the electron distribution of a water molecule in the liquid [5].

Recently, x-ray absorption spectroscopic (XAS) measurements [6] have been interpreted to imply that there may be a flaw in these traditional assumptions. In essence the idea is that when a proton forms a hydrogen bond with the oxygen on another molecule, the bonding oxygen pushes electron density away from the proton it is bonding to and towards the oxygen and the other proton on the same molecule; figure 1(b). Hence the charge distribution becomes asymmetric by an amount x $(0 \leqslant x \leqslant 1.0)$ and the ability of the other proton to form hydrogen bonds is reduced. Such a radical change to our view of how water molecules bond affects our picture of what makes water structure form the way it does: an asymmetric charge distribution might give rise to a chain-like structure rather than the network structure that is traditionally assumed.

The purpose of the present study is to analyse existing neutron and x-ray diffraction data on water assuming that the charge distribution on the water molecule has varying degrees of asymmetry, and to determine what evidence there is, based on these diffraction data, for such a charge asymmetry in the liquid state. We make no comment on the XAS experiment itself and the interpretation of the XAS data. There is already a significant literature building up on the interpretation of the XAS data [6, 7].

2. Method

The method of analysis uses empirical potential structure refinement (EPSR) [8] to perform a series of simulations of water and compares them with the existing neutron and x-ray data. At the heart of the EPSR method is a reference potential which is used to provide prior knowledge about the structure of the water molecule itself and the likely interaction potential between water molecules. In principle the reference potential can be as complicated as can be conceived, incorporating polarizability and other many-body effects, though in practice it usually takes a simple Lennard-Jones plus Coulomb interaction form. The Lennard-Jones interactions serve to prevent atomic overlap and to represent the dispersive forces between molecules, while the

Coulomb interactions occur between specific sites on the water molecule, which may or may not coincide with the nuclear positions, depending on the particular interaction potential being used. EPSR uses this potential at the outset to form an initial distribution of molecules in the computer simulation box, then perturbs it iteratively, using the diffraction data as a guide. Using as many diffraction data sets as possible, one has the best chance of obtaining on the computer a model of what the real liquid looks like at the molecular level.

The diffraction data are represented by a series of distinct structure factors, $F_d(Q)$, which are defined by

$$F_d(Q) = \sum_{\alpha,\beta\geqslant\alpha} (2-\delta_{\alpha\beta})c_\alpha c_\beta b_\alpha b_\beta H_{\alpha\beta}(Q) \tag{1}$$

where the Faber–Ziman partial structure factors $H_{\alpha\beta}(Q)$ are defined by

$$H_{\alpha\beta}(Q) \equiv S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^\infty r^2(g_{\alpha\beta}(r)-1)\frac{\sin Qr}{Qr}\,\mathrm{d}r. \tag{2}$$

$g_{\alpha\beta}(r)$ are the site–site radial distribution functions, c_α is the atomic fraction of component α, and b_α is either the scattering length (neutrons) or the Q dependent electron form factor (x-rays). For x-rays the diffraction data are usually normalized to either $[\sum_\alpha c_\alpha b_\alpha^2(Q)]$ or $[\sum_\alpha c_\alpha b_\alpha(Q)]^2$, while for neutrons the data are normally left unnormalized.

To use the diffraction data within EPSR, the partial structure factors are labelled $j = 1, N$, and the data sets are labelled $i = 1, M$. On the basis of the scattering equation (1), weights are assigned as $w_{ij} = (2-\delta_{\alpha\beta})c_\alpha c_\beta b_\alpha^{(i)} b_\beta^{(i)}$, $j = 1, N$, where $b_\alpha^{(i)}$ is the scattering length or form factor for component α in data set i, and j refers to one of the site–site partial factors ($j = 1$ refers to OO, $j = 2$ refers to OH, etc). In the present case there are more data sets ($M = 6$) than partial structure factors ($N = 3$), although in the majority of examples the reverse is true, namely $M < N$, which means that the inversion of the w_{ij} is indeterminate. Even when $M \geqslant N$, as at present, the data may contain systematic errors which reduce their ability to form an accurate reconstruction of the partial structure factors. To circumvent this difficulty, a feedback factor f $(0 \leqslant f < 1)$ is introduced to create a set of pseudo-weights:

$$w'_{ij} = f w_{ij}, \qquad 1 \leqslant i \leqslant M \tag{3}$$

for the data, with additional terms for the simulation:

$$w'_{ij} = (1-f)\delta_{(i-M)j}, \qquad M+1 \leqslant i \leqslant M+N. \tag{4}$$

