

A REAPPRAISAL OF WHAT WE HAVE LEARNT DURING THREE DECADES OF COMPUTER SIMULATIONS ON WATER

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Abstract

Due to its ubiquity in our environment (near or far remote) water is the most investigated liquid of the literature. Since the advent of molecular simulations in the sixties the key point of the theoretical studies on water is the description of its force field. During the last three decades a cohort of model potentials have been published and tested by computer simulations. Our purpose is to appraise what have been accomplished during all these years and what deserves to be improved. In addition we attempt to give some guidance for future investigations.

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I - INTRODUCTION

Water is certainly the most investigated liquid by numerical methods since the advent of molecular simulations in the sixties. In view of the continuous flow of theoretical literature published nowadays on water and aqueous solution (about 1 paper/day) it seems worthwhile to step back in order to appraise what has been accomplished during the last three decades and what deserves to be improved.

The reason for the irrepressible interest about water is due to its ubiquity in our environment (near or far remote). Among the large variety of research areas where a deep understanding of the behaviour of water is required one may quote, for instance, the industrial applications of supercritical water for synthesis and toxic waste destruction [1], the environmental sciences (solubility of atmospheric gases in sea water [2], presence of vast amounts of gas hydrates under the sea floor [3]), the geosciences (role of water in rheology of magmas and in volcanic eruptions), the planetary sciences (water under extreme conditions of T and P is found in the mantle of giant planets like Uranus and Neptune [4]) and biology (water is a unique medium for biointeractions [5]). Incidentally one notes that in many cases

water is either far from ambient conditions or is confined or even interfacial, all situation that tells for really accurate water models.

Thus the main goal in physics and chemistry of water is first, to reproduce and to understand quantitatively the evolution of water properties over a large range of thermodynamic conditions and next, to ensure the transferability of this description to various environments (aqueous solution, interfaces ,...). So the purpose of many studies published in the literature during the last thirty years is the quest of a microscopic model for water susceptible to fulfil the above task.

In this context it is useful to summarize briefly some milestones which have put rythm into the saga of water. This story starts in the effervescence of the thirties,

1932 - Spectroscopic proofs of the V-shaped geometry of H_2O [6].

1933 - Bernal and Fowler propose the first realistic interaction potential for water [7].

----- End of the pre-computer era -----

1953 - Metropolis, Rosenbluth and Teller present the Monte Carlo sampling scheme [8].

1957 - Alder and Wainwright perform the first molecular dynamics simulation [9].

1969, 1971- Barker and Watts [10] and Rahman and Stillinger [11] publish the first computer simulations of liquid water.

1976 - Clementi et al. [12] derive a pair potential for water from ab initio calculations.

1981, 1983 - Determination of accurate and simple (ready to use) pair potentials for liquid water [13-15].

1993 - First ab-initio calculation of liquid water [16].

It is noteworthy that as early as 1933, Bernal and Fowler [7] proposed a simple electrostatic model for water where the center of negative charges is moved off the oxygen and towards the hydrogens (positively charged) at a point located on the bisector of the HOH angle. This simple representation, in addition to a repulsion-dispersion term (rare gas like) centred on the oxygen, was supposed to be able to explain the tetrahedral arrangement of water molecules in the liquid state. In fact this picture was actually prophetic, and its correctness waited nearly fifty years before to be proved by computer simulation [15]. From that time an impressive number of interaction potentials primarily designed for simulation has been introduced in the literature, most of them being empirical. It is our purpose to review this matter before we discuss the advances, the difficulties and the possible ways for improvement.

II – WHAT POTENTIAL FOR SIMULATED WATER ?

1-The opposing forces.

There is a number of excellent review articles and critical reports on computational models of water (for recent papers see [17-19]), and we don't intend to be redundant in going into details about the formalism used to describe intermolecular interactions and the computational methodologies involved in Monte Carlo (MC) and molecular dynamics (MD) simulation (for a textbook see [20]). We prefer to focus our attention on the philosophy which underlies the models and their ability to yield useful results. In Table I is presented a

chronological list of the interaction potentials published since the Bernal and Fowler (BF) model in 1933 until these days. Each potential is identified by its name (acronym) in current use in the literature. Although we have tried to be as exhaustive as possible, some models can miss either by ignorance or because they are only a minor variation of an already mentioned potential. When a modification of a given potential is judged more significant we indicate the year of introduction of this new version. An overwhelming majority of the models are empirical and are based on the widely accepted opinion that the hydrogen bond is essentially the result of a competition between an attractive interaction potential energy, well approximated by classical electrostatic interactions, and a repulsive electronic energy [61]. The charge distribution of the water molecule is generally modelled by point charges on the nuclei (e.g. SPC [14]), and occasionally in using one or several additional fictive sites located in the plane of the molecular frame (e.g. BF [7], TIP4P [15]) or out of it (e.g. lone pairs in BNS [22] and ST2 [23]). The electronic repulsion between molecules is mostly accounted for by a Lennard-Jones potential centered on the oxygen which incorporates in addition the dispersion energy. Some noticeable exceptions exist for which the repulsion and the dispersion terms are treated separately from each other (e.g. TIPS [13]) or when an exponential function is preferred to the Lennard-Jones repulsive term (e.g. NSPCE [52]). As we will see later on the implications of these choices are not negligible. The potential parameters (charges and repulsion-dispersion parameters) are fitted to reproduce some gas phase properties (e.g. the dipole moment, the dimer interaction energy, etc...) or to recover some liquid state properties at ambient conditions (e.g. heat of vaporization, density, etc...) by performing a MC or a MD calculation. Very early [22] it appeared that an enhanced dipole moment greater than the gas phase value (1.855 D [62]), was necessary to reproduce at best a number of liquid state properties. Thus many empirical models which have been developed since thirty years have this property (see Table I). Another way to describe more realistically the interactions in water is to introduce the flexibility of the molecule by allowing intramolecular vibrations. This can be done either by supplementing an existing rigid model for water with harmonic or anharmonic potentials for bond length and bond angle (e.g. SPC/F [30]), or by defining a new family of potential just for this very purpose (e.g. the central force models [24,26,48,53]). The intramolecular potential is chosen so as to reproduce the value of the three vibration modes of the isolated molecule and to account for their frequency shift in going from the gas phase to the liquid phase. However a number of flexible models predict a narrowing of the HOH bond angle in the bulk liquid (from 104.5° in the gas phase to approximately 100° in the liquid, e.g. CF [24,26]), an undesirable effect due to the packing of molecules and which is at variance with experimental data [63]. In fact the formation of hydrogen bonds tends to redistribute the valence electrons around the oxygen atom, a charge transfer which leads to a small relaxing of the HOH angle. Finally also notice that the combination of an angular narrowing with a bond elongation due to hydrogen bonding may lead to a significant increase of the dipole moment of the molecule in the liquid (see Table I). This has to be bear in mind when it is the question to compare flexible models with rigid ones.

Table. Main water models of the literature developed since 1933. In the following R is for rigid, F for flexible, D for dissociable and P for polarizable. Values of the dipole moment in the gaseous phase and in the liquid phase are indicated by μ_g and μ_l , respectively.

Acronym (date)	Reference	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
BF (1933)	7	empirical	R	4	2.0	2.0
R (1951)	21	empirical	R	5	1.84	1.84
BNS (1971)	22	empirical	R	5	2.17	2.17
ST2 (1973,1993)	23	empirical	R	5	2.35	2.35
CF (1975,1978,1995)	24	empirical	F	3	1.86	1.98
MCY (1976)	25	ab initio	R	4	2.19	2.19
DCF (1978,1980,1993)	26	empirical	F,D,P	3	1.855	-
PE (1979)	27	empirical	P	1	1.855	2.50
SPC (1981)	14	empirical	R	3	2.27	2.27
TIP3P (1981,1983)	15	empirical	R	3	2.35	2.35
RWK (1982)	28	empirical	F	4	1.85	1.89
TIP4P (1983)	15	empirical	R	4	2.18	2.18
BJH (1983)	29	empirical	F	3	1.87	1.99
SPC/F (1985)	30	empirical	F	3	2.27	2.42
MCYL (1986)	31	ab initio	F	4	2.19	2.26
SPC/E (1987)	32	empirical	R	3	2.35	2.35
WK (1989)	33	empirical	R	4	2.60	2.60
SPCP (1989)	34	empirical	P	3	1.85	2.90
CKL (1990)	35	empirical	F,P	4	1.88	2.20
MCHO (1990)	36	ab initio	P	6	2.12	≈ 3.0
NCC (1990)	37	ab initio	P	6	1.85	2.80
NEMO (1990,1995)	38	ab initio	P	5	2.04	2.89
PTIP4P (1991)	39	empirical	P	4	1.85	2.80
SPC/FP (1991)	40	empirical	F,P	3	1.85	2.44
PSRWK (1991)	41	empirical	P	4	1.88	2.63
KJ (1992)	42	empirical	P	4	1.85	-
NCCvib (1992)	37b	ab initio	F,P	6	1.85	3.11
ASP-W (1992,1998)	43	ab initio	P	3	1.85	2.90
RPOL (1992)	44	empirical	P	3	2.02	2.62
CPMD (1993,1999)	45	DFT+CP	F,D,P	nucl.+el.	1.87	2.95
PPC (1994)	46	ab initio	P	4	2.14	2.51
SPC/FQ (1994)	47	empirical	P	3	1.85	2.83
TIP4P/FQ (1994)	47	empirical	P	4	1.85	2.62
KKY (1994)	48	empirical	F,D	3	2.38	2.21
SQPM (1995)	49	valence bond	P	4	1.85	2.62
SCDP (1996)	50	empirical	P	4	1.85	2.87
TAB/10D (1998)	51	SCF+MD	P	5	1.85	2.65
NSPCE (1998)	52	empirical	R	3	2.18	2.18
NCF (1998)	53	empirical	F	3	1.85	1.90
MCDHO (2000)	54	ab initio	F, P	4	1.85	3.01
TIP5P (2000)	55	empirical	R	5	2.29	2.29
SPC/HW (2001)	56	empirical	R	3	2.41	2.41
DEC (2001)	57	empirical	R	3	1.85	1.85
SWFLEX (2001)	58	empirical	P	4	1.85	2.59
POLARFLEX (2001)	59	valence bond	F,P	3	1.85	2.55
POL5 (2001)	60	ab initio	P	5	1.85	2.71

