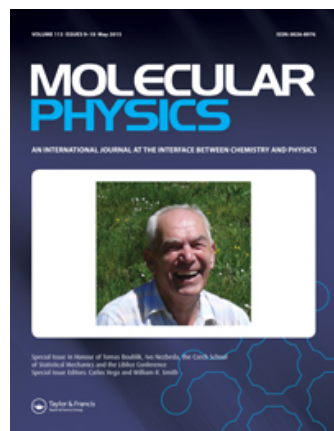


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INVITED ARTICLE

Water: one molecule, two surfaces, one mistake

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In order to rigorously evaluate the energy and dipole moment of a certain configuration of molecules, one needs to solve the Schrödinger equation. Repeating this for many different configurations allows one to determine the potential energy surface (PES) and the dipole moment surface (DMS). Since the early days of computer simulation, it has been implicitly accepted that for empirical potentials the charges used to fit the PES should also be used to describe the DMS. This is a mistake. Partial charges are not observable magnitudes. They should be regarded as adjustable fitting parameters. Optimal values used to describe the PES are not necessarily the best to describe the DMS. One could use two fits: one for the PES and the other for the DMS. This is a common practice in the quantum chemistry community, but not used so often by the community performing computer simulations. This idea affects all types of modelling of water (with the exception of *ab initio* calculations) from coarse-grained to non-polarisable and polarisable models. We anticipate that an area that will benefit dramatically from having both, a good PES and a good DMS, is the modelling of water in the presence of electric fields.

Keywords: computer simulation; water; force fields; dielectric constant; electric field; potential energy surface

1. Introduction

Water is a simple molecule: just two hydrogens and one oxygen. Still it has a fascinating behaviour related to the possibility of forming tetrahedral hydrogen-bonded network structures [1–7]. The hydrogen bond, a directional and rather strong intermolecular interaction (when compared to van der Waals forces), is responsible for the special properties of water. Moreover, the hydrogen atoms are light; therefore, nuclear quantum effects are important. Understanding the properties of water from a molecular point of view is certainly important. Computer simulations can be useful for that purpose, and they started with the seminal papers of Barker and Watts [8] in 1969 and of Rahman and Stillinger [9] in 1971. Since the seminal paper of Bernal and Fowler [10,11], water is often described by a Lennard–Jones (LJ) centre and several charges. The model of Bernal and Fowler was modified by Jorgensen *et al.* [12] to obtain the popular TIP4P model. Abascal and Vega [13] have shown that the parameters of the TIP4P can be modified to yield a new model, TIP4P/2005. TIP4P/2005 is a rigid non-polarisable model and one may wonder how far can one go in the description of water with such a simple model. Recently, we have calculated a number of properties for this model and compared them to experimental results [14]. The comparison has been extended to other popular rigid non-polarisable water models such as SPC/E [15], TIP3P [12] and TIP5P [16]. These are also rigid non-polarisable models and they differ from TIP4P/2005 in the way the

partial charges have been arranged [14,17]. The comparison revealed some useful information. Not all water models are equally successful in describing the experimental properties. From the considered models, TIP4P/2005 provided the best results. However, since the model is rigid and non-polarisable, it cannot describe all the experimental properties of water. Thus, our feeling is that TIP4P/2005 represents the limit of the description of water that can be achieved by using rigid non-polarisable models. It is a decent model, but to go beyond that, new physical features (and not simply new parameter sets) must be incorporated.

We found a property with a somewhat surprising behaviour: the dielectric constant. We found two puzzles while considering the dielectric constant of water. First, certain models were able to describe the dielectric constant of water at room temperature and pressure. This is the case of TIP3P [12] and TIP5P [16]. However, for some other models, the dielectric constant was low when compared to experiment increasing in the order TIP4P, TIP4P/2005, SPC [18] and SPC/E [15]. Second, Rick and co-workers [19–22] and Lindberg and Wang [23] and ourselves [24–26] computed the dielectric constant of ice Ih. The surprising result was that, for this phase, all these water models predicted a dielectric constant value lower than the experimental one, sometimes by a factor of two. The first reaction to explain these results is to assign the discrepancy to the approximate description of the intermolecular potential. This is reasonable, but still this hypothesis should explain why all models

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fail in describing the dielectric constant of ice Ih. Experimentally, the dielectric constants of ice Ih and water at the melting point are quite similar, that of the solid phase being slightly higher [27]. The importance of this experimental finding may not have been fully appreciated, and may be quite relevant, since it may affect the way we approach the modelling of water. At the melting point, the tetrahedral order of liquid water is quite high (that would explain the maximum in density), and it is even difficult to find order parameters (required for nucleation studies [28,29]) that distinguish between liquid-like and solid-like arrangements around a central molecule [30–33]. If ice Ih and water are quite similar at the melting point, it is difficult to explain why all models fail in describing the dielectric constant of ice Ih. We found that, for TIP4P models, the dielectric constant of ice Ih was similar to that of liquid water (and this is in agreement with the experiment), whereas the predicted value was too low for both phases when compared to experiments [25]. At this point, we proposed in 2011 an explanation as to why TIP4P/2005 was unable to reproduce the dielectric constant of water related to the failure of the model to describe the ‘real’ water dipole moment in condensed phases. Not surprisingly, the title of our 2011 paper was ‘The dielectric constant of water and ices: a lesson about water interactions’ [25]. This is probably true, but in this paper, we will present some evidence illustrating that maybe we did not obtain the ultimate consequences of the ‘lesson’.

2. ABCD in the modelling of water

Let us consider a system with N molecules of water. Since each water molecule has three atoms, we need to define the position of the $3N$ atoms of the system, \mathbf{R}^{3N} . $E^0(\mathbf{R}^{3N})$ (which defines the potential energy surface, PES) is the energy of the system. We shall define the intermolecular potential energy U as follows:

$$U(\mathbf{R}^{3N}) = E^0(\mathbf{R}^{3N}) - NE_{\text{H}_2\text{O}}^0. \quad (1)$$

where we have taken zero of energies as the energy of a system of N isolated water molecules ($NE_{\text{H}_2\text{O}}^0$). The superscript zero indicates that there is no electric field present.

It is useful for pedagogical reasons to classify the different approaches in the modelling of water into four groups (or teams) which we will label as A, B, C and D. They differ in the way U is obtained. In Table 1, the main four treatments in the modelling of water are presented.

If you solve the Schrödinger equation to obtain E^0 , then your treatment is of type A or B. In group A, the motion of the nuclei is also treated from a quantum perspective. In group B, one uses classical statistical mechanics to describe the motion of the nuclei on the PES (i.e. the nuclei are regarded as classical objects). Approach B is often denoted as Car–Parrinello simulation [34] and approach A as

Table 1. Different approaches in the modeling of water.

	A	B	C	D
Electrons	Electronic structure calculations	Electronic structure calculations	Analytical expression for $E^0(\mathbf{R}^{3N})$	Analytical expression for $E^0(\mathbf{R}^{3N})$
	+	+	+	+
Nuclei	Path integral simulations	Classical statistical mechanics	Path integral simulations	Classical statistical mechanics

‘full quantum’. Within classical statistical mechanics, the positions of the nuclei are governed by

$$-\nabla_{\mathbf{R}_i}(E^0(\mathbf{R}^{3N})) = m_i \frac{d^2 \mathbf{R}_i}{dt^2}, \quad (2)$$

$$p(\mathbf{R}^{3N}) \propto e^{-\beta E^0(\mathbf{R}^{3N})}, \quad (3)$$

where the first expression (Newton’s law) is to be used in molecular dynamics (MD) simulations and the second one in Monte Carlo (MC) simulations, being $p(\mathbf{R}^{3N})$ the probability of having a certain configuration of the nuclei. The approach A is described in [35] and some examples for water within the approach B can be found in [36,37]. Notice that in approaches A and B, the energy is obtained ‘on the fly’ for each configuration either by solving the Schrödinger equation or by performing density functional theory (DFT) calculations.