The resulting matrix ($M + N$ rows by N columns) can always be inverted in the least squares sense (provided that $f < 1$), with greater emphasis on the data as f approaches unity. By choosing different values of f the effect of systematic errors in the diffraction data on the outcome of the simulation can be tested [9]. Inversion of the matrix, w'_{ij}, allows us to combine the diffraction data and simulation results to generate a perturbation to the site–site empirical potential at each iteration of the simulation loop.

As stated above it is traditionally assumed that the protons are identical so that the charge imbalance is the same for the two protons. In the present work we assume that the protons are distinct, labelled HW1 and HW2, while the oxygen atom is labelled OW. Starting from the case where HW1 and HW2 have the same charge, case a2, the charge on HW1 is progressively reduced by an amount xe, where e is the electron charge, and the charge on HW2 increased by a corresponding amount, cases a2_2, a2_3, a2_4, until with case a2_6 HW1 has no charge, and HW2 has all the charge ($x = 1$). This has to be done in a manner such that the overall charge on the water molecule is zero, and the energy of the simulation is roughly constant. Table 1 lists the main parameters of these asymmetric potentials. Note that a small Lennard-Jones term is used for the protons to prevent them approaching one another unphysically closely in the

Table 1. The asymmetric simple point charge model for liquid water. In this potential both water oxygen and water hydrogen atoms are given Lennard-Jones parameters: $\varepsilon_{\mathrm{OW}} = 0.585$ kJ mol^{-1}, $\sigma_{\mathrm{OW}} = 3.166$ Å, $\varepsilon_{\mathrm{HW}} = 0.0325$ kJ mol^{-1}, $\sigma_{\mathrm{HW}} = 1$ Å. The fitting factor R_{f} measures the quality of fit to the data, defined by $R_{\mathrm{f}} = \sum_i \sum_j (D_i(Q_j) - F_i(Q_j))^2 / \sum_i N_Q(i)$, where M is the number of data sets, and $N_Q(i)$ is the number of Q values for the ith data set.

Potential	x	q_{OW} e	q_{HW1} e	q_{HW2} e	μ D	R_{f}	E_{pot} (kJ mol^{-1})
a2	0	−0.848	+0.424	+0.424	2.42	0.0061	−42
a2_2	0.224	−0.810	+0.262	+0.548	2.55	0.0063	−45
a2_3	0.473	−0.785	+0.207	+0.578	2.64	0.0066	−50
a2_4	0.706	−0.680	+0.100	+0.580	2.64	0.0068	−43
a2_6	1	−0.600	+0.000	+0.600	2.83	0.0069	−45

asymmetric case. Note also that one consequence of this charge imbalance is that the dipole moment of the water molecule increases in the simulation, in line with what has been seen in some *ab initio* simulations of water [10].

The data sets used here include five neutron diffraction data sets [11] for mixtures of light and heavy water, namely (1) pure H_2O, (2) 75:25 H_2O:D_2O, (3) 50:50 H_2O:D_2O, (4) 25:75 H_2O:D_2O, and (5) pure D_2O, and an x-ray diffraction data set for pure H_2O, (6) (Hura *et al* [12]). It should be noted here that whereas the reference potential can distinguish between HW1 and HW2, the diffraction data cannot be used to do this, since as far as the diffraction experiment is concerned they have identical scattering properties. Therefore any perturbations to the reference potential induced by the data will be the same for HW1 and HW2. As will be seen below however, these perturbations are in fact not large enough to overcome the underlying charge asymmetry.