Many empirical potentials are pairwise additive although they take into account many body effects to some extent in an effective way (through the value of the dipole moment, for instance). Among the many body contributions, the dipole induced dipole mechanism is believed to play the leading role [64]. A simple way to implement it is to develop a model in which the water molecule (rigid or flexible) is approximated by a set of point charges whose the magnitudes are chosen so that to reproduce the dipole moment (and eventually the quadrupole) of the gas phase and to assign a point polarizability to the oxygen atom. A number of models have been proposed along those lines (e.g. SPCP [34], CKL [35], PTIP4P [39], KJ [42], RPOL [44]) but we will see that the results are rather deceptive. The problem of polarization effects was reformulated recently [47] in terms of fluctuating charges which take into account the intramolecular charge transfer induced by the local field. Based on the electronegativity equalization principle this method is an elegant way to improve the accuracy of simple empirical potentials (e.g. SPC/FQ and TIP4P/FQ [47]).

In view of the complexity of the interactions in water, some authors have attempted to extract the force field from ab initio calculations, the resulting potential function being an analytical fit of the results (e.g. MCY [25], MCHO [36], NCC [37], NEMO [38], ASP-W [43]). In general the ab initio calculations are performed on dimers and more scarcely on trimers and higher order clusters (e.g. MCDHO [54]), a procedure which precludes what really happens in the bulk liquid. Moreover the intermolecular interaction energy is a very small fraction of the total energy of the fragments, a situation which requires very accurate ab initio calculations to be reliable. Last but not least, the analytical fit, generally based on distributed charges and polarizabilities can deviate substantially from the potential energy surface really evaluated and hence may generate some inaccuracies. For these reasons other authors prefer to restrict the quantum calculation to a particular mechanism as, for example, the quantum treatment of the electronic polarization. Thus the response of a single molecule to an electric field can be evaluated through a quantum-chemical calculation, the response function (polarization) being parametrized with the help of fluctuating and moving charges (e.g. PPC [46], MCDHO [54]). Alternatively, the valence bond approach has been used to evaluate at each step of a molecular dynamics calculation the ground state polarization energy associated with a set of interacting water molecules (e.g. SQPM [49], POLARFLEX [59]). The use of a limited number of quantum polarization states renders this method very effective provided that a convenient empirical model is used as a framework.

Still more ambitious are the works whose the objective is to implement an electronic structure calculation of liquid water in a computer simulation (MD). An operational procedure consists to use the simple self consistent field description of quantum chemistry to determine the evolving charge distribution of bulk water during a classical MD simulation (e.g. TAB/10D [51]). Although this method formally accounts for electronic penetration effects and polarizability, electron exchange and correlation energy have to be incorporated in an ad hoc way via Lennard-Jones potential for example, with parameters fitted on some gas phase and/or liquid state properties. But the most successful ab initio calculation for water is the Car-Parrinello molecular dynamics scheme (CPMD [65]). In this calculation the electrons are

treated within the Hohenberg-Kohn-Sham density functional theory (DFT) where generalized gradient approximations to the exchange-correlation energy are used. In the framework of the Born-Oppenheimer approximation, the crux of the method is that it leads to an operable molecular dynamics scheme for electronic orbitals. Nevertheless this method is very demanding in computer resources (only small systems of a few tens of molecules are investigated [45]) and the accuracy of the results depend strongly on the exchange-correlation functional used (see [66]).

2-Properties of simulated water .

A usual criterion to choose a model potential among all those presented in Table I is its ability to reproduce at best by computer simulation the properties of real water. For a long time the reproduction of water properties at ambient conditions (298 K, 1 bar) was the only concern and it is only at the end of the eighties that the accuracy of the models has begun to be tested for conditions away from ambient [67-69]. In order to quantify the level of accuracy reaches by the different models we have selected (somewhat arbitrarily) from the simulation data of the literature seven properties namely, the density of the liquid, the heat of vaporization, the self diffusion coefficient, the atom-atom pair distribution functions, the temperature of maximum density, the critical parameters and the dielectric constant. Of course many others quantities have been evaluated by simulations (e.g. the second virial coefficient , the surface tension coefficient , the isothermal compressibility , the heat capacity , ..) but we believe that the properties chosen for discussion are sufficiently representative for our purpose.

a-Liquid density.

In Fig.1 are presented the values of the density of water simulated at ambient conditions (298K, 1 bar) in using various potentials. For a better legibility the simulation data are regrouped according to the kind of potential used (top panel : rigid models; middle panel : flexible models; bottom panel : polarizable models). One sees that the target value (0.997 g/cm^3) is reached by a number of models (e.g. TIP4P [15], SPC/E [32], TIP5P [55], DEC [57]) while others predict either a too small value (e.g. CF [24], MCY [25], NEMO [38]) or a too large one (e.g. BF [7], RWK [28], NCC [37]). For information notice that an overpressure of 500 bar increases the density of real water by 0.02 g/cm^3 . In fact a good agreement is mostly an indication that the potential parameters were fitted to reproduce the experimental density. On the other hand when the density is not used in the fitting procedure, as for instance with ab initio potentials (e.g. MCY [25], MCYL [31], NEMO [38]), the results are rather deceptive. A further analysis shows that the density of the liquid is very sensitive to small inaccuracies in the determination of the exchange-correlation energy (notice that in the case of CPMD calculations [45] using DFT, the smallness of the system size and the absence of long range correction to the exchange-correlation energy prevents a reliable evaluation of the pressure). So in the present state of the art a model potential cannot produce an accurate value of the density at ambient conditions without further adjustments of the potential parameters.

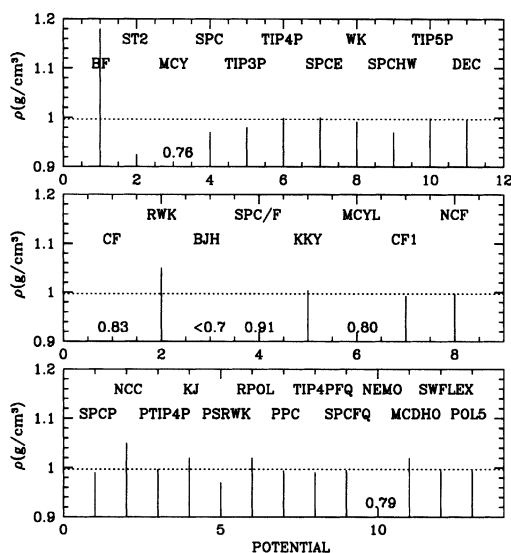


Figure 1. Density of simulated water at 298K and 1bar for different model potentials (see Table):top panel (rigid models), middle panel (flexible models) and bottom panel (polarizable models). The dotted line indicates the experimental value for H_2O (0.997g/cm³).

b-Heat of vaporization.

An important quantity which quantifies the importance of hydrogen bonding in water is the heat of vaporization ΔH_{vap} , i.e the enthalpy difference between the vapour and the liquid in coexistence with each other. To evaluate this quantity by computer simulation it is convenient to make the distinction between intermolecular and intramolecular degrees of freedom, namely

$$\Delta H_{vap} = (U_g^{int,ra} - U_l^{int,ra}) + (U_g^{inter} - U_l^{inter}) + P(V_g - V_l) \quad (1)$$

where $(U_g^{int,ra} - U_l^{int,ra})$ corresponds to the difference in energy of a water molecule in the two phases and $(U_g^{inter} - U_l^{inter})$ is the variation of the intermolecular energy associated with the vaporization process. If all the degrees of freedom are treated classically (as it is generally the case) and provided the temperature is sufficiently low for the vapour to be considered as ideal (e.g. at room temperature) then the following relation holds,

$$\Delta H_{vap} = \Delta E_0 - E_l^{pot} + RT \quad (2)$$

where ΔE_0 is the formation energy difference of a water molecule in the two phases and E_l^{pot} is the intermolecular potential energy of the liquid phase only. In the case where the molecules are assumed rigid (e.g. SPC, TIP4P, ..), Eq.(2) leads to the simple relation,

$$\Delta H_{vap} = -E_l^{pot} + RT \quad (3)$$

To be complete notice that if all the degrees of freedom are treated quantum mechanically (we will discuss this point more thoroughly later on) then,

$$\Delta H_{vap} = \Delta E_0 + \Delta E_{ZPE} - U_l^{inter} + 4RT \quad (4)$$

where ΔE_{ZPE} is the difference in zero point energy of a water molecule in the two phases and U_l^{inter} is the intermolecular energy ($U = E^{pot} + E^K$) of the liquid evaluated quantum mechanically in using the path integral formalism [70].