Teams C and D use analytical expressions for the PES. These analytical expressions can be obtained in two completely different ways. The analytical expressions can be obtained by fitting *ab initio* results obtained for water clusters and/or liquid configurations. We shall denote this type of potentials as analytical *ab initio* potentials. The second possibility is to propose an analytical expression for the potential with some free parameters that can be chosen to reproduce some selected thermodynamic properties. We shall denote this second class as empirical potentials. Thermodynamic properties (i.e. enthalpy, Gibbs free energy, etc.) are functionals of $U(\mathbf{R}^{3N})$. One could state that in analytical *ab initio* potentials, the parameters of the fit are determined to reproduce $U(\mathbf{R}^{3N})$, whereas in empirical potentials, the parameters are determined to reproduce certain functionals of $U(\mathbf{R}^{3N})$ (i.e. density, enthalpy, diffusion coefficients).

It is important when developing analytical potentials that ‘representative configurations’ of the system are selected for the fit. By representative we mean configurations with a reasonable statistical occurrence (i.e. with a non-negligible value of their Boltzmann factor). Thus, the target, in principle, is not to reproduce the energy of any arbitrary configuration (including, for instance, configurations of very high energy where the water molecules overlap significantly), but rather properly describe the energy of those configurations of the \mathbf{R}^{3N} space which have a reasonable

probability of being found. Obviously, the value of the potential parameters may depend on the configurations used for the fit either explicitly as when using *ab initio* inspired potentials, or implicitly as when using empirical potentials, where the properties and the selected thermodynamic states determine implicitly which configurations are entering in the fit.

When the description of the intermolecular energy is done with an analytical expression and nuclear quantum effects are used to describe the motion of the nuclei, your approach is of type C [38–46]. Simulations of analytical *ab initio* potentials should be performed within the framework C, since when your PES was designed to reproduce *ab initio* results, you should expect to reproduce water properties only when nuclear quantum effects are included. In team D, an analytical expression is used to describe the PES and the nuclear quantum effects are neglected (i.e. it is assumed that the motion of the nuclei can be described by classical statistical mechanics). In the case of empirical potentials, you could use approach C or D. In fact, you could determine the potential parameters to reproduce the experimental properties when nuclear quantum effects are included or you could determine the parameters of the potential to reproduce the experimental properties within classical simulations. It is important to point out that if one has a good empirical potential model of water of type D (i.e. one using classical statistical mechanics) and one tries to use it within the formalism of type C (i.e. including nuclear quantum effects), the model will not work. This is because then, nuclear quantum effects will be counted twice, once through the fitting to experimental properties and the other through the use of quantum simulations [45,46]. Group D is by far the most popular. For this reason, it is useful to classify the types of models that are often found within this family of potentials.

1. *Ab initio* potentials. For these models, analytical expressions are used to reproduce either high-level *ab initio* results for small water clusters (TTM2-F [47], TTM3-F [48], CCpol23 [49,50]), or DFT results of condensed matter (neural network potentials [51]) or both as for the MB-pol model [52]. Certainly, quantum calculations are performed to develop these potentials. However, instead of solving the Schrödinger equation on the fly to determine the energy of each configuration (as you would do in teams A and B), here you assume that the fit used to reproduce the results of some water clusters and/or some selected configurations, can be used for any configuration. Obviously, assuming that a good fit obtained for a small cluster water should also work in condensed matter is an approximation. In the case of neural network potentials [51,53,54], your results are obtained for condensed matter, but it is not clear if a neural network trained at a certain density and phase will also work for other densities and/or phases.
2. Empirical potentials. The family of empirical potentials is large and several sub-classes could be identified. Our classification of empirical models is based on the way electrostatic interactions are described.
 - (a) Coarse-grained models. The term coarse grained is typically used for potential models that do not use partial charges in the description of the PES [55]. Examples are the primitive model of water of Kolafa and Nezbeda [56–58] and its modifications often used in combination with Wertheim's statistical associating fluid theory (SAFT) [59–65], the Mercedes Benz model [66], the mW model [67] and the ELectrostatics-BASed (ELBA) model [68]. This last model does not have partial charges but incorporates an ideal dipole moment on the oxygen atom.
 - (b) Non-polarisable models. In these models, an LJ centre (or similar [69]) is located on the position of the oxygen atom. Models differ in the number and location of the partial charges: three charges located on the atoms (TIP3P, SPC), three charges with one charge out of the atom positions (TIP4P family), four charges [16] (TIP5P) or five charges [70] (NvDE). In these models, the magnitude of the partial charges does not depend on the local environment.
 - (c) Polarisable models. These are similar to the non-polarisable models, but now the partial charges (or the molecular dipole moments) depend on the environment [71–76]. Typically polarisability is introduced either by allowing each molecule to develop an induced dipole moment in response to the local electric field or by using the concept of charge transfer where part of the charge of one molecule (atom) is transferred to the neighbouring molecules (atoms) [77]. Strictly speaking, polarisable models are not analytical potentials (in a mathematical sense) as the energy must be obtained through an iterative process. However, they are only one order of magnitude, more expensive (from a computational point of view) than non-polarisable models, in contrast to quantum calculations of type A or B which are about four orders of magnitude slower. For this reason, we have included polarisable potentials in team D. Notice also that some of the *ab initio* potentials are polarisable.

Within each type of potentials described in group D (i.e. analytical potentials), one could find two subsets,

one in which the molecules are treated as rigid entities (rigid models) and those in which flexibility is incorporated (flexible models).

Non-polarisable models are by far the most used in the modelling of water. For these models, $U(\mathbf{R}^{3N})$ is usually described as

$$U(\mathbf{R}^{3N}) \simeq \sum_{i=1}^{i=N-1} \sum_{j=i+1}^{j=N} 4\epsilon_{\text{LJ}}[(\sigma/R_{ij})^{12} - (\sigma/R_{ij})^6] + \sum_{i=1}^{i=N-1} \sum_{j=i+1}^{j=N} \sum_{\alpha} \sum_{\beta} \frac{q_{i\alpha} q_{j\beta}}{4\pi\epsilon_0 R_{i\alpha j\beta}}, \quad (4)$$

where the indices α , β run over the partial charges of each molecule, and there is only one LJ centre per molecule (located on the oxygen atom). One of the main conclusions of the last 20 years is that empirical non-polarisable potentials such as SPC/E, TIP4P-Ew [78] or TIP4P/2005 [13] which overestimate the vapourisation enthalpy ΔH_v provide a better description of water than those that try to reproduce it. The vapourisation enthalpy can be estimated (when far from the critical point) as $\Delta H_v = -\langle U_l \rangle + nRT$, where $\langle U_l \rangle$ is the residual internal energy of the liquid and n is the number of moles. For this reason, models as SPC/E, TIP4P-Ew and TIP4P/2005 underestimate $\langle U_l \rangle$ and only get closer values to experiment for ΔH_v when an ‘ad hoc’ term, the polarisation energy, is added [15,79]. Why models that do not reproduce the vapourisation enthalpy provide a better description of water properties? A possible explanation is that these models try to reproduce the gradient of the intermolecular energy (i.e. the forces) rather than the absolute values of the intermolecular energy, providing an overall better description of the landscape for the liquid phase of the intermolecular energy. A graphical summary of this idea is presented in Figure 1. In the sketch of this figure, it is qualitatively illustrated how a potential may describe well U but not its gradient (as for instance TIP4P), whereas another model may describe reasonably well the gradient but not U (as, for instance, TIP4P/2005). It is now clear that for non-polarisable models of water models, it is not possible to simultaneously reproduce both U and the gradient of U , and that a better water model is obtained when reproducing the gradient rather than the energy. If your description of the gradient of U is reasonable, then the configurations generated along the Markov chain of the MC run or along the trajectory in the MD run, would indeed be representative of those appearing in real water. Having values of U in the liquid phase, shifted by a constant relative to the exact ones, will not influence the relative probabilities between two different configurations in this phase since it is proportional to the Boltzmann factor of their energy difference, and this difference remains unchanged if the energy of both configurations is shifted by a constant. The drawback is that this shift would be much smaller in the gas phase. Therefore, liquid–vapour co-existence properties (vapour pressures,