3. Results

The EPSR fits to these data were performed using 1800 water molecules in a cubic box of dimension 37.7725 Å at a temperature of 298 K. A feedback factor of $f = 0.7$ was used for all simulations. The fits to the data for cases a2 ($x = 0$) and a2_6 ($x = 1.0$) are shown in figure 2, and the corresponding fit parameters, R_{f}, are shown in table 1. Bearing in mind that there are small differences in structure between H_2O and D_2O which both neutron and x-ray diffraction experiments are likely to be sensitive to [13], the overall quality of fit is good, even though some small discrepancies can be seen. The slight worsening trend in R_{f} with increasing asymmetry seen in table 1 is not obvious in figure 2 and so is probably within the systematic uncertainties of the data and should not be treated as significant. The main point is that with the asymmetric charge distribution for the reference potential the fits do not get noticeably worse. Hence at this level it appears that the diffraction data are not sensitive to whether a charge imbalance occurs or not. Indeed one could imagine that different molecules could have different degrees of charge asymmetry and we would still get adequate fits.

The consequence for the radial distribution functions is of course profound, however. These are shown in figure 3 for the cases $x = 0$ and 1. The other reference potentials are intermediate between these two cases. Now, because the protons are distinguishable, there are six partial $g(r)$s to display instead of the usual three. Clearly as the charge imbalance between the protons increases the HW1 proton becomes progressively less strongly hydrogen bonded, while the HW2 proton becomes more strongly bonded.

The OW–OW function seems to vary somewhat between the different potentials, with the asymmetric potential producing a sharper peak at lower r, followed by a more pronounced

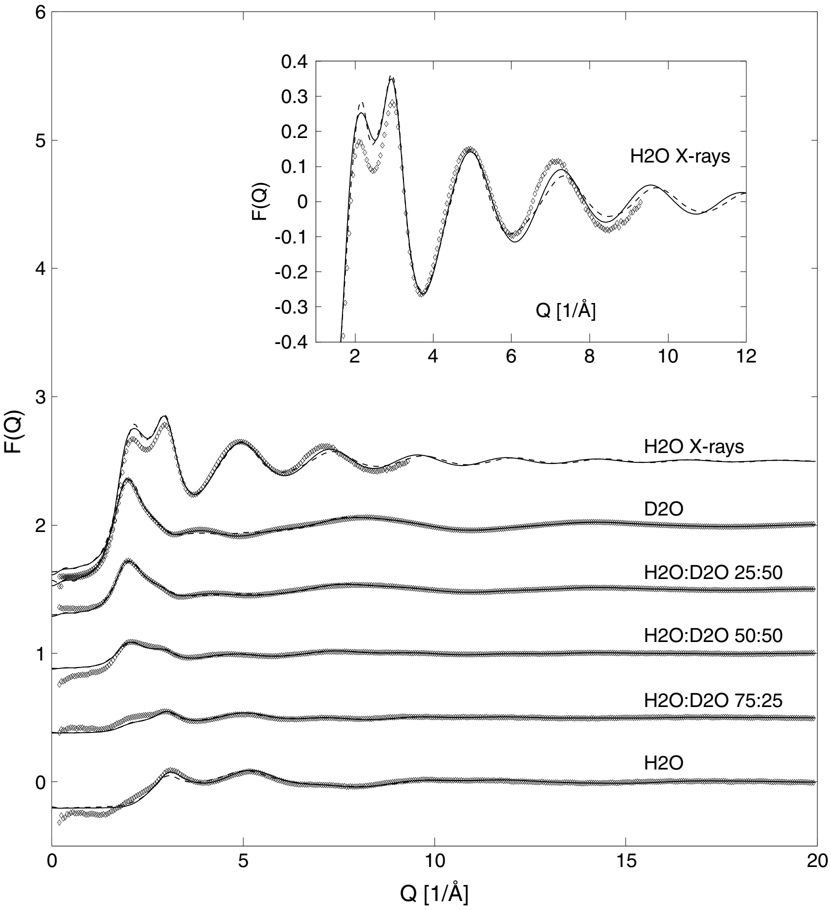

Figure 2. EPSR fits to neutron and x-ray diffraction data (diamonds) for the case of $x = 0$ (symmetric charge distribution, solid line) and $x = 1$ (full asymmetry, dashed line). The x-ray data are shown at the top, and the neutron data for different mixtures of H_2O and D_2O are shown in the five graphs below this one. The inset shows the x-ray fit in more detail.