An important point is to determine what is the most relevant target value of ΔH_{vap} to use in a computer simulation. For a model potential dealing with rigid molecules a common practice is to use the experimental value for light water in Eq.(3) ($\Delta H_{vap}^{H_2O} = 10.52$ kcal/mol at 298K, see [71]). Unfortunately this procedure is not rigorously correct when one deals with classical mechanics as it is the case of most of the simulation works of the literature. Actually the isotope effects are not negligible in liquid water and especially for ΔH_{vap} (10.52 kcal/mol for H_2O , 10.87 kcal/mol for D_2O and 10.93 kcal/mol for T_2O , see Ref.[72]). So it is more judicious to compare the result of a classical calculation with the value of ΔH_{vap} expected for an hypothetical *classical* water. Using the literature data for the isotopic waters we have recently estimated [57] the heat of vaporization of such a classical water to be around 11.0 kcal/mol. Consequently, we recommend to use the latter value as a benchmark in classical simulations for water instead of using the value for H_2O of 10.52 kcal/mol (e.g. in [57]). In Fig.2 are presented the results of the simulation literature for ΔH_{vap} at room temperature obtained with a number of model potentials (the presentation is the same than in Fig.1). Two reference values are indicated, the one generally used in the simulation works and corresponding to light water (10.52 kcal/mol, dotted line), and the one we recommend (11.0 kcal/mol, full line). Since the latter value was introduced only lately it is expected that a simulation result agrees with it only by chance (e.g. ST2 [23a]). In fact a majority of models leads to the value of 10.52 kcal/mol because this value was used as an input data in the fitting procedure (e.g. SPC [14], TIP3P [15], TIP4P [15], TIP5P [55], RPOL [44], PPC [46], TIP4P/FQ [47], SPC/FQ [47], TAB/10D [51]). On the other hand when the deviation between the reference value and the calculated one exceeds approximately ± 0.5 kcal/mol (e.g. MCY [25], MCYL [31], NCC [37], KJ [42],...) it is most often an indication that the liquid state properties were not used to determine the potential parameters. For instance a first principle MD calculation based upon the Car-Parrinello method leads to a value of 7.38 kcal/mol [73], a deceptive result in the absolute but nevertheless very encouraging if one considers that it is an ab initio result for the liquid state.

At this stage it is noteworthy that there is a point at issue in the literature concerning the comparison between computer simulations based upon intermolecular pair potentials using enhanced dipoles (i.e. greater than the gas phase value of 1.85D, see Table I) and experimental data. It has been convincingly argued [32] that in order to take into account the self polarization energy coming from the use of an enhanced (rigid) dipole, a proper comparison with the experimental data needs to correct correspondingly the target value for the intermolecular potential energy of the simulated liquid (an approximate evaluation leads to $\Delta E_{pol} = (\mu_l - \mu_g)^2 / 2\alpha$, see [32]). But the consequence of this procedure is to increase by a significant amount (around +1.0 kcal/mol, according to the model used) the value of ΔH_{vap} produced by the empirical potential. This increase expresses the fact that the effective dipole moment is the same in the two phases while it is not for real water or when the polarization mechanism is treated explicitly. So it is not surprising to see that the SPC/E model, for which the above correction is built-in, leads to a value of ΔH_{vap} which exceeds significantly the experimental value (the same holds true for SPCHW [56], SPC/F [30]). We will see later on that this overestimation of ΔH_{vap} has an important effect on the critical properties of the simulated water.

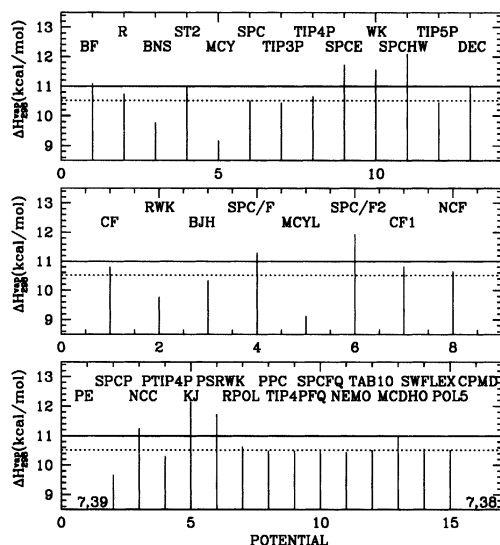


Figure 2. As Fig.1 but for the heat of vaporization at room temperature. The dotted line indicates the experimental value for light water while the continuous line is the one expected for classical water (see text).

c-Diffusivity.

Among the transport coefficients of water, the self diffusion coefficient is the one for which MD studies have paid much attention. Since it measures the mobility of water molecules it is an indicator of the influence of hydrogen bonds on the translational motions. In Fig.3 are reported the MD results of the literature at ambient conditions. It is noteworthy that in general, the interaction potentials for water are not parametrized to reproduce the value of the self diffusion coefficient. The horizontal line indicates the experimental value for light water at ambient ($2.3 \cdot 10^{-5} \text{cm}^2/\text{s}$ [74]). Notice that at room temperature the influence of quantum effects on the self diffusion coefficient seems to be appreciable as suggested by some calculations (quantization tends to increase the mobility, see [53,75]), though a definite conclusion is difficult to extract from experimental data [76]. In this context one can just indicate what models certainly overestimate the diffusivity (e.g. BF [7], BNS [22], SPC [14], TIP3P [15], TIP4P [15], SWFLEX [58]) and what models are reasonably accurate (essentially all the other ones presented in Fig.3).

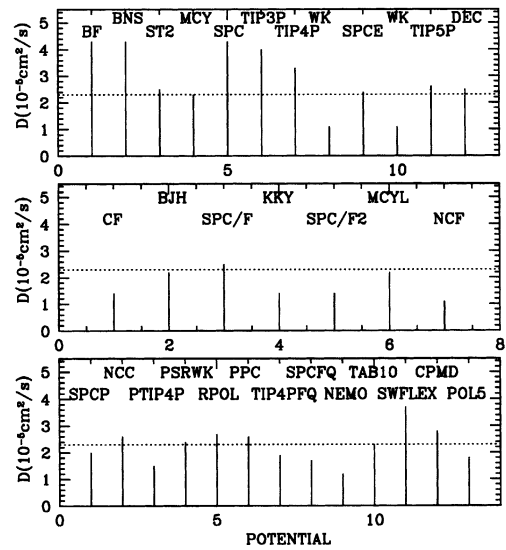


Figure 3. As Fig.1 but for the self diffusion coefficient at ambient conditions. The dotted line indicates the experimental value for light water (see text).

c- Structure.

Among all the properties of liquid water, the most distinctive one is its microscopic structure. Thus the ability of a model potential to reproduce with accuracy the structure data coming from X-ray and neutron scattering studies is quite essential. On the other hand the latter techniques have seen their accuracy to increase progressively in the long run and it is only recently that X-ray and neutron scattering data on liquid water are found to be in a reasonable agreement with each other [77]. To better estimate the degree of accuracy reached by the water models of the literature, it is useful to briefly summarize the specificity of each technique before to compare with the simulation results. An X-ray scattering experiment probes the electronic density distribution within the fluid. In the case of water the measured scattering cross section reveals essentially the position of oxygen atoms and marginally that of hydrogen atoms [78]. This is due to the weighting functions expressed in terms of atomic scattering factors which strongly favour the oxygen atoms with respect to the hydrogens in the scattering intensity. For a long time neither the change in electron density upon formation of a water molecule from isolated oxygen and hydrogen atoms (a redistribution which is responsible of the gas phase dipole of 1.85D), nor the electronic redistribution induced by the liquid state (responsible of an average dipole lying in the range 2.6-3.0 D, see [77,79]) were properly taken into account in the data analysis. Thus the conjunction of appropriate modifications into data extraction with the advent of new image detectors (CCD) and intense X-ray sources (synchrotron) make present day experimental data much more accurate.

As for neutron scattering experiment it gives information on the distribution of nuclei within a liquid sample. Due to the large difference between the coherent scattering lengths of deuterium and proton, respectively, heavy water is generally preferred to light water for a neutron scattering experiment. However the isotopic substitution technique takes advantage of this difference to extract the nucleus-nucleus pair correlation functions ($g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$) from diffraction measurements on heavy water, light water and their mixtures in various proportions. The assumption behind this method is that the structure of the two isotopic waters is identical. In fact simulation studies using path integral techniques [53,75,80-82] and experimental works [83] have shown that this is not the case, heavy water being slightly more structured than light water (which found expression in more pronounced peaks in the atom-atom pair correlation functions). Unfortunately from a quantitative point of view, the isotope effects evaluated by path integral simulations are found to be potential dependent [53,75,80-82] while they are difficult to measure accurately [83]. Nevertheless their influence have to be considered when extracting structure data from an isotopic substitution experiment.