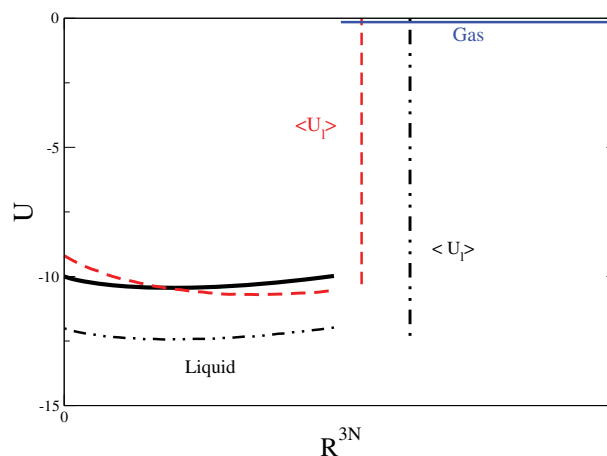


Figure 1. Sketch of the PES as obtained from first principles for the liquid (configurations on the left-hand side, black solid line) and vapour (configurations on the right hand side, blue solid line). Certainly R^{3N} is multidimensional; therefore, our presentation as a one-dimensional object (x -axis) is only a sketch. Red dashed lines: sketch of the PES for a model reproducing the values of $\langle U_l \rangle$ (the average residual internal energy of the liquid) and the vapourisation enthalpy ΔH_v , but not the gradient of U , as TIP4P. Black dashed–dotted lines: sketch of a model reproducing the gradient of U but neither $\langle U_l \rangle$ nor ΔH_v as TIP4P/2005. Vertical lines represent the value of $\langle U_l \rangle$ which is one of the main contributions to the vapourisation enthalpy.

vapourisation enthalpies) will be affected reflecting that the relative probabilities between configurations of these two phases will not be described properly.

After presenting the different options (ABCD) in the modelling of water there is an interesting question: should one use the approach A, or B, or C or D when modelling water? Obviously, you should use the approach that is more convenient for the problem you have in mind. Therefore, there is no unique answer to this question. Depending on the problem it may be more convenient to use the approach A, B, C or D. For instance, it is difficult to think how empirical potentials can contribute to problems where water is involved in chemical reactions, or when computing electronic spectra. At the same time, it is difficult that approach A or B can attack problems involving hundreds or thousands of water molecules or very long times (for instance, nucleation and supercooled water [80–82] or the conformational changes in proteins). Our point of view is that the four approaches are complementary. In fact, it is becoming more common now to be at conferences about water where scientists of the four types of modelling are presenting their results. These four approaches in the modelling of water will continue in the future.

Another different question is as follows: which approach provides an overall better description of water after ignoring chemical reactions and electronic spectra? In principle, results of approach A should be the only ones able to describe all the experimental properties of water. The

Table 2. Scoring summary of the TIP4P/2005 (see Table IV of [17] for further details) and surface (PES, DMS or both) required to determine the property. Strictly speaking for the dielectric constant, the PS is also needed. However, the contribution of this surface to the final value of the dielectric constant is small (of about 1% in condensed phases of water). TMD, T_m and T_c stand for the temperature of maximum density at room pressure, the normal melting temperature of ice Ih and the critical temperature, respectively. EOS refers to the equation of state.

Property	TIP4P/2005	Surface
Enthalpy of phase change	5.0	PES
Critical point properties	7.3	PES
Surface tension	9.0	PES
Melting properties	8.8	PES
Orthobaric densities and TMD	8.5	PES
Isothermal compressibility	9.0	PES
Gas properties	0.0	PES
Heat capacity at constant pressure	3.5	PES
Static dielectric constant	2.7	PES + DMS (+PS)
T_m -TMD- T_c ratios	8.3	PES
Densities of ice polymorphs	8.8	PES
EOS at high pressure	10	PES
Self-diffusion coefficient	8.0	PES
Shear viscosity	9.5	PES
Orientalional relaxation time	9.0	PES
Structure	7.5	PES
Phase diagram	8.0	PES
Final score	7.2	

approach A is, in principle, exact. However, the reader may be surprised to learn that the results of approaches A and B are still far from describing the experimental properties of water. The reason is that we are not solving the Schrödinger equation exactly. Reliable methods such as MP2 or coupled cluster become too expensive (except for small water clusters [83]) and they are not feasible right now for the system sizes and simulation times required to obtain the thermodynamic properties. Computationally, cheaper methods such as DFT use approximate functionals. Typically, a set of letters is designed to describe the approximated functionals used in the calculations as for instance PBE0, B3LYP [84–87].

A possible way of tracking progress in the field is to perform an extensive comparison between calculated and experimental values for a number of selected properties. We recently propose such a comparison and suggested a criterion to obtain a numerical score [17]. When agreement with experiment is good, you obtain a high score. When agreement with experiment is low, you obtain a low score. Results for TIP4P/2005 are shown in Table 2. As it can be seen that TIP4P/2005 got a score of 7.2 points out of the 10. In our opinion obtaining a higher score in the test means that you are describing better the PES of water.

The water test includes the comparison to experimental properties of the gas, liquid and solid phases of water. Therefore, the water test evaluates the capacity of the model to reproduce the PES under quite different conditions. The PES depends formally on \mathbf{R}^{3N} , but for systems under pe-

riodic boundary conditions, the volume of the system V should also be provided. When performing a simulation at a certain value of N , V and T only configurations having a non-negligible statistical weight will be found. Let us denote this subset of configurations as \mathbf{R}^{3N*} . Obviously, the subset of explored configurations will be a function of the number density of the system $d = (N/V)$, the temperature and, in the case of solid phases, the geometrical constraints imposed by the lattice Ω . Therefore, \mathbf{R}^{3N*} is a function of d , T and Ω . Recently, it has been shown how a polarisable model [74] was able to obtain a higher score than a good non-polarisable one in the water test. That makes sense and points out the existence of progress in the field. The main reason for the higher score was an improvement in the score for those properties that depend on the description of the PES at low values of the density (properties of the gas, the virial coefficients, vapour pressure, critical pressure), while keeping a good score for condensed matter properties. Non-polarisable models are designed to describe the condensed matter phases but are unable to describe the properties of the gas.

In this section, we have presented different possible approaches in the modelling of water. The central idea of this paper is related to the way the dielectric constant should be computed, when modelling water within the approaches C and/or D. In Section 4, we will describe how the dielectric constant is commonly obtained in computer simulations and in experiments. But before, and to illustrate the reasons behind the main point of this paper, it seems pertinent to summarise some basic ideas of quantum chemistry. In particular, how the energy of a system can be obtained from quantum calculations, both in the absence and in the presence of an electric field.

3. A little bit of Quantum Chemistry: potential energy and dipole moment surfaces

We shall start by presenting two of the most important surfaces in the modelling of water, the PES and the dipole moment surface (DMS). We shall first explain how they are obtained from quantum calculations, and second, we will discuss which properties are determined by the PES and which ones by the DMS.