tail than the symmetric potential. The inset to figure 2 shows the x-ray data and fits in more detail. In particular, we note that there are small differences both between fit and data, and between the symmetric and asymmetric potentials near $Q = 2$ Å^{-1} and for $Q > \sim 6$ Å^{-1}. Attempts to remove these differences by increasing the amplitude of the empirical potentials were unsuccessful. Differences between fit and data could be a consequence of some intrinsic limitation in the EPSR technique, but equally could be due to the finite accuracy of the data themselves in these regions. The differences between simulated x-ray structure factors are almost certainly a consequence of the difference in shape of the main OW–OW peak in figure 3 between these two potentials, there being little else different between these simulated functions in both Q and r spaces.

Table 2 shows the coordination numbers for the different radial distribution functions, and table 3 shows the estimated hydrogen bond probabilities and numbers, based on the restricted definition of a hydrogen bond given in the *Science* paper [6]. Clearly within this definition the number of hydrogen bonds per molecule diminishes markedly with increasing charge

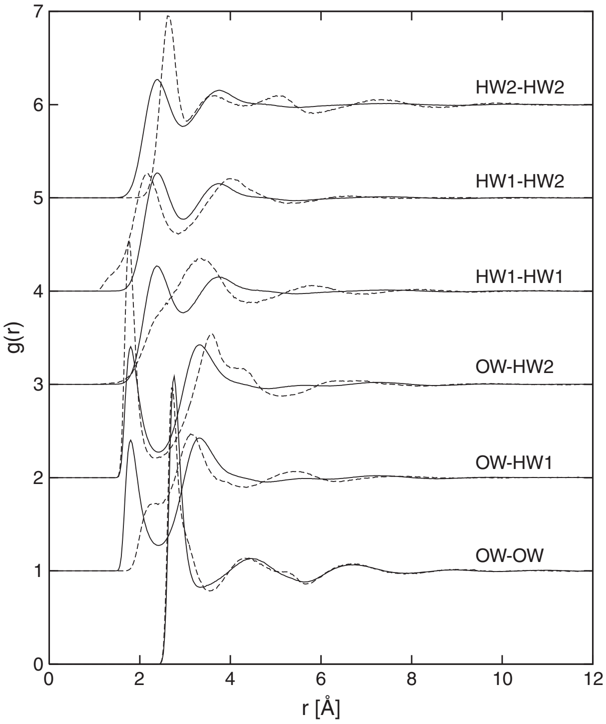

Figure 3. Site–site radial distribution functions for the cases of $x = 0$ (symmetric charge distribution, solid lines) and $x = 1$ (fully asymmetric charge distribution, dashed lines).

Table 2. Running coordination numbers for the asymmetric potentials (with EPSR refinement). The integration range for each site–site distribution is given in parentheses.

Potential	OW–OW (0–3.5 Å)	OW–HW1 (0–2.4 Å)	OW–HW2 (0–2.4 Å)	OW–HW (Total)
a2	5.3	1.0	1.0	2.0
a2-2	5.3	0.7	1.1	1.8
a2-3	5.3	0.7	1.1	1.8
a2-4	5.3	0.7	1.1	1.8
a2-6	5.2	0.7	1.2	1.9

Table 3. Mean number of hydrogen bonds per water molecule according to the definition given in [6].

Potential	No of H bonds
a2	2.9
a2_2	2.6
a2_3	2.5
a2_4	2.3
a2_6	2.2

asymmetry, but the coordination numbers do not change appreciably. We note however that even with the fully symmetric potential the hydrogen bond number is significantly lower than the reported value for conventional simulations of water [6].