Coming back to simulated water it must be emphasized that during more than two decades the computer simulations using empirical potentials were calibrated with the help of inaccurate structure data. More precisely in their pioneering work Narten and Levy [78] using X-ray data assigned a value of ≈ 2.2 to the first peak of $g_{OO}(r)$ (see also [84-87]) while later on Soper and Philips [88] recommended a value of 3.1 from their own analysis of neutron diffraction data. But subsequent X-ray [77,79] and neutron studies [89,90] have shown that the above discrepancy was due not only to the experimental uncertainties but for a large part

to the data treatment. The most recent X-ray scattering data [79] leads to a value around 2.8 for the first maximum of $g_{OO}(r)$ and located at a slightly smaller O-O distance (2.75Å) than expected previously (2.80-2.85Å). In fact although the deviation between X-ray and neutron data tends to reduce with time, it is still too large (2.8 for $g_{OO}^{\max}(r)$ by X-ray instead of around 2.3 by neutrons [89-91]). In addition the quantum effects are clearly overlooked in all these studies since light and heavy water are assumed to be identical from the structural point of view. As for the O-H and H-H pair correlation functions only the isotopic substitution technique (using H_2O/D_2O mixtures) coupled to a neutron diffraction experiment is able to evaluate each of them. Despite many studies [88-92], some uncertainties subsist concerning the respective magnitude of the peaks and for a better accuracy we recommend to use the total pair correlation function (for D_2O , $G(r)=0.489g_{DD}(r)+0.421g_{OD}(r)+0.09g_{OO}(r)$) when it is the question to assess some simulation results. As a matter of fact for pure (heavy) water each peak of the atom-atom correlation functions gives rise to a well defined feature (peak or shoulder) on the total pair correlation function. Hence a good reproduction of this latter one is a stringent test for computer simulations (for an illustration see Fig.4).

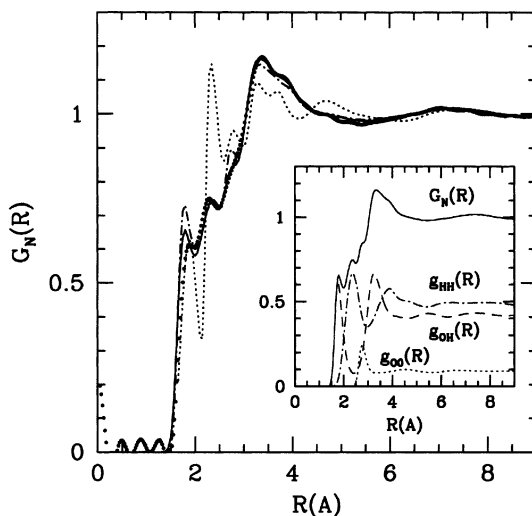


Figure 4. Intermolecular pair correlation function for heavy water at ambient conditions as

evaluated for a neutron diffraction experiment (see text). The dotted curve is obtained from the NCF model [53], the dashed-dotted curve from the SPC/E model [32], the full curve from the DEC model [57] and the black dots are the neutron data of Bellissent-Funel et al. [93]. The insert shows the decomposition of the total pair correlation function in its partial components (only results for the DEC model are presented). Notice that the NCF model deviates significantly from the experimental data specially around 2-2.5Å, a feature due to an overstructuring of $g_{HH}(r)$. By comparison SPC/E is a much better model despite some deviation around 1.80, 2.80, 3.40, and 3.80Å, respectively. As for the DEC model, it reproduces fairly well all the details of the neutron diffraction data.

We have analysed the simulation works of the literature in comparing their structure data at ambient conditions with the X-ray data of Sorensen et al. [79] for $g_{OO}(r)$ and the neutron data of Bellissent-Funel et al. for $G(r)$ (see Fig.8 in [93]). To facilitate the comparison we have assigned to each water model a mark : -1 if the comparison is really bad (this is the case when the hydrogen bond peak at 4.5Å on $g_{OO}(r)$ is not reproduced, e.g. KJ [42], NSPCE [52]), +1 if the comparison is just acceptable (e.g. SPC [14], TIP3P [15]), +2 if there is a good agreement (e.g. SPC/E [32], TIP4P [15]) and +3 if the comparison is accurate (e.g. TIP5P [55], DEC [57]). One sees in Fig.5 that a few models give a poor description of the water structure while a great majority is acceptable or good and that only two of them are really accurate (TIP5P and DEC) even if there is still some room for improvement. In this respect the level of accuracy reached by the CPMD calculations [45] is not yet fully settled since it varies with the exchange-correlation functional used [66,94], the system size (32 water molecules in [45a,66,94a], 54 in [95] and 64 in [45b]) and some other computational details.

Away from ambient conditions, the structure of water has also been investigated in the supercritical state during the last few years. After some controversy mainly due to experimental difficulties [96,90,93,97] it is now well established that dense supercritical water ($T \approx 673\text{K}$ and $\rho \approx 0.66\text{ g/cm}^3$) is no longer characterized by a 3D hydrogen bond network but is composed of monomeric, dimeric, and trimeric species as also as higher order aggregates in a much smaller proportion. It is interesting to notice that the simulations have played an important role in predicting nicely the evolution of the water structure upon heating. From a quantitative point of view, and although the accuracy of the neutron diffraction data available [93,96b,97] is not yet fully satisfactory, one can state that empirical potentials using an enhanced dipole moment (e.g. SPC/E, TIP4P,...) overestimate somewhat the structure of supercritical water while a recent CPMD calculation [98] produces a good reproduction of the available data. Besides the explicit introduction of the polarizability in empirical models (e.g. in [99-101]) or the recourse to a more elaborated intermolecular pair potential (e.g. DEC [57]) lead to some improvements.

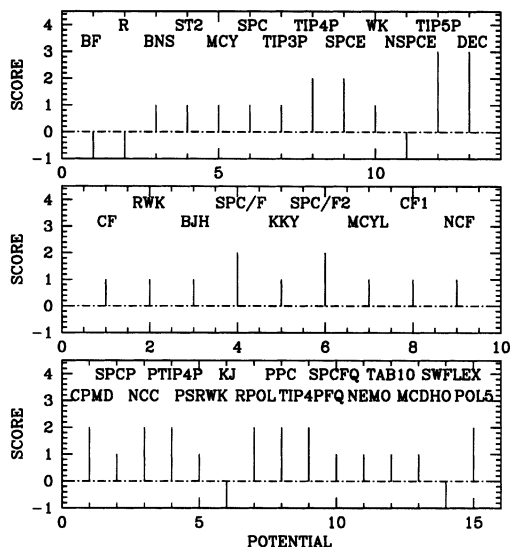


Figure 5. Ability of the model potentials to reproduce structure data of liquid water at ambient conditions (see text): -1 suggests a bad description, +1 when it is acceptable, +2 when the description is good and +3 when the agreement is excellent (see Fig.4 for an illustration).

c- Density maximum.

Among all the anomalous properties of water, the density maximum near 4°C is certainly the most commonly known. Here again the quantum effects are not negligible since the density maximum shifts perceptibly in temperature according to the considered isotopic water (from 4°C for H_2O to 11.2°C for D_2O , and 13.4°C for T_2O , see [72]). Correspondingly the value of the density maximum decreases very slightly with the sequence $H_2O > D_2O > T_2O$ which indicates an enhancement of the hydrogen bond network. A number of simulation works [46,53,55-57,102-106] have been devoted to the localization of the density maximum (if any). The results of these studies and the experimental data are reported in Fig.6. One sees that the results are potential dependent, some models exhibiting a density maximum in the supercooled region (e.g. SPC/E [103], TIP4P [104], DEC [57], SPC/HW [56]) whereas some others are more realistic (e.g. PPC [46], TIP5P [55], TIP4P/FQ [106], TIP4P/BSV [105], NCF [53]). However in the framework of a classical calculation the target value for the density maximum is likely around 14°C (13.4°C for T_2O) and not 4°C as it is currently accepted in simulation studies (a noticeable exception is the SPC/HW model [56]).

specially designed for D_2O). Notice also that a few models of the literature show any density maximum (e.g. SPC [104], TIP3P [104], NEMO [38b]), the density increasing monotonically when the temperature is decreasing. Finally all the models analysed in this section exhibit a systematic trend namely, the density decreases too quickly when the temperature is raised above room temperature. This implies that the density of the liquid along the saturation curve will be systematically underestimated with respect to the behaviour of real water.

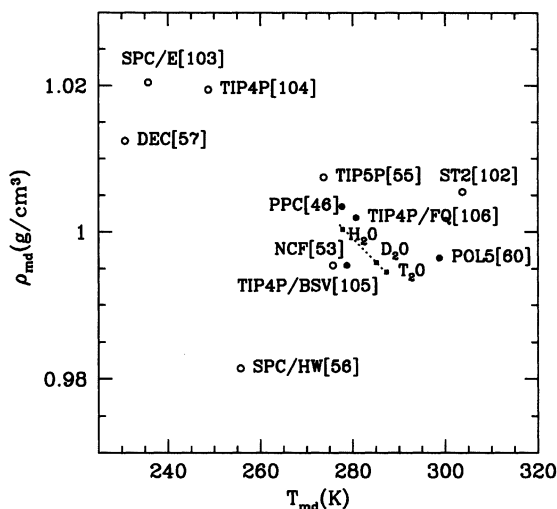


Figure 6. Temperature of maximum density predicted by a number of models (references are indicated in square bracket): circles (nonpolarizable models) and full dots (polarizable models). Values for H_2O , D_2O and T_2O are indicated along the dotted line which is used as a guideline.

d- Critical parameters.