Within the Born–Oppenheimer approximation one should solve the Schrödinger equation for a certain fixed configuration of the nuclei of the system $\mathbf{R}^{3N} = \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{3N}$. The positions of the n_e electrons are denoted as $\tau^{n_e} = \tau_1, \tau_2, \dots, \tau_{n_e}$ (obviously, for water, $n_e = 10N$), where τ_i stands for the coordinates of position and spin of electron i (i.e. $\mathbf{r}_i s_i$). In the absence of an electric field (E_{el}), the energy of the system can be obtained by solving the Schrödinger equation:

$$\hat{H}^0 \Psi^0(\tau^{n_e}; \mathbf{R}^{3N}) = E^0(\mathbf{R}^{3N}) \Psi^0(\tau^{n_e}; \mathbf{R}^{3N}) \quad (5)$$

The superscript ⁰ indicates the absence of an electric field. The hat indicates an operator. Unless other thing is

stated, we shall focus on the ground state, so that the energy and wave function refer to that of the ground state. Notice that \hat{H}^0 includes the internuclear Coulombic repulsion energy. The total dipole moment of the system \mathbf{M}^0 is obtained as follows [86,87]:

$$\mathbf{M}^0(\mathbf{R}^{3N}) = e \left(\sum_{\gamma} Z_{\gamma} \mathbf{R}_{\gamma} - \int \mathbf{r} \rho^0(\mathbf{r}) d\mathbf{r} \right) \quad (6)$$

where e is the magnitude of the electron charge, Z_{γ} is the atomic number of atom γ and ρ^0 is the electron density at point \mathbf{r} , which can be easily obtained from the wave function as [86]

$$\rho^0(\mathbf{r}) = n_e \int \cdots \int \Psi^*(\mathbf{r}, s_1, \tau_2, \dots, \tau_{n_e}) \times \Psi(\mathbf{r}, s_1, \tau_2, \dots, \tau_{n_e}) ds_1 d\tau_2, \dots, d\tau_{n_e} \quad (7)$$

Notice that both the energy and the dipole moment of the system depend on the positions of the nuclei; therefore, they are functions of \mathbf{R}^{3N} . Determining E^0 for different configurations of the nuclei provides the PES, $E^0(\mathbf{R}^{3N})$. Determining the dipole moment for different positions of the nuclei provides the DMS, $\mathbf{M}^0(\mathbf{R}^{3N})$. The existence of two different surfaces when describing properties of a system is well known in the quantum chemistry community [88,89], but probably less well known in the community performing condensed matter simulations with empirical potentials.

The energy E^0 and the dipole moment \mathbf{M}^0 are observable so that in principle they can be measured. There is an operator for each of these two magnitudes, and it is easy to determine their values once the wave function is known. However, the dipole moment of each individual molecule (in a certain \mathbf{R}^{3N} configuration) cannot be measured experimentally and there is no operator linked to the dipole moment of a single molecule in condensed matter. The same is also true for the total quadrupole moment of a system. It can also be determined experimentally by using an inhomogeneous electric field. However, it is not possible to determine the quadrupole moment of each individual molecule (in a certain \mathbf{R}^{3N} configuration), and there is no operator linked to the quadrupole moment of a molecule in condensed matter. The problem when determining the molecular dipole/quadrupole moment of a molecule in condensed matter is that for each point of the space \mathbf{r} , with an electronic density $\rho^0(\mathbf{r})$, one must decide somewhat arbitrarily to which molecule of the system this point \mathbf{r} belongs. There is no unique way of doing that and for this reason there is no unique way of determining the dipole moment of a molecule in condensed matter [87,90,91]. The dipole moment of an individual molecule is not needed either to compute the energy of a certain configuration or to compute the total dipole moment of the system in a certain configuration. However, it may be useful to rationalise the obtained results. Defining the dipole moment of a molecule

in condensed matter is useful as a pedagogical concept, as it allows one to better understand the properties of condensed matter. In the same way, the partial charge of an atom in a molecule cannot be measured. In fact, there is no operator to determine partial charges. Partial charges are only useful to obtain a graphical simple picture of the charge distribution within the molecule or eventually to obtain an initial educated first trial in the design of empirical potentials. Although partial charges cannot be determined in a unique way, it is certainly possible to conceive that a certain prescription yields partial charges that can be used with success in the development of a force field for a given molecule.

Let us now apply a uniform static electric field \mathbf{E}_{el} . Let us assume that the electric field is applied along the z -direction and its modulus is E_{el} . The energy of the system for a certain configuration of the nuclei \mathbf{R}^{3N} is obtained by solving the Schrödinger equation:

$$\begin{aligned} (\hat{H}^0 - E_{\text{el}} \hat{M}_z) \Psi(\tau^{n_e}; E_{\text{el}}, \mathbf{R}^{3N}) \\ = E(\mathbf{R}^{3N}, E_{\text{el}}) \Psi(\tau^{n_e}; E_{\text{el}}, \mathbf{R}^{3N}) \end{aligned} \quad (8)$$

The total dipole moment of the system M is obtained as follows:

$$\mathbf{M}(\mathbf{R}^{3N}) = e \left(\sum_{\gamma} Z_{\gamma} \mathbf{R}_{\gamma} - \int \mathbf{r} \rho(\mathbf{r}) d\mathbf{r} \right) \quad (9)$$

where ρ (without any subscript) is the electron density in the presence of the field, which can be obtained easily from the wave function. It follows from Equation (8) that the energy of the system in the presence of the external field can be written as follows:

$$E(\mathbf{R}^{3N}, E_{\text{el}}) = \int \Psi^* \hat{H}^0 \Psi d\tau^{n_e} - E_{\text{el}} M_z \quad (10)$$

According to this, the energy can be divided into two contributions. The first one is the intermolecular energy, and the second one is the contribution due to the interaction of the system with the external field. Notice, however, that even the first term depends on the external electric field since the wave function Ψ depends on the external field and it is not identical to Ψ^0 . If the external field E_{el} is weak, one can use quantum perturbation theory using the external field as the coupling parameter to estimate the energy of the system. In that case (to the second order in E_{el}) one obtains

$$\begin{aligned} E(\mathbf{R}^{3N}, E_{\text{el}}) = E^0 - E_{\text{el}} M_z^0 \\ + E_{\text{el}}^2 \sum_j \frac{|\int (\Psi^0)^* \hat{M}_z \Psi_j^0 d\tau^{n_e}|^2}{(E^0 - E_j^0)} + \cdots \end{aligned} \quad (11)$$

where the subindex j labels the excited states of the system in the absence of the external field. The previous equation

can be written as follows:

$$E(\mathbf{R}^{3N}, E_{\text{el}}) = E^0 - E_{\text{el}} M_z^0 - \frac{1}{2} E_{\text{el}}^2 \alpha_{zz}^0 + \dots \quad (12)$$

where α_{zz} is the zz -component of the polarisability tensor. It follows that

$$M_z^0(\mathbf{R}^{3N}) = - \left(\frac{dE(\mathbf{R}^{3N}, E_{\text{el}})}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} \quad (13)$$

$$\begin{aligned} \alpha_{zz}^0(\mathbf{R}^{3N}) &= \left(\frac{dM_z(\mathbf{R}^{3N}, E_{\text{el}})}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} \\ &= - \left(\frac{d^2 E(\mathbf{R}^{3N}, E_{\text{el}})}{dE_{\text{el}}^2} \right)_{E_{\text{el}}=0} \end{aligned} \quad (14)$$

The energy of the system in the absence of the external field E^0 defines the PES. The first derivative of the energy with respect to the external field (at zero external field) defines the DMS (M_z^0). Strictly speaking, the DMS is formed by three different surfaces (i.e. M_x^0 , M_y^0 , M_z^0). The second derivative of the energy with respect to the external field is the polarisability surface (PS) [92]. Obviously, the PS is formed by nine components and is a tensor. Each component represents a different second derivative (xx , xy , \dots , zz). For this reason, the PS is formed by nine surfaces. Notice that the polarisability is related to the derivative of the polarisation of the system with respect to the external field. After introducing the PES and DMS, it is interesting to raise the following question: which properties are obtained from the PES and which one from the DMS?

In Table 2, a list of the properties that can be obtained once the PES is known is presented. As can be seen, the knowledge of the PES is enough to compute practically all experimental properties of the system. In fact, to perform MC simulations, one only needs to know the energy of each configuration (and its gradient too in the case of molecular dynamics). The only property that cannot be evaluated, even after the PES is known, is the dielectric constant. To determine the dielectric constant, both the PES and the DMS are needed (and also the PS, although the contribution of this surface in the case of water is rather small). In the absence of the electric field, all properties of water can be obtained from the PES. In this case, you should not care at all about the DMS and PS because without the presence of the electric field they play no role! In the physics of water (or in that of any other substance or system), the dielectric constant is a property that matters only when applying an electric field to the sample. Due to this particularity, it is interesting to discuss in some detail the procedure used to determine the dielectric constant both in experiments and in computer simulations.