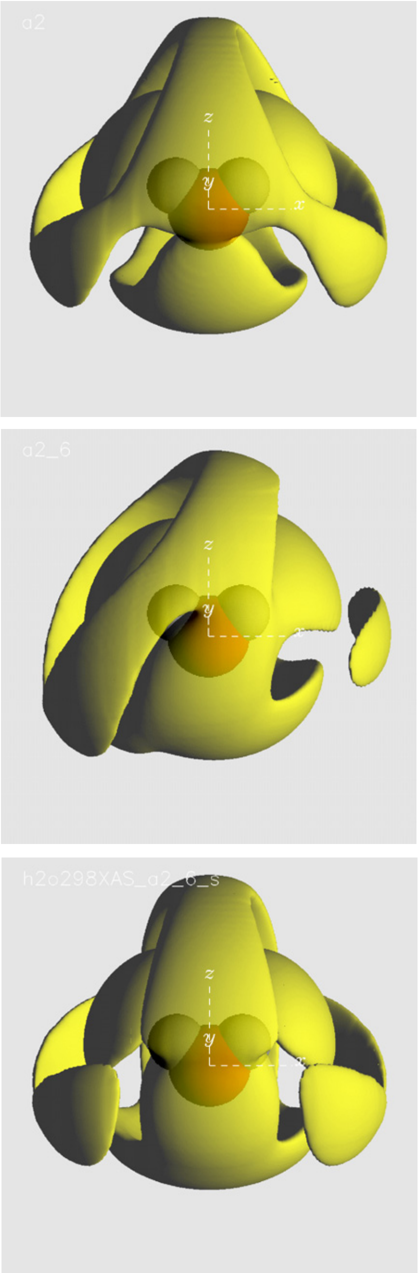

Figure 4. Spatial density functions for water oxygen atoms about a central water molecule; (top) charge symmetry, $x = 0$; (middle) full charge asymmetry, $x = 1$; and (bottom) same as (middle), but symmetrized by reflection in the z–y plane. Note that the HW1 atom lies in the plane defined by the positive x-axis and the z-axis, which points midway between the two protons.

Figure 4 shows the spatial density function for water [14] for the cases (a) $x = 0$ and (b) $x = 1$. The asymmetry in the local structure induced by the charge imbalance is clearly visible in this representation. Also shown in (c) is the case where the charge distribution is the

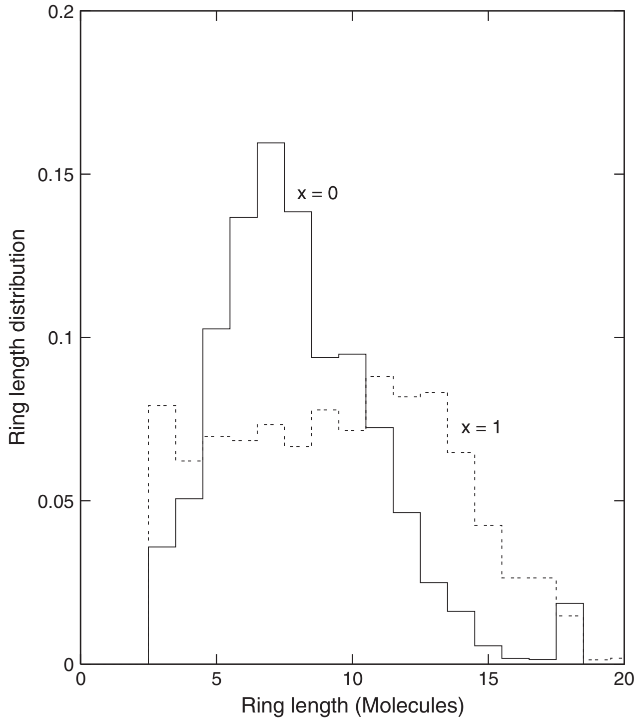

Figure 5. Ring distributions for the simulated boxes of water molecules. Two water molecules are regarded as ‘bonded’ if the oxygen atom on one molecule is separated by 3.3 Å or less from the oxygen atom on a second molecule, while at the same time one of the hydrogen atoms on the first molecule is separated by 2.4 Å or less from the same second molecule oxygen atom. Rings are then counted on the basis of the ‘shortest path’ criteria [16]. The solid line is for $x = 0$, and the dashed line is for $x = 1$.

same as $x = 1$, but the spatial density function has been symmetrized about the z–y plane, by averaging the positive and negative halves of (b) about this plane. Note the similarity between cases (a) and (c).