Due to the presence of hydrogen bonds, water shows a high critical temperature ($T_C^{H_2O} \approx 647.1K$, Ref.[107]), the isotope effect being not completely negligible ($T_C^{D_2O} \approx 643.8K$, Ref.[107]). The evaluation of the liquid-vapour coexistence curve and the critical parameters

of water models started at the end of the eighties [67,69], and became an important test of validation. There are essentially three ways to locate the critical point by computer simulation. The simplest but very tedious way consists to perform a series of MD or MC calculations at different state points distributed all over the expected region of the phase diagram. In using an analytical equation of state, a least-square fitting of the points permits to locate the critical point (e.g. in [108]). The accuracy of the results will depend crucially on the number of points really evaluated, the statistical uncertainties and the flexibility of the fitting function. A more elegant method is to ensure via the Gibbs ensemble [109] the equilibrium between a vapour phase and a liquid phase. Although this method is not free from uncertainties (especially close to the critical point) it is the most commonly used for water. Finally, the direct method consists to perform a MD calculation of the liquid-vapour equilibrium in treating explicitly the liquid-vapour interface [110], the molecules migrating freely from one phase to the other during the simulation. All three methods have been used and they lead to very similar results, as expected (for SPC/E see [108,111,112]).

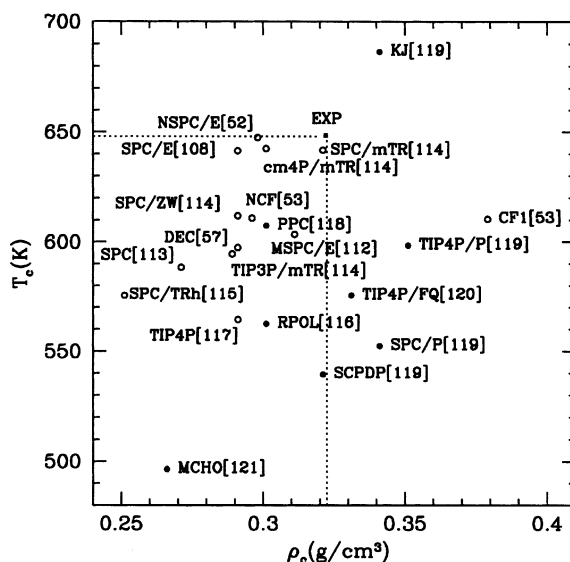


Figure 7. Critical point of simulated water : circles (nonpolarizable models) and full dots (polarizable models). The experimental critical point indicated by EXP is the one for light water.

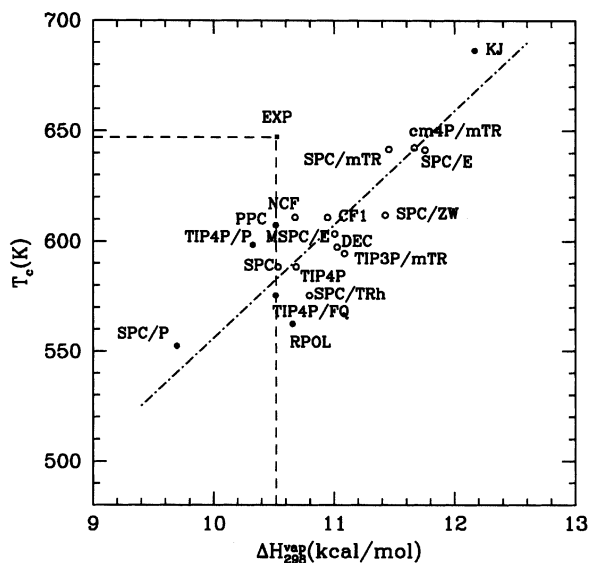


Figure 8. Critical temperature versus heat of vaporization at room temperature for the models presented in Fig.7. The dashed-dotted curve is just a guideline for the eyes. For a better viewing the MCHO model [121] is absent from this figure because it is characterized by a low critical temperature (495K) and a weak heat of vaporization (around 8.0 kcal/mol due to a strong overestimation of the liquid pressure). Nevertheless these latter values fit well with the above correlation.

In Fig. 7 are collected, as exhaustively as possible, the critical parameters (T_c, ρ_c) associated with different interaction potentials for water. The results obtained with polarizable models are indicated by full dots whereas those obtained with nonpolarizable models are represented by circles. Notice that the statistical uncertainties are of the order of $\pm 15\text{K}$ for T_c and $\pm 0.03\text{ g/cm}^3$ for ρ_c , respectively. The aimed critical parameters are those for light water, considering that the isotope effects are well within the simulation uncertainties (the critical parameters of an hypothetical classical water should lie around $T_c \approx 642\text{K}$ and $\rho_c \approx 0.32\text{ g/cm}^3$). The calculated points are scattered over a rather large region and the general

tendency is an underestimation of the critical temperature (with one exception, the KJ model [42,119]). Nevertheless a few models are closer to the critical point of real water than others (e.g. SPC/E [108], NSPC/E [52], cm4P/mTR [114], SPC/mTR [114]). More astonishing is that polarizable models are not better than nonpolarizable models in spite of their more rigorous way to treat the polarization effects. In order to find some clues to understand the above puzzling data we have redrawn the critical temperature of each model as a function of its heat of vaporization at room temperature. The results are shown in Fig.8. A net correlation between T_C and ΔH_{vap} shows up in the figure and so whatever is the kind of potential (polarizable or not). This is expected if one remembers that in mean field theories the critical temperature is related to the magnitude of the interaction energy in the liquid near the melting point (this explains why the critical temperature increases strongly when going from van der Waals to polar and ionic fluids). Nevertheless it is noteworthy first, that the correlation (see the dotted line in Fig.8) misses the experimental point (647 K and 10.5 kcal/mol for H_2O) by a significant amount (underestimation of T_C) and next, that the models which come close to the true critical temperature (e.g. SPC/E [108], SPC/mTR [114], cm4P/mTR [114]) overestimate the heat of vaporization by roughly 1.5 kcal/mol. These results suggest that something is lacking in the way to develop empirical potentials and particularly when it is the question to treat explicitly the polarization effects. Moreover the attempts made to improve the description of the liquid-vapour coexistence curve by re-parametrizing or by modifying somewhat the existing models (e.g. NSPC/E [52], MSPC/E [112]) are not successful since generally they diminish the agreement originally obtained at ambient conditions with these models.

e-Dielectric constant.

The high dielectric constant of liquid water ($\epsilon_{H_2O}=78.4$ and $\epsilon_{D_2O}=78.1$ at 298K and 1 bar [122]) is an important property that a microscopic model for water must reproduce to be credible. Unfortunately the evaluation of the dielectric constant by computer simulation (MD) comes up against two difficulties . First, it is a slowly converging quantity near ambient conditions [123] and next, its value depends on the manner the long range interactions are taken into account (Ewald sum or reaction field), even though the theoretical basis for the calculations are well established [20]. In this context we have chosen to compare the simulation results performed in the framework of periodic boundary conditions with Ewald summation (the reaction field method is more uncertain and tends to give a slightly smaller value for ϵ , see [124]). The results of the literature obtained at ambient conditions with polarizable (full dots) and nonpolarizable (circles) models are collected in Fig.9 as function of the dipole moment in the liquid phase (see Table I for μ_l), following the suggestion made by Sprik some years ago [41]. Although the points are scattered over a large region and that the statistical uncertainties are significant ($\approx \pm 10\%$ but this is difficult to assess, see for example the compilation data for SPC/E in [125]), it is clear that, on average, larger the dipole higher the dielectric constant. In fact, the results are distributed over two distinct regions, according

to the type of potential used. More precisely, the polarizable models tend to overestimate the dielectric constant while the nonpolarizable models tend to underestimate it, even if some of them are quite successful (e.g. CF [24d], TIP5P [55], SPC/F [75], WK [41], PPC [46], TIP4P/FQ [47]). Thus a rapid look at the Fig.9 could suggest that a good model for water should exhibit a dipole moment around 2.4D to reproduce accurately at once the value of the dielectric constant and the other properties of water. Unfortunately things are not so simple as we will see in the following.

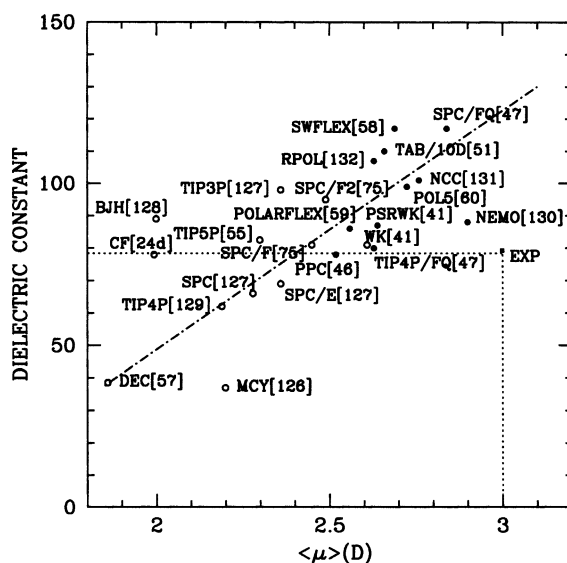


Figure 9. Dielectric constant of a number of models at room temperature as function of the average dipole moment in the liquid phase (see also Table): circles (nonpolarizable models) and full dots (polarizable models). For polarizable models $\langle \mu \rangle$ is evaluated from $\sqrt{\langle (m+p)^2 \rangle}$ where m is the permanent dipole moment and p is the induced one. The dashed-dotted line is just a guide for the eyes, the horizontal dotted line is the experimental value of ϵ for light water and the vertical dotted line located at $\langle \mu \rangle = 3.0$ D is the upper limit value expected for real water (the true value is likely somewhere between 2.6 and 3.0 D, see the text).