4. The dielectric constant

In experiments, the dielectric constant is obtained from the relation between the polarisation ($\langle P_z \rangle$) and the electric field:

$$\langle P_z \rangle = \frac{\langle M_z \rangle}{V} = \chi E_{\text{el}} = \epsilon_0(\epsilon_r - 1)E_{\text{el}} \quad (15)$$

where χ is the susceptibility, ϵ_0 is the permittivity of vacuum and $\epsilon_r = \epsilon/\epsilon_0$ (the ratio of the permittivity of the medium with respect to vacuum) is the dielectric constant. In general, the electric field acting on the sample, E_{el} , is not identical to the applied external field E_{ext} , as surface charges are formed at the interfaces of the sample, and these surface charges generated an additional contribution to the field [93,94]. However, if the sample is confined within a conductor (i.e. the dielectric around the sample has an infinite dielectric constant), then E_{el} becomes identical to E_{ext} . For simplicity, we shall assume that this is the setup used both in experiments and in the calculations, so that E_{el} and E_{ext} are identical (i.e. we are using conducting boundary conditions). For weak electric fields, the relation between $\langle P_z \rangle$ and E_{el} is linear and the slope defines the value of the dielectric constant. Therefore,

$$\begin{aligned} \epsilon_r &= 1 + \frac{1}{\epsilon_0} \left(\frac{d\langle P_z \rangle}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} \\ &= 1 + \frac{1}{\epsilon_0 V} \left(\frac{d\langle M_z \rangle}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} \end{aligned} \quad (16)$$

Let us now assume that the motion of the nuclei can be described using classical statistical mechanics (the formalism can be easily extended to the case where one incorporates nuclear quantum effects). Then (in the NVT ensemble),

$$\langle M_z \rangle = \frac{\int M_z(\mathbf{R}^{3N}, E_{\text{el}}) e^{-\beta E(\mathbf{R}^{3N}, E_{\text{el}})} d\mathbf{R}^{3N}}{\int e^{-\beta E(\mathbf{R}^{3N}, E_{\text{el}})} d\mathbf{R}^{3N}} \quad (17)$$

Notice that both $M_z(\mathbf{R}^{3N}, E_{\text{el}})$ and $E(\mathbf{R}^{3N}, E_{\text{el}})$ are functions of the position of the nuclei and of the electric field. If the zero of energies was chosen as the energy of N isolated water molecules in the absence of the field, then this change, of course, would not affect the value of $\langle M_z \rangle$. To evaluate ϵ_r , all that is needed is to evaluate the derivative of $\langle M_z \rangle$ with respect to E_{el} at zero external field (see Equation (16)). By using the expression obtained to first order from quantum perturbation theory for $E(\mathbf{R}^{3N}, E_{\text{el}})$, one obtains

$$\begin{aligned} \epsilon_r &= 1 + \frac{1}{\epsilon_0 V} \left\langle \left(\frac{dM_z(\mathbf{R}^{3N}, E_{\text{el}})}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} \right\rangle \\ &\quad + \frac{\beta}{\epsilon_0 V} (\langle (M_z^0)^2 \rangle_0 - \langle M_z^0 \rangle_0^2) \end{aligned} \quad (18)$$

where the $\langle X \rangle_0$ represents the canonical average of property X over configurations generated in the absence of the electric field. Although the discussion can be formulated for a general case, for simplicity, let us focus on an isotropic phase (for instance, a liquid phase). In this case, the value of $\langle M_z^0 \rangle_0$ is zero (there is no net polarisation in the absence of the field), and the directions x, y, z are equivalent, so that better statistics is obtained by averaging the results over the three axes. The final expression is as follows:

$$\begin{aligned} \epsilon_r &= 1 + \frac{1}{\epsilon_0 V} \left\langle \left(\frac{dM_z}{dE} \right)_{E_{el}=0} \right\rangle_0 + \frac{\rho}{\epsilon_0 3kT} \frac{\langle (\mathbf{M}^0)^2 \rangle_0}{N} \\ &= \epsilon_{r,\infty} + \frac{\rho}{\epsilon_0 3kT} \frac{\langle (\mathbf{M}^0)^2 \rangle_0}{N} \end{aligned} \quad (19)$$

This is the expression in the SI system of units. To obtain the corresponding formula in the CGS (often used in simulations), one should replace ϵ_0 by $1/(4\pi)$ in the previous expression. The dielectric constant is the sum of three contributions. The first one is a constant with value one. The second contribution accounts for the average change of the polarisation of the system for an instantaneous configuration when an external field is applied. The sum of these two terms is usually denoted as $\epsilon_{r,\infty}$. The third contribution accounts for the polarisation induced in the system by the alignment of the permanent dipole moments of the molecules with the external electric field. Let us briefly comment on the value of $\epsilon_{r,\infty}$. It can be determined from experiments by using an electric field of high frequency. In fact, when the electric field has a high frequency, the permanent dipole moment of the molecules of water is unable to align with the external field within the time scale of one oscillation. For this reason, it is possible to determine $\epsilon_{r,\infty}$ from experiments by using high-frequency electric fields. It can also be determined from theoretical calculations. The value of $\epsilon_{r,\infty}$ for water is of about 1.8 both for pure water and for ice Ih [95,96]. Since the dielectric constants of liquid water and ice Ih at the melting point are 88 and 94, respectively, it is clear that, in condensed matter, the largest contribution to the dielectric constant comes by far from the last term on the right-hand side of Equation (19). The dielectric constant of water is high, not because the external field significantly changes the polarisation of individual configurations, but because it significantly changes the probability of each individual configuration in the ensemble by increasing the probability of configurations with large polarisation.

The way to compute ϵ_r in computer simulation is rather straightforward. One performs simulations in the absence of the electric field. One only needs the PES to perform those simulations. You store in the hard disk, say, 10,000 independent configurations for later analysis. For each configuration, one evaluates its dipole moment \mathbf{M}^0 (which is obtained from the DMS) and the derivative of M_z with

respect to the external field evaluated at zero external field (which is obtained from the PS). Obviously, expressions for the DMS and PS are needed. After obtaining the average over the 10,000 configurations, one obtains the value of the dielectric constant. In summary, one only needs the PES to generate the trajectory over the phase space, and then for the analysis leading to the dielectric constant one also needs the DMS and PS.

Now we will present the main point of this paper.

5. One molecule, two surfaces

The PES and the DMS are the two functions that depend on \mathbf{R}^{3N} . They are two surfaces on the imaginary plane where \mathbf{R}^{3N} are the independent variables. Both PES and DMS can be obtained from the wave function.

5.1. One side of the mistake: transferring from the PES to the DMS

Empirical potentials are simple expressions designed to describe (although in an approximate way) the PES. They usually contain parameters for the LJ part of the potential, and parameters (i.e. partial charges) to describe Coulombic-like interactions.

Now it is time to introduce the ‘dogma’ that has been used implicitly by a number of people (including the author of this paper) [17,97,98]. The ‘dogma’ states that ‘the partial charges’ used to describe empirically the PES should also be used to describe empirically the DMS. According to the ‘dogma’, it should be done in this way, and it would not be legal, possible or correct to do something different.

But ... if the PES and the DMS are two surfaces, why should we use the same set of fitting parameters to describe two different functions? Let us assume that both the PES and the DMS are known from *ab initio* calculations. In the case we are using partial charges to describe empirically the PES and/or DMS, one would expect that the parameters providing the best fit (i.e. with the minimum of the average square deviation) for the PES would, in general, be different from those obtained to reproduce the DMS. Therefore, there is no conceptual reason why one could not use a different set of partial charges to describe the PES and the DMS (in contrast with the ‘dogma’ that states that they should be identical). The main point of this paper is to point out that the implicit assumption that one should use the same partial charges to describe the PES and the DMS is a ‘conceptual’ mistake. Let us analyse whether leaving the ‘dogma’ presents some technical difficulties. When performing simulations using an empirical PES, one stores a set of configurations on the hard disk. It is clear that now you can use whatever expression you want to obtain the dipole moment of the stored configurations. There is no technical difficulty in doing that. One can write a program to generate the configurations from a certain PES, and another one reading these configurations and obtaining

the DMS using a different set of parameters. In fact, one does not need two programs. One could do that within one program. It is enough to have two subroutines, one for the PES (which enters in the Markov chain or when computing forces) and another one for the DMS (which enters to compute the dipole moment of each configuration). In the case the PS is also considered, then another subroutine for the PS is needed. Of course, the current popular programs (Gromacs [99], DLPOLY [100], Lammmps [101], ...) do not allow one to do that because they have been written respecting the ‘dogma’. However, modified versions of these codes leaving the dogma can be easily written.