Finally figure 5 shows the ring distributions for the cases $x = 0$ and 1. Case (a) has a form similar to what has been calculated for network glasses [15], while case (b) implies much larger rings on average. It is clear that the ring structures are quite different for the two liquids: such radical change in structure is not evident directly from the diffraction data.

4. Discussion

What do we learn from this analysis?

(a) Within the limits imposed by the data and modelling analysis there do not appear to be any major inconsistencies between a model which assumes charge asymmetry on the water molecule and the various diffraction data sets, x-ray and neutron. This by itself does not prove that the asymmetric model is correct, nor that the symmetric model is incorrect, but simply that both symmetric and asymmetric models for water can probably be made consistent with the diffraction data.

(b) On close inspection, there do appear to be some small differences between the symmetric and asymmetric potentials in the simulated x-ray structure factor particularly for the region $Q > \sim 6$ Å^{-1} (figure 2, inset). Either the present x-ray data are not accurate enough to distinguish between these functions, or the EPSR method fails at this point. Whatever the reason, the differences between the two potentials show up in the shape of the main peak of $g_{\mathrm{OWOW}}(r)$; figure 3. This suggests that there is in fact a way to test the asymmetric model experimentally: since the x-ray diffraction pattern is generated from the electron density distribution around the water molecule, and since the asymmetry effect is primarily an effect of the electrons, a precise and accurate x-ray experiment in the region $2 < Q < 20$ Å^{-1} might be able to distinguish between the two scenarios. This however is not an easy experiment to perform on account of the uncertainties associated with knowing exactly which x-ray form factor to use, and with correcting for Compton scattering in this region of the x-ray diffraction pattern.

(c) The HW1 and HW2 functions change markedly with increasing charge asymmetry, but do so in such a manner that the mean of the different distributions (OW–HW1 + OW–HW2, etc) does not change very significantly. The neutron data cannot distinguish between HW1 and HW2 and so ‘see’ only this average environment. This no doubt explains why the neutron diffraction data are apparently rather insensitive to the symmetry of the reference potential.

(d) The spatial density functions and ring distributions indicate that charge asymmetry does radically alter the local environment of a water molecule, but note that the *average* spatial density function, figure 4 (bottom), is quite similar to the symmetric charge distribution case, figure 4 (top). With an asymmetric charge distribution the length of distinct chains and rings increases markedly compared to that when the charges are symmetrically distributed.

(e) The question about numbers of hydrogen bonds is distinct from that concerning the coordination numbers: the latter do not change appreciably with charge asymmetry, whereas the former depend rather sensitively on precisely what definition is used. Looking at the O–HW1 $g(r)$, the peak near 1.8 Å rapidly goes away with increasing charge asymmetry, but there is always a shoulder, even in the case when the charge on HW1 is zero. Hence the hydrogen bonds in water probably range from strong to weak and it is not necessarily possible to draw a sharp boundary between what is strong and what is weak.

5. Conclusion

Neutron and x-ray diffraction data on water under ambient conditions have been subjected to empirical potential structure refinement using a range of interaction models, which assume varying degrees of asymmetry in the charge distributions on the water molecule proton sites. The results show that the data cannot readily be used to distinguish between these models, even though they do have radically different radial distribution functions.

It remains to be seen whether the asymmetric charge distribution for the water molecule as tested out here is borne out by further observations and computer simulations. At face value the notion that the electron distribution responds quickly and sensitively to the local environment of a water molecule is not unreasonable. Given that the diffraction experiment in principle at least probes the local order at an instant in time, it is possible to argue that the charge distribution seen by neighbouring molecules might well be asymmetric. If this were true then the local order in water would indeed be distinct from the network structure that is traditionally assumed and more chain-like or ring-like. Unfortunately *ab initio* simulations of water, which in principle could throw some light on this question, are still not accurate enough to give a definite answer to this question [5]. A new x-ray experiment is proposed that could in principle test for the asymmetry effect.