A piece of information is given by the analysis of the results obtained via the nonpolarizable models. It may seem astonishing that the CF model [24d] and the WK model [33] both lead to $\epsilon \approx 80$ when their respective dipole moment (rigid) are very different (2.0D for CF and 2.6D for WK, respectively). Actually, among the empirical pair potentials, the CF model is peculiar because it uses the dipole moment of the gaseous phase (the small enhancement from 1.85D to 2.0D coming essentially from the narrowing of the HOH angle in the liquid) but supplemented by an ad hoc short range attractive interaction to ensure a tetracoordination in the liquid at room temperature (see [24b]). On the contrary with the WK model the water structure is realized solely by the use of an enhanced dipole of 2.6D, a common feature to many models (e.g. TIP4P, SPC,...). Thus, although the two aforementioned models exhibits the same dielectric constant, they must differ significantly for each other in some way. Another example of unexpected behaviour is given by TIP3P and SPC/E which have the same enhanced dipole moment (2.35D) but show a very different dielectric constant (≈ 68 for SPC/E and ≈ 97 for TIP3P, see [127]). A detailed analysis [127] has shown that a different HOH bond angle in the two models (109.5 for SPC/E, 104.5 for TIP3P) is responsible of these results.

In order to be more quantitative we introduce the definition of the dielectric constant which is used when performing a MD simulation with periodic boundary conditions and Ewald summation [133],

$$\epsilon - \epsilon_\infty = \frac{4\pi}{3} \frac{\langle M^2 \rangle}{V k_B T} \quad (5)$$

where \mathbf{M} is the total dipole moment of the simulation cell and ϵ_∞ is the high frequency dielectric constant (a fluctuating term $\langle M \rangle^2$ is also neglected in Eq.(5)). For models using rigid dipoles of magnitude μ_i the above relation writes

$$\epsilon - 1 = \frac{4\pi\rho}{3k_B T} \mu_i^2 g_K \quad (6)$$

where $g_K = \frac{1}{N} \langle \sum_i u_i \sum_j u_j \rangle$ is the Kirkwood factor and u_i is an unitary vector along the permanent dipole of molecule i. Hence the dielectric constant is a measure of the orientational correlations throughout the liquid ($g_K=1$ when dipoles are randomly distributed). In order to compare the nonpolarizable models of Fig.9 on the same footing we introduce the renormalized dielectric constant ϵ_R ,

$$(\epsilon_R - 1) = (\epsilon - 1) \frac{\mu_g^2}{\mu_i^2} \quad (7)$$

where $(\epsilon - 1)$ is given by Eq.6, $\mu_g (=1.85D)$ is the gas phase dipole moment, and μ_i is the effective dipole of the model under investigation. Thus ϵ_R is nothing but the dielectric constant of the model when substituting μ_i for μ_g in Eq.6. Accordingly, if all models gave

rise to the same orientational correlations (i.e. with the same g_K) then they should exhibit the same value for ϵ_R . The result of this simple substitution is shown in Fig.10. The values of ϵ_R are very scattered and no clear tendency is coming out. This means that the angular correlations differ substantially from one model to another. Moreover a good reproduction of the water dielectric constant is not necessarily the indication that the model is accurate. Actually, the dielectric constant has never been used as a target property during the fitting of the potential parameters. Consequently the fact that a model using an enhanced dipole moment reproduces the dielectric constant with accuracy must be considered as mostly coincidental. A further analysis shows that the situation is still more confusing if one emphasizes that the dielectric constant takes into account an extended orientational order which is not easily identifiable in the local structure as deduced from the pair correlation functions (see previous paragraph). For instance TIP5P [55] and DEC [57] models produce very similar local structures (the g_{ij} 's are almost identical in the two models) when their respective renormalized dielectric constant are quite different ($\epsilon_R \approx 53$ for TIP5P and ≈ 38 for DEC for a related discussion see also [127]). On the other hand, light and heavy waters have virtually the same dielectric constant, while their local structure differs in a visible way. So to assess and to improve the existing models it is important to estimate the target values for ϵ_R and μ_i , respectively.

To do that one can imagine the following procedure. Let us suppose that we have access to a set of microscopic configurations of water molecules representative of real water at ambient conditions. For instance this set could be extracted from structure data on real water in using a highly accurate reverse Monte Carlo calculations (for a presentation of the RMC see [134]). From these microscopic configurations (i.e. the translational and orientational coordinates of each molecule) one is able to evaluate the renormalized dielectric constant, ϵ_R , by assigning a rigid dipole moment of 1.85D to each molecule (see Eq.6). Next, the effective dipole moment, μ_i , can be deduced from Eq.7 knowing that $\epsilon = 78.4$ at ambient conditions. Unfortunately, such a calculation is not yet at hand even if some recent improvements in reverse Monte Carlo methods give some hope for the future [134]. An alternative way, more approximate, is based upon Eq.(5) which can be rewritten under the following form,

$$\epsilon - \epsilon_\infty = \frac{4\pi\rho}{3k_B T} \langle \mu^2 \rangle G_K \quad (8)$$

$$\text{where } G_K = \frac{\langle M^2 \rangle}{N \langle \mu^2 \rangle} \quad (9)$$

is the generalized Kirkwood factor. In the above equations, $\mu = m + p$, is the individual dipole composed of a permanent contribution (m) plus an induced dipole (p) whereas, $M = \sum_i \mu_i$, is

the sum of all individual dipoles in the liquid sample. Notice that G_K is not identical to g_K figuring in Eq.6 since it takes into account the polarization effects which are non additive and

distance dependent. However it is convenient to connect these two quantities by introducing an effective dipole moment, μ_{eff} , through the relationship

$$\langle \mu^2 \rangle G_K = \mu_{eff}^2 g_K \quad (10)$$

where the right member can be identified to the term $\mu_l^2 g_K$ figuring in Eq.6.

Just as we have defined a renormalized dielectric constant for nonpolarizable models (see Eq.(7)) we generalize this definition to polarizable models, namely

$$(\epsilon_R - 1) = (\epsilon - \epsilon_\infty) \frac{\mu_K^2}{\mu_{eff}^2} . \quad (11)$$

To evaluate ϵ_R for real water from the above relation (i.e. the value of the dielectric constant if the dipole of each molecule was rigid and equal to 1.85D, all things being equal by other respects) we have to know the value to assign to μ_{eff} . Since this value cannot be extracted directly from experiment (except the procedure evoked earlier using a reverse Monte Carlo), it can be evaluated by computer simulations by applying Eq.(10). We have performed this calculation in using simulation data of the literature for different model potentials (SPC[135], SPC/E[136], DEC[57]) and found that μ_{eff} is about 83-87% of the average dipole moment $\mu = \sqrt{\langle (m+p)^2 \rangle}$. Notice that in a different context Nyman et al. [137] found that $\mu_{eff} \approx 0.95\mu$ in comparing effective and polarizable intermolecular potentials (NEMO models). So in using the conservative value of 0.9 for the ratio μ_{eff}/μ , it remains to evaluate μ for real water. Although there is debate about the latter value, lately, several studies independent from each other evaluate μ around 2.9-3.0D. Thus a re-evaluation of the average dipole moment in hexagonal ice [138] leads to a value of 3.09A instead of the commonly used benchmark value of 2.6D [139]. To match X-ray with neutron scattering data of liquid water at ambient conditions it has been shown [77] that an average dipole moment around 2.9D is needed. Finally, an ab initio MD calculation [45b] evaluates the average dipole moment in the range 2.9-3.0D in using a refined partition scheme of the charge distribution in the liquid (notice that other partition schemes can lead to different results [140-142], see also later on for a discussion). So in assuming a value around 2.9-3.0D for the average dipole moment of liquid water, that leads to a value around 2.6-2.7D for μ_{eff} , and a renormalized dielectric constant ϵ_R ranging from 37-40. It is patent by inspecting Fig.9 and 10 that very few models succeed to come close or to reproduce the above values. Thus the effective (nonpolarizable) models exhibit, in general, a too small value of their effective dipole and a too large value of ϵ_R and when they succeed to reach the experimental value $\epsilon=78$ it is likely due to a cancellation of errors in the product $(\epsilon_R - 1)\mu_{eff}^2$ (see Eq.(7)). However, notable exceptions are the WK and the DEC models, respectively. Indeed both show a value of ϵ_R in the expected range (41 for WK [41] and 37 for DEC [57]) while the effective dipoles of the two models are quite close to the expected value for real water (2.6D for WK and 2.68D for DEC after evaluation of the induced contribution, see in [57], as compared with 2.6-2.7D by our evaluation). As for the

polarizable models, they generally overestimate to a large extent the value of the dielectric constant (see Fig.9). In fact, they overestimate the angular correlations (ϵ_R is too large see Fig.10) and their average dipole moment μ is often too small, although some models succeed to reproduce approximately the dielectric constant (e.g. PPC [46], TIP4P/FQ [47], POLARFLEX [59], NEMO [130]).