In the design of empirical potentials for water, we probably misunderstood the role of the dielectric constant. The dielectric constant is not the property to look at to obtain a good PES. It depends on two surfaces and when one fails in describing ϵ_r , one does not know whether this is due to a good PES combined with a bad DMS, to a bad PES combined to a good DMS or to the combination of a bad PES and a bad DMS (although in this last case there is the possibility that one describes quite well the experimental value if the errors in the two surfaces cancel out partially). We suggest the following procedure. One first tries to develop an empirical expression for the PES, by reproducing as many experimental properties as possible (but eliminating the dielectric constant from the test). Once you have a good PES, then you fit your empirical expression for the DMS by fitting to the experimental values of the dielectric constant.

Once one leaves the ‘dogma’, there are many possibilities. For instance, one could use a model like TIP4P/2005 for the PES and use quantum chemistry, or a polarisable model to determine \mathbf{M}^0 and the polarisability for the configurations stored on the hard disk. In fact, such approach has been used recently by Hamm to determine the two-dimensional Raman THz spectra of water [102,103] and make a comparison with the experimental results. Also, Skinner and co-workers [104] found that it was possible to describe the low-frequency region of the infra-red (IR) spectrum of water and ice Ih by using a non-polarisable model for the PES and a polarisable model for the DMS. In the future, it may be very interesting to determine \mathbf{M}^0 from first principles for the configurations obtained by using an empirical potential. There are some lessons to be learnt from that. Probably, we have not fully appreciated the fact that the PES and the DMS are two different surfaces and there is no reason why both of them should be described by the same set of charges, parameters or methodologies.

As far as we know, the dogma was challenged in at least three recent papers. In our previous work, we used the ‘charge scaling’ method (see discussion about this method later) for the DMS [25,26]. The group of Skinner has also presented recently an example of ‘departure from the dogma’. Skinner and co-workers developed the E3B model [105], a model that adds three body forces to a TIP4P-

like model. The addition of three body forces in principle should improve the description of the PES. However, it was found that the E3B model did not improve the description of the dielectric constant of water. Why? Because once again the same set of charges was used to describe the PES and the DMS. However, quite recently, Skinner and co-workers used the E3B model for the PES and a polarisable model to describe the DMS with reasonable agreement with the experimental results [104]. Probably, these two works can be regarded as the first excursions away from the ‘dogma’. The idea is also ‘in the air’ in the recent papers of Leontyev and Stuchebrukhov [106–108], where they suggested that the charges to be used in the PES of a non-polarisable model correspond to the scaled charges of a polarisable model (assuming that they mean that the charges of the non-polarisable model are used to obtain the PES and the charges of the polarisable model are for the DMS). We do hope that many more examples like these (i.e. leaving the dogma) will come.

If one solves the Schrödinger equation exactly (as nature does), then from the exact wave function one obtains both the exact PES and DMS. The power of approaches A and B is that as one gets a better and better wave function (or functional), one will be able to obtain from the wave function (or from the electronic density) both an accurate PES and DMS. The assumption that a simple empirical potential is able to describe all features of the PES is somewhat optimistic, although one must admit that it is amazing how much can be described by such a simple approach. However, even admitting that an empirical potential with partial charges can do a reasonable job in describing the PES, assuming that the same partial charges are good to describe the DMS, is simply ‘too much’. It is interesting to point out that the collaboration between teams A/B and D could be very useful to obtain accurate values for ϵ_r .

We have described above how it is possible and simple to determine ϵ_r without invoking the ‘dogma’ from the expressions obtained from linear response theory. The dielectric constant can also be obtained by applying a weak electric field. Once again, for simplicity, we shall assume that the field acts on the z -axis and shall use conducting boundary conditions. Then, one has [26,94]

$$\epsilon_r = 1 + \frac{\langle M_z \rangle}{\epsilon_0 E_{el} V} = 1 + \frac{1}{\epsilon_0 E_{el} V} \frac{\int M_z e^{-\beta E(\mathbf{R}^{3N}, E_{el})} d\mathbf{R}^{3N}}{\int e^{-\beta E(\mathbf{R}^{3N}, E_{el})} d\mathbf{R}^{3N}} \quad (20)$$

For a weak electric field, one can use the first-order perturbation theory both for $E(\mathbf{R}^{3N}, E_{el})$ and for M_z :

$$\epsilon_r = 1 + \frac{1}{\epsilon_0 E_{el} V} \left\langle M_z^0 + \left(\frac{dM_z}{dE_{el}} \right)_{E_{el}=0} E_{el} \right\rangle_{E^0 - E_{el} M_z^0} \quad (21)$$

To evaluate this expression, one needs to store on the hard disk configurations generated according to the Boltzmann distribution of $E^0 - E_{\text{el}} M_z^0$ (so that the PES and DMS are needed). Once these configurations are saved, you simply evaluate the average of the value in the bracket (which requires to know both the DMS and the PS). Many standard MD and MC programs allow one to apply an external electric field. The codes were written to obey the ‘dogma’; therefore, the same partial charges and/or multipoles are used for the PES and the DMS. It is generally stated that for non-polarisable models, the PS is zero. In the case of polarisable models, the PS is described by a simple electrostatic model describing how the DMS changes with the electric field. However, these codes could be easily modified to deviate from the ‘dogma’, by simply allowing different treatments when describing the PES, DMS and PS. As discussed previously, the contribution of the PS to ϵ_r for water at room temperature and pressure is small (of about 1 %), so that the error introduced by neglecting this contribution is small.

We shall now illustrate a very simple example where we abandon the dogma. Although more complex treatments could obtain much better results, the ‘ λ ’ scaling is probably the simplest example to illustrate the ideas of this paper at work.

5.2. The λ scaling

Let us assume that to describe the PES one is using, in addition to the traditional LJ parameters, a set of partial charges. We shall denote the partial charges used to describe the PES as q_{PES} . Let us now assume that to describe the DMS one is using a set of charges that are identical to those used to describe the PES (and located at the same position) but scaled by a factor λ . Then, it follows that

$$q_{\text{DMS}} = \lambda q_{\text{PES}} \quad (22)$$

We shall denote with subscript λ the properties that will follow when using the scaled charges for the DMS (while using the original charges for the PES) and by PES the properties that will follow when using the same charges for the PES and DMS. It follows that

$$\mathbf{M}_{\text{DMS}}^0 = \lambda \mathbf{M}_{\text{PES}}^0 \quad (23)$$

Implementing the ideas described above (and assuming for simplicity that the PS contribution is zero), one obtains

$$\epsilon_{r,\lambda} = 1 + \frac{\rho \lambda^2}{\epsilon_0 3kT} \frac{\langle (\mathbf{M}_{\text{PES}}^0)^2 \rangle}{N} \quad (24)$$

$$\epsilon_{r,\lambda} = 1 + (\epsilon_{r,\text{PES}} - 1) \lambda^2 \quad (25)$$

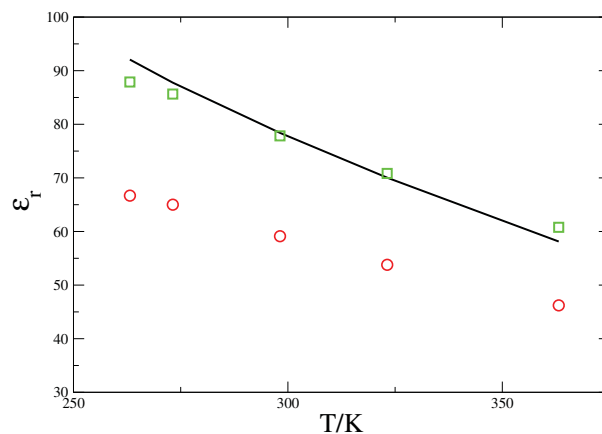


Figure 2. Dielectric constant of liquid water at room pressure as a function of the temperature. Line: experimental results. Circles: results for TIP4P/2005 from [94], and from the λ scaling (with $\lambda = 1.15$) as obtained in this work (squares).

where we denote $\epsilon_{r,\text{PES}}$ as the value that will follow from evaluating the dielectric constant in the traditional way (i.e. using the same partial charges for the PES and DMS). Several previous studies suggested that the dipole moment of water in condensed matters is of about 2.66 D [22,109–115]. In the TIP4P/2005 model, all molecules have a dipole moment of 2.305 D. Then, the value of λ that follows from this reasoning is $\lambda = (2.66/2.305) = 1.15$. Let us now evaluate the dielectric constant of water using this scaling.