Acknowledgments

It is a pleasure to acknowledge discussions with A Nilsson, L G M Petterson and M Odelius. My thanks to G Hura and T Head-Gordon for supplying the x-ray data in numerical form, and to D Bowron for a thoughtful reading of the final manuscript.

References

[1] Rahman A and Stillinger F H 1971 *J. Chem. Phys.* **55** 3336
[2] Jorgensen W L, Madura J D and Swenson C J 1984 *J. Am. Chem. Soc.* **106** 6638–46
Berendsen H J C, Grigera J R and Straatsma T P 1987 *J. Phys. Chem.* **91** 6269
[3] Isaacs E D, Shulka A, Platzman P M, Hamann D R, Bariellini B and Tulk C A 1999 *Phys. Rev. Lett.* **82** 600–3
Romero A H, Silvestrelli P L and Parinello M 2001 *J. Chem. Phys.* **115** 115–23
Ragot S, Gillet J-M and Becker P J 2002 *Phys. Rev.* B **65** 235115
[4] Chialvo A A and Cummings P T 1996 *J. Chem. Phys.* **105** 8274
Svishchev I M, Kusalik P G, Wang J and Boyd R J 1996 *J. Chem. Phys.* **105** 4742
Sorenson J M, Hura G, Glaeser R M and Head-Gordon T 2000 *J. Chem. Phys.* **113** 9149–61
[5] Grossman J C, Schwegler E, Draeger E W, Gygi F and Galli G 2004 *J. Chem. Phys.* **120** 300–11
Schwegler E, Grossman J C, Gygi F and Galli G 2004 *J. Chem. Phys.* **121** 5400–9
[6] Wernet Ph, Nordlund D, Bergmann U, Cavalleri M, Odelius M, Ogasawara H, Näslund L Å, Hirsch T K, Ojamäe L, Glatzel P, Pettersson L G M and Nilsson A 2004 *Science* **304** 995–9
Nilsson A, Wernet Ph, Nordlund D, Bergmann U, Cavalleri M, Odelius M, Ogasawara H, Näslund L Å, Hirsch T K, Glatzel P and Pettersson L G M 2005 *Science* **308** 793a
[7] Hetenyi B, De Angelis F, Giannozzi P and Car R 2004 *J. Chem. Phys.* **120** 8632–7
Smith J D, Cappa C D, Wilson K R, Messer B M, Cohen R C and Saykally R J 2004 *Science* **306** 851–3
Smith J D, Cappa C D, Wilson K R, Messer B M, Cohen R C and Saykally R J 2005 *Science* **307** 793b
Mantz Y A, Chen B and Martyna G J 2005 *Chem. Phys. Lett.* **405** 294–9
Näslund L-Å, Lüning J, Ufuktepe Y, Ogasawara H, Wernet Ph, Bergmann U, Pettersson L G M and Nilsson A 2005 *J. Phys. Chem.* B **109** 13835–9
[8] Soper A K 1996 *Chem. Phys.* **202** 295–306
Soper A K 2001 *Mol. Phys.* **99** 1503–16
[9] Soper A K 2005 *Phys. Rev.* B **72** 104204
[10] Silvestrelli P L and Parrinello M 1999 *J. Chem. Phys.* **111** 3572–80
[11] Soper A K 2000 *Chem. Phys.* **258** 121–37
[12] Hura G, Sorenson J M, Glaeser R M and Head-Gordon T 2000 *J. Chem. Phys.* **113** 9140–8
[13] Hart R T, Benmore C J, Neuefeind J, Kohara S, Tomberli B and Egelstaff P A 2005 *Phys. Rev. Lett.* **94** 047801
[14] Kusalik P G and Svishchev I M 1994 *Science* **256** 1219–21
[15] Rarivomanantsoa M, Jund P and Jullien R 2001 *J. Phys.: Condens. Matter* **13** 6707–18
Van Ginhoven R M, Jónsson H and Corrales L R 2005 *Phys. Rev.* B **71** 024208
[16] Franzblau D S 1991 *Phys. Rev.* B **44** 4925–30