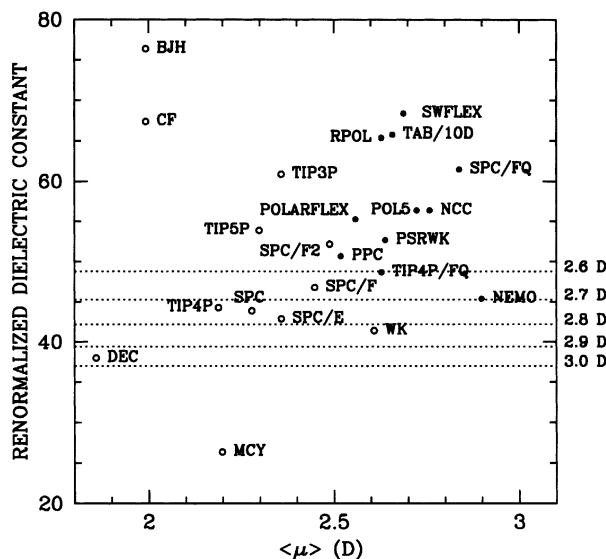


Figure 10. As Fig.9 but for the renormalized dielectric constant ϵ_R defined in Eq.7 for nonpolarizable models (where $\mu_i = \langle \mu \rangle$) and in Eq.11 for polarizable models (where $\mu_{eff} = 0.9 \langle \mu \rangle$, see text), respectively. The horizontal lines correspond to the values of ϵ_R expected for real water in assigning different values of its average dipole moment within the range 2.6-3.0D. For example if the average dipole of real water is believed to be around 2.9-3.0D then only the DEC model is able to reproduce the correct value for ϵ_R (37 in that case). In the same way if the average dipole of real water is between 2.8 and 2.9D then the WK model is relevant, and so on.

III - WHAT HAVE WE LEARNT ?

Retrospectively two main lessons can be drawn from this brief survey. The first one is that very early it was clear that a semi-quantitative reproduction of the water properties could be obtained by computer simulation in using a simple empirical intermolecular potential for water. The good compromise between simplicity and accuracy was a determining factor to popularise the simulation studies and especially in the fields where water plays a major role (ionic solutions, hydrophobicity, hydration of biological molecules,...). Nevertheless in the details we have seen that the models of the literature are not free of inaccuracies. Thus the value of their effective dipole moment is mostly inadequate to evaluate the dielectric constant. In the same way no model succeeds to reproduce at once the temperature of maximum density and the critical point of real water. Concerning this latter one, if some attempts [52,112,114] show a slight improvement it is in general to the prejudice of another property (for instance the structure near ambient conditions). More generally, the attempts made in the literature to improve the force field for simulated water lead most of the time to disappointing results. For example it has been frequently argued that the introduction of the flexibility of the molecules could improve the description of water in some ways. Actually, most of the effects on the structure, diffusivity and dielectric constant are due to a slight enhancement of the dipole moment in the liquid phase, effects which can be recovered almost completely (but not totally) by simply renormalizing the dipole of the original (rigid) model. Much more astonishing and very frustrating is the fact that the explicit introduction of the molecular polarizability does not lead to a significant improvement. In particular neither the coexistence curve nor the critical point are better described by polarizable models with respect to nonpolarizable ones in spite of a real improvement observed for the second virial coefficient (see [43b,143]), and to a lesser extent for the structure in the supercritical region [99,100]. On the other hand, the influence of the polarizability cannot be skipped when it is question of dielectric properties. However we have seen that no model succeeds to reproduce at one the magnitude of the dielectric constant and the one estimated for the average dipole moment (permanent + induced) in liquid water. Even more troublesome is that the situation does not improve systematically at higher temperatures [144] on the contrary to nonpolarizable models [145]. So something goes wrong when dealing with the polarization effects in water. In the next paragraph we will give some clues for improvement.

Despite our mixed opinion about the level of accuracy achieved by the model potentials of the literature, it must be recognized that a vast amount of information has been obtained thanks to simulation studies during the last three decades. For example one of the major advances has been to quantify the evolution of the hydrogen bond network with the thermodynamic conditions from the supercooled state [146-148] to the supercritical region [108,149] in passing by the ices [150-154]. One important point raised by these studies is that the results are generally robust in the sense that qualitatively they are not potential dependent, although it must never be overlooked that the phase diagrams associated with the models may not only differ from each other but also from the one of real water.

The fact that no model potential is able to reproduce in every details the properties of real water despite thirty years of active research leaves a taste of incompleteness. Moreover, if the ultimate goal of all this quest is to develop a force field sufficiently accurate to be really helpful, not only to understand the real nature of water but also for many other fields (from biochemistry to chemical engineering), then one has to continue the search for improvement. However, owing to the difficulties encountered in the past to improve the empirical potentials, it is justified to ask the question : is there still room for improvement ? In the following we give some clues which could suggest that the answer is yes.

IV – IN SEARCH OF IMPROVEMENT.

There is a large amount of *ab initio* calculations in the literature devoted to the study of the force field between water molecules (from the simple hydrogen-bonded dimer [155] to clusters of several molecules [156]). As discussed earlier the results are often deceptive when it is the question to describe the liquid phase, because small inaccuracies in the quantum treatment may lead to large deviation for the water properties after implementation in a MD (or MC) simulation. Although the recent progress made with density functional theory in the framework of the CPMD calculation [45,94,95,98] is quite impressive, this type of calculation will be always very time consuming, and non competitive with respect to the empirical models as soon as more realistic system size and larger time scale are needed (only a few ten of molecules during a few ps are currently simulated). Nevertheless the *ab initio* calculations are quite relevant when it is the question to tackle all the subtleties of the quantum interactions. Thus to build an accurate empirical potential for water presupposes to know all the elementary interactions which contribute to hydrogen bonding (HB), a knowledge that only the *ab initio* calculations can reveal. So in this context the following questions merit to be raised.

-Is the hypothesis of a negligible covalency in HB correct ?

Quantum mechanical calculations show that HB can be understood as the competition between the attractive interaction potential energy and the repulsive internal electronic kinetic energy of the water molecules [61]. This is because the former term can be approximated by classical electrostatic energy and the latter term by an heuristic analytical function that the empirical potentials are assumed to be well founded. Recently this picture of the hydrogen bond was challenged by an X-ray experiment measuring the Compton profile anisotropies of ordinary ice Ih [157]. In this study it was concluded that the hydrogen bond in ice is partly covalent which discards the recourse to a purely electrostatic bonding model for condensed phases (solid or liquid). However, a partial covalent character of the hydrogen bond in ice is not, *a priori*, in contradistinction with the claim of an absence of covalency in the hydrogen-bonded gas phase dimer if one considers that the O-O distance is 2.75Å in ice (and very close to that in the liquid, 2.75-2.80Å [79]) as compared to 2.98Å in the dimer [156]. The above result has had a large impact in the community and several theoretical evaluations [158,159] have been published ever since then. It occurs that the interpretation of

the Compton profile was erroneous, the ab initio calculations showing without ambiguity the antibonding character of the overlap effects in ice. So as far as we know covalency is negligible in water.

-Is the point charge approximation accurate enough to reproduce the electronic charge distribution ?

Curiously enough most of the models for water are based on a point charge description of the molecular charge distribution when it is well known since many years that the electrical potential emanating from a water molecule is much better approximated by diffuse spherical charge densities in addition to point charges on the nuclei [160,161]. As a result, the interaction energy of two molecules with overlapping charge distributions cannot be well reproduced by point multipoles, especially when the equilibrium separation of the partners is rather short (around 2.80 Å in liquid water). So clearly, these charge penetration effects have to be included in the force field for water.

-Is the choice of a Lennard-Jones repulsion-dispersion term relevant ?

Generally the repulsion-dispersion interaction between water molecules is simply accounted for by a Lennard-Jones term centered on the oxygen. The latter potential was originally designed for closed shell systems and is not particularly adapted for water. For example it is known that this term is responsible in a number of models of a too large value for the first peak of the oxygen-oxygen pair correlation function. Moreover, when one knows that the pressure of the simulated fluid is very sensitive to small changes of the dispersion interaction (a few per cent leads to variations of hundred bars), the fact that it is not possible with the LJ potential, to modulate the repulsion and the dispersion terms independently from each other, prevails the model to be accurate enough (for the lack of flexibility of the LJ potential see [52]). Actually, in quantum-mechanical calculations, the exchange-repulsion energy coming from the Pauli exclusion principle is closely related to the penetration energy between electronic clouds discussed above [162]. Thus the functional form of the repulsion energy is more adequately described by overlap integrals and gaussian functions (see e.g. in [163]) than by the too stiff $1/r^{12}$ repulsive term of the LJ potential.

-Is the charge transfer significant in HB ?

Basically there are two kinds of charge transfer (CT) mechanisms, an intramolecular one between atoms (or atom and bond) of the same molecule and an intermolecular one which may ultimately lead to ion pair formation. However, there is still debate about the role of the CT energy in water because this is not always a well defined quantity in perturbational approaches of quantum chemistry (see [164]). Sometimes the CT energy is included with the polarization mechanism in the so called induction term, while in other formalisms CT and polarization appear naturally. When the partition between intermolecular and intramolecular charge transfer can be done unambiguously it is shown that the charge flow between molecules is unimportant [140,164] whereas the intramolecular

charge redistribution becomes significant when two hydrogen-bonded molecules approach each other [165]. More precisely, as the two molecules approach in an hydrogen-bonded configuration, the oxygen charge becomes more negative and the hydrogen charges more positive, the net result being to render the two molecules more polar [165]. Notice that this enhancement of the polarity is distinct from the one attributed to dipolar polarizability.

-Why is the introduction of the polarizability so deceptive ?