The results obtained are presented in Figure 2. The dielectric constant of liquid water for TIP4P/2005 was taken from the recent work by Kolafa and Viererblova [94]. As can be seen, the description of the dielectric constant of water is now much better. At 298 K, the predicted value of $\epsilon_{r,\lambda}$ is 77.8, which should be compared to 78.5 which is the experimental value. Also, the variation of the dielectric constant with temperature is now in better agreement with the experimental results [116]. With respect to ice Ih, the value of λ required to bring the simulation results of TIP4P/2005 into agreement with the experiments is $\lambda = 1.41$, which implies that the dipole moment of the molecules of water in ice is about 3.25 D, in reasonable agreement with previous estimates [22,110–115]. It is not possible to reproduce simultaneously the dielectric constant of liquid water and ice Ih using an unique value of λ . The use of the λ scaling would modify the score of TIP4P/2005 model in the block of dielectric properties (of course, it will not affect the score in the rest of the properties). If a unique value of λ is used for the fluid and ice (i.e. $\lambda = 1.15$), then the score for the three properties of the dielectric constant block would be 10 (liquid), 3 (Ih) and 3 (ratio of the dielectric constant of ice and water); therefore, the average of this block would be 5.3. Using two different values for λ (one for ice and another one for liquid) would dramatically increase the score of this section, since basically one would now reproduce

the experimental results. Thus, the use of the λ scaling will increase the global score of TIP4P/2005 from 7.2 to 7.4 (when using the same value of λ for all phases) and to 7.6 when using a different value of λ for the liquid water and for ice. It is probably true that all previous discussions [17,97,98] about the ability of water models to describe the dielectric constant should be revised, since all the reported values were obtained under the implicit assumption that the charges used to describe the PES should also be used to describe the DMS. Recently, the TIP4P model has been modified to obtain a ‘special purpose’ model that improves the description of the dielectric constant [117] of water (while still using the ‘dogma’). Further work is needed to analyse if the improvement [117] in the description of ϵ_r is at the cost of deteriorating somewhat the PES, leading to an overall lower score in the water test (as compared to TIP4P/2005). Polarisable models, in principle, should improve the description of the dielectric constant of water, although further work is needed to analyse if the improvement obtained for the liquid phase does also extend to the solid phases [22]. Notice also that the use of the ‘dogma’ is also present in polarisable models, since the charges/multipoles used to describe the PES are also used to describe the DMS.

Even in the case of polarisable models leaving the ‘dogma’ may result in an improved description of the dielectric properties of water (so the main point of this work does not only apply to non-polarisable models). In any case it seems that when using polarisable models (especially those using diffusive partial Gaussian charges [71,75] rather than point like partial charges), the differences between the optimum set of charges needed to reproduce the PES and those needed to reproduce the DMS are smaller than when using non-polarisable models. Thus with polarisable models, the need to use different charges for the PES and DMS is reduced considerably. However, the option of using different approaches to describe both surfaces is still possible and the benefits of such a treatment remains to be explored. Obviously, in a quantum treatment, the same electron density should be used to compute both the DMS and PES (in fact, in DFT, the energy is obtained once the electron density is known). However, an empirical polarisable model is not identical to a quantum treatment; therefore, the option of using different approaches for the PES and DMS could still be beneficial. Further work on this issue is needed before establishing definite conclusions.

The failure of all non-polarisable models in describing the dielectric constant of ice Ih was the ‘smoking gun’, announcing that something was totally wrong in our treatment of dielectric properties. The dielectric constant of ice Ih was not computed often for water models and that may explain our delay in understanding the situation. TIP4P/2005 was successful in describing many properties of water indicating that it has a reasonable PES. The fact that the dielectric constant of both ice Ih and water was incorrect, but always

much lower than the experimental value, was a clear indication that there should be a reason for that. In our 2011 paper, we indicated that this was a failure of the model, and that it was a consequence of the fact that the model is non-polarisable. In this work, we go one step further. Our point is that there was something wrong but ‘in our mind’. LJ centres, partial charges and polarisable models that respond to a local electric field are just approximations aimed to describe the PES, which, of course, can only be obtained from quantum mechanics. Forcing these entities to reproduce simultaneously, two surfaces obtained from the quantum treatment (PES and DMS) was in, retrospective, a naive hope.

5.3. The other side of the mistake: transferring from the DMS to the PES

Let us consider a diluted solution of NaCl in water in the absence of an electric field. The dipole moment of a certain configuration is given by Equation (6). In Equation (6), the first sum goes over all the nuclei of the problem, and the second contribution is an integral over the electronic cloud. This formula is exact. Let us assume, however, that we want to provide an empirical (and simple) expression for the dipole moment of the configuration considered. The electronic cloud around an ion in vacuum is spherical, but not in water, since the solvation of the ions by the water molecules distorts the electronic cloud. As stated previously, the electronic cloud cannot be distributed exactly among the atoms of the system. However, a scheme like Atoms in Molecules [91] (AIM) provides a reasonable partitioning of the space. One may expect that integrating the electronic cloud around the ion (in the region assigned to the ion by a procedure such as AIM) and adding the charge of the nucleus of the ion, one would obtain a contribution not too far away from +1 for the Na^+ and -1 for Cl^- . What about the water contribution? The water molecules in contact with the ions will have a distorted electronic cloud, but if the solution is highly diluted, most of the molecules of water will not be in contact with the ions, and one approximation for the contribution of the water molecules to the dipole moment of the entire system is to use the same charge distribution that provided a good DMS for pure water. Therefore, an approximate empirical approximation for the dipole moment of a certain configuration in a diluted solution of NaCl in water would be

$$\mathbf{M}^0 \simeq \mathbf{M}^0_{\text{H}_2\text{O}} + \mathbf{M}^0_{\text{NaCl}} \simeq \mathbf{M}^0_{\text{H}_2\text{O}} + e \left(\sum_{\text{Na}^+} \mathbf{R}_{\text{Na}^+} - \sum_{\text{Cl}^-} \mathbf{R}_{\text{Cl}^-} \right) \quad (26)$$

In other words, we obtain the polarisation as the sum of two contributions – one due to water and the other one due

to the ions. This is, of course, an approximation. The DMS should be obtained from the electron density obtained after solving the Schrödinger equation. However, the approximation described above can be regarded (for diluted solutions) as reasonable.

We can now focus on the PES of the salt solution. Let us assume that water–water interactions are described with a certain water potential model. What to use for the ion–ion and ion–water interactions? In the solid phase, it has been shown [118,119] that the interactions between the ions are well described by a short-range repulsion plus a Coulombic interaction between the ions using the charges +1 (for Na^+) and -1 (for Cl^-). In fact, lattice energies (and densities) are well described with this approach. Let us assume that we use the same approach for the ion–ion interactions in the solution. The only remaining question now is as follows: what should we use for the ion–water interactions?