To answer this question we have to reconsider the assumptions made when using polarizable models. In empirical models (e.g. SPC/P[34], PTIP4P[39], RPOL[44],...) it is assumed that the molecular polarizability is unaffected by the liquid phase and can be identified to its gas phase value ($\bar{\alpha}_w = 1.45 \text{ \AA}^3$ [166]). Recently several attempts have been done by quantum chemical approach to evaluate the perturbation generated by the condensed phase on electric properties of the water molecule and especially on its molecular polarizability. Depending on the method used to treat the solvent around the probe molecule, the results of these calculations [167-170] show generally a small reduction of the mean polarizability in the liquid as compared with the gas phase value (from 10%-15% [167,168], except in [169] where a very slight increase is observed). In addition when a decrease of the polarizability is observed, this reduction takes place essentially in the plane of the molecule (along the hydrogen bonds) and is caused by the cumulative contribution of the exchange, charge transfer and polarization interactions. Nevertheless, whether this reduction is real or not, it seems to have only a small effect on the average dipole moment which is always found strongly enhanced by the presence of the surrounding medium (in the above studies, $\mu \approx 2.65\text{--}2.70D$). To tell the truth, the variety of the quantum methods used in the literature to evaluate the average dipole moment of a water molecule in condensed phase produces a large dispersion of the results (e.g. 2.33D in [167], 2.43 D in [141], 2.65 D in [168] , 2.70D in [169], 2.95D in [45b]) and renders any definitive conclusion very risky. So in this context we think that the use of the gas phase value for $\bar{\alpha}_w$ when evaluating the polarization effects by computer simulation is not the primary source of uncertainty even if one has to keep in mind the above discussion.

A priori more problematic is the recourse to the point polarizable dipole approximation in polarizable models. As a matter of fact, it is frequently emphasized that the point dipole approximation could be violated at the short distances involved by hydrogen bonding and could lead to an overpolarization (or even a polarization catastrophe). This hypothesis was recently challenged [171] by an analysis based upon the comparison between a classical calculation using the point dipole approximation and performed on a water dimer modelled by an empirical model (TIP4P like) and a quantum evaluation (MP4 level) of the total dipole moment of the dimer. This study shows that both calculations are in good agreement with each other and that the point dipole approximation seems to be fairly adequate even at the shortest distance probed in simulations of liquid water (i.e. for $R_{O..H} \approx 1.5\text{\AA}$). However the conclusion is based upon a limited range of configurations (only one orientation

of the molecules is investigated) and the induced contribution to the total dipole is generally small except at distances of interest for the hydrogen bond where precisely one begins to notice some significant deviations between quantum and classical calculations. So our conclusion will be more conservative in emphasizing that this work does not show any clear failure of the point dipole approximation. Anyhow, even if this latter approximation is accurate, the value of the induced dipole moment will be relevant only if the electric field emanating from the neighboring molecules is adequately described by the model potential. But there is a serious doubt about the ability of models using point charges to reproduce the water electric potential (see the first point of the above discussion and Refs.[160,161]). In fact, as discussed earlier, the potential parameters are generally fitted on thermodynamic and structural properties of the liquid state and the resulting electrical potential is only a by product of this fitting.

In summary, with our present knowledge and in a first approximation, it is not necessary to question neither the point dipole approximation nor the use of the gas phase value of the dipolar polarizability when dealing with polarizable models. On the other hand it is not certain that the electric field produced by the charge distribution of the model is accurate enough to give relevant results for the induced dipole. Furthermore the latter polarization mechanism is not the only one which contributes to the dipole moment in the liquid phase. The intramolecular charge transfer induced by the hydrogen bond has also to be taken into account (see the corresponding point of this discussion). Finally, let us emphasize that because of the variety of the theoretical approaches in quantum calculations (supermolecules, perturbational, DFT) it is difficult to compare without ambiguity the results coming from different methods, a situation which renders problematic the implementation of induction effects in empirical models.

-How to deal with quantum effects ?

As evoked previously light (H_2O) and heavy (D_2O) water are not two identical liquids due to quantum delocalization (see section II.b). Although relatively small (a few percent at room temperature depending on the investigated quantity [72,76,83]), their differences are conceptually important for two reasons. First, this nonequivalence has important consequences for example in biology (D_2O is toxic [172] and affects the stability of proteins [173]). Next, the interaction potentials for water are generally implemented in classical simulation codes which do not make the difference between isotopic waters. So the comparison between classical simulation results and experimental data may be questionable in the details. A more rigorous procedure would be to develop a model potential specially designed for classical simulation and whose the parameters would be fitted to reproduce the properties of the most classical water that we know, namely T_2O . The next step would be to implement the resulting force field in a simulation code for H_2O incorporating path integral technique [70] in order to account for quantum delocalisation (notice that this procedure can

also be implemented in CPMD calculations [174]). The ultimate goal is to produce a model potential capable of reproducing by simulation all the properties of the isotopic waters.

-What about transferability ?

Although the importance of this topic might deserve an entire review article, for obvious reasons we will restrict our discussion to a few comments. In dealing with aqueous solutions it is usual to distinguish hydrophobic solutes (e.g. rare gases, CO_2 , O_2 , CH_4 , ...) for which the solute-water interactions are weak (i.e. much smaller than the water-water interactions), from hydrophilic solutes (e.g. ions, polar molecules) for which the solute-water interactions are stronger or comparable to the water-water interactions [175]. Obviously, all a gradation of behaviour exists in between these two categories (e.g. benzene). One of the characteristics of the hydrophobic solutes is their low solubility in water [176], and many computer studies have been devoted to the determination of their solubility at infinite dilution (or Henry constant). For a number of simple hydrophobic solutes (rare gases, methane) the simulations using an empirical model for water (e.g. SPC/E) and a simple Lennard-Jones potential for the solute (the solute-water potential parameters being generally deduced from the Lorentz-Berthelot combining rules) are in good agreement with experimental data over a large range of temperature (e.g. [177]). In that case the transferability of the water model seems to be established. This conclusion is not surprising if one recalls that the hydrophobic hydration characterizes essentially the property of water to accommodate a hard sphere, a mechanism which involves only the force field of water. However when it is the question to investigate the interaction between two hydrophobic solutes in water [178,179] and the phase behaviour of these solutes (e.g. alkanes) in aqueous solution, the simulation results become less accurate and especially when the size of the solute increases (e.g. [180,181]). In this case the solute-water interactions may become important to stabilize (or destabilize) solute-solute association, a situation where transferability begins to be questionable.

When the solute under investigation shows an hydrophilic character, the solute-water interactions becomes preponderant for hydration properties. For example, a recent simulation study [182] of tetrahydrofuran-water mixtures (THF is a polar molecule related to the ribose and deoxyribose sugars of nucleic acids) has shown that the phase diagram associated with these mixtures is extremely sensitive to the THF-water interactions. Thus the use of the TIP4P model for water with a model for THF originally designed for the pure liquid is unable to reproduce the liquid-liquid coexistence curve observed for the mixture (the experimental phase diagram is characterized by a region of immiscibility delimited by a closed loop in the concentration-temperature representation). To recover the experimental behaviour it is essential to modify the charge distribution of THF molecules when they interact with the water molecules. This example, among others, illustrates the limitation of empirical models whose the effective charges are scaled for a given environment. Of course it is often possible to re-parametrize carefully the potential parameters but this is a tedious process (e.g. in [183] for the hydration of amines). The use of polarizable models [184] seems more promising since it can take into account, at least partly, the specificity of the solute-

water interaction. Nevertheless, even in this framework, there is no guarantee of success if the other terms of the force field are not optimized for cross interactions (e.g. [184]). For strong solute-water interactions as encountered with simple ions (Li^+ , Na^+ , Cl^- , ..) or charged groups, the recourse to polarizable models becomes unavoidable [185]. But here also, other mechanisms as for example the charge transfer may be important [186], and the very notion of a transferable model is becoming questionable. In this context it is understandable that some authors have a more pragmatic approach and propose a water model specifically developed for simulations of aqueous solutions (for hydration of biological macromolecules see [187]), giving up all idea of transferability.

V – CONCLUSION.

In spite of thirty years of computer simulations on water, one may have a mixed feeling about what have been accomplished. On the one hand, one is impressed by the amount of works which has been published and the sum of information concerning the modelling of water. The fact that it is possible to describe the force field of water by simple empirical models easy to implement in a simulation code is not for nothing in the success encountered by simulation studies in many fields. On the other hand, one has a taste of incompleteness if one considers that not a water model available in the literature is able to reproduce with a great accuracy all the water properties. Despite many efforts to improve this situation, very few significant progress can be asserted. In return, this difficulty demonstrates the extreme complexity of the water force field in the details, and their influence on the macroscopic properties of the condensed phase.

In the last part of this review we have attempted to give some guidance for improvement. In brief we believe that the joint introduction of diffuse charges, polarization and charge transfer plus an optimized repulsion-dispersion term is a prerequisite for developing a better model. Thus the DEC model [57] which appeals to diffuse charges without resorting to an enhanced dipole moment (the gas phase value is used) supports this view. In the same way the recent attempts made to combine fluctuating charges (mimicking charge transfer) and polarizable dipoles (POL5 [60]) are quite interesting in the above perspective. In the meantime it will be necessary to pursue the investigations by *ab initio* methods and especially by CPMD calculation where the introduction of new exchange-correlation functionals [94,188] could lead to significant improvements. Finally, from the experimental point of view, the accuracy of the structure data coming from X-ray and neutron scattering experiments leaves yet to be desired and especially what concerns the non equivalence between light and heavy water. We may reasonably hope that in a near future new experimental investigations should help to clarify the situation. This is the price to pay for developing a better potential for water.

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