To accurately describe the property of a mixture of two components (1 and 2) one needs to describe correctly not only the 1–1 and 2–2 interactions, but also the 1–2 interactions. To obtain the 1–2 interactions, one should use a quantum treatment. However, quite often, the 1–2 interactions are estimated by simply applying certain empirical prescriptions denoted as combining rules that allows one to estimate the 1–2 interactions once one knows the 1–1 and 2–2 interactions. For instance, Lorentz–Berthelot (LB) rules are often used to describe the LJ interactions between different type of atoms, and when they do not provide satisfactory results, deviations from LB rules are introduced [120]. Concerning the Coulombic part of the potential, we are quite rigid. For instance, for the ion–water interaction, we will simply apply Coulomb law between the charges of the ions and the charges of the water model. If the reader agrees with the statement that 1–2 interactions cannot be obtained exactly from 1–1 and 2–2 interactions, then this idea should extend to all types of contributions to the 1–2 energy (i.e. short-range repulsion, long-range dispersion and Coulombic interactions). The hydration energy of an ion at infinite dilution is mostly due to the interaction between the ion and the first hydration layers. One could obtain the hydration free energy from a quantum calculation. However, when water is described by an empirical model, it may be the case that to reproduce the hydration free energy of the ion solvated by water, the choice of +1 or -1 for the ions may not be the best to reproduce *simultaneously* the hydration free energy and the density of the solution. It could be the case that reducing the charge of the ions improves the description of the hydration energies. Moreover, reducing the charge of the ions may improve the description of the ion–ion correlations at large distances in diluted solutions, if the dielectric constant of the water model is lower than the experimental value and one, as usual, uses the charges of the PES of water to describe the Coulomb interactions with the ion (instead of the probably better option of using the charges of the DMS of water since, in

the particular case of very large distances, the effect of the ion on water is essentially identical to that of an electric field). Reducing the charge of the ion may certainly deteriorate the description of the ion–ion interaction (so that you should not use this model to describe solids or highly concentrated solutions), but it may significantly improve the description of the salt solution properties at low to moderate concentrations.

The idea of using partial charges different from +1 and -1 (or $+ze$ in general) for ions is not new in the literature. It has also been suggested by other authors [106,121]. The idea has not been very popular, probably because of the resistance to use different charges in the DMS and in the PES (i.e. the ‘dogma’). Once you leave the ‘dogma’, the flexibility increases. Instead of attacking this approach from the very beginning, we believe that this question should be decided in the battle field. The battle field in modelling is the description of the properties of real systems. Does one describe better the experimental properties when using different charges to describe the PES and DMS surfaces? Do we describe better the properties of solutions by using charges different from +1 or -1 for the ions? It should be mentioned that properties of the solution as density, diffusion coefficients, vapour pressure, osmotic coefficients, chemical potentials and activity coefficients depend only on the PES and not on the DMS.

Certainly, further work is needed to analyse this issue in detail. In particular, there are two problems that would be particularly useful to obtain certain conclusions. The first is the determination by computer simulation of the chemical potential and activity coefficients of salts in explicit water. Few studies have been presented so far dealing with this problem [122–126] and further work is certainly needed. Reproducing the Debye–Hückel limit (which is valid for concentrations below 0.01 m) is nice but certainly not enough. For instance, in the case of NaCl, we must analyse the behaviour of the activity coefficient for concentrations up to 6.14 m (the solubility limit). A second problem is that of determining the solubility limit of a salt in water by computer simulations. Besides the technical difficulties (quite a few), it is a very hard test for force fields as one needs to simultaneously describe the salt in the solid phase (many salt models do not even get right the melting point [127]), a good description of the solvent and a good description of the water–solvent interaction. No force field so far reproduced the experimental value of the solubility of NaCl in water [122,128–132] (the best prediction of the solubility deviates from the experimental value by a factor of two). It is clear that we have a problem.

In agreement with the previous reasoning, Kann and Skinner [121] have shown recently that using partial charges smaller than +1 and -1 for the ions in salt solutions, it is possible to describe the variation of the diffusion coefficient of water with salt concentration (increasing with concentration in the case of structure breakers or chaotropes, and

decreasing with concentration in the case of structure makers or kosmotropes). The key step was to leave the dogma. Leontyev and Stuchebrukhova [106–108] suggested that to describe the PES of salt solutions, the charge of the ions should be scaled by $1/\sqrt{\epsilon_\infty}$ (i.e. $\frac{1}{\sqrt{1.8}} = 0.75$). This is an interesting suggestion. In any case, the charge of the ions to be used in the PES can be considered as an empirical parameter to be fitted to reproduce as many properties of the solution as possible.

That further work is needed to analyse this is even more obvious when one takes into account that, for NaCl, no model using charges of +1 and –1 for the ions has been proposed so far that describes simultaneously the density, chemical potential and melting point of the NaCl solid, the experimental values of the chemical potential of NaCl in solution up to high concentrations (i.e. the standard chemical potential and activity coefficients), and the solubility limit.

6. Discussion

We shall now discuss several issues that arise once one leaves the ‘dogma’.

6.1. The generalised hyper-surface

We shall denote as surfaces those magnitudes that depend on the positions of the nuclei only. The function $E(\mathbf{R}^{3N}, E_{\text{el}})$ depends on both the position of the nuclei and of the magnitude of the external field, and is a hyper-surface. As was stated previously, the energy of a certain configuration in the presence of an electric field in the z -direction can be approximated (using quantum perturbation theory) as follows:

$$E = E^0 - M_z^0 E_{\text{el}} - \frac{1}{2} \alpha_{zz}^0 (E_{\text{el}})^2 + \dots \quad (27)$$

It is now clear that the hyper-surface E (when truncated in second order) depends on three surfaces, the PES (i.e. E^0), the DMS (i.e. M_z^0) and the PS (i.e. α_{zz}^0). The polarisation of the system in the presence of the external field is given as follows:

$$M_z = M_z^0 + \left(\frac{dM_z}{dE_{\text{el}}} \right)_{E_{\text{el}}=0} E_{\text{el}} + \dots = M_z^0 + \alpha_{zz}^0 E_{\text{el}} + \dots \quad (28)$$

From the discussion of this paper, it follows that one could use a different empirical expression to describe E^0 , M_z^0 and α_{zz}^0 . They are three different surfaces after all. Let us illustrate this idea with a simple example where we use the TIP4P/2005 for the PES, the λ scaling for the DMS and

the Clausius–Mossoti approximation for the PS:

$$E = E^{\text{TIP4P/2005}} - \lambda M_z^{\text{TIP4P/2005}} E_{\text{el}} - \frac{1}{2} \left(\sum_{j=1}^N \alpha_{j,zz} \right) E_{\text{el}}^2 + \dots \quad (29)$$

where $\alpha_{j,zz}$ is the component zz of the polarisability of molecule of water j . If one assumes that α is isotropic (a reasonable approximation for water [133]), and one takes the value from the gas (i.e. $\alpha_{\text{H}_2\text{O}}$), one obtains an ever simpler expression as follows:

$$E = E^{\text{TIP4P/2005}} - \lambda M_z^{\text{TIP4P/2005}} E_{\text{el}} - \frac{N}{2} \alpha_{\text{H}_2\text{O}} E_{\text{el}}^2 + \dots \quad (30)$$

This expression combines a good PES (i.e. TIP4P/2005) with a much more reasonable description of the variation of the energy of the system with the external field (both in the linear and quadratic terms on the field). Notice that each contribution has units of energy (for instance, in the SI, M_z has units of C m, α of C m²/Volt and E_{el} of Volt/m). The expression of the hyper-surface when one follows the ‘dogma’ is simply that of the previous expression with $\lambda = 1$ and $\alpha_{\text{H}_2\text{O}} = 0$. It is clear that when compared to experiments, the ‘hyper-surface’ generated when following the ‘dogma’ is much worse than the expression we have just written, the most obvious consequence being an improvement in the description of the dielectric constant.

An interesting practical remark is that if the quadratic term on the field is neglected then the first order term can be written (when using the λ scaling) either as $[(\lambda M_z^{\text{TIP4P/2005}}) E_{\text{el}}]$ or $[M_z^{\text{TIP4P/2005}} (\lambda E_{\text{el}})]$. That means that if one uses a standard MC or MD program, where the DMS is obtained from the charges of the PES, then the results obtained when applying an electric field E'_{el} in simulations (obeying the ‘dogma’) corresponds to those obtained when applying an electric field $E_{\text{el}} = E'_{\text{el}}/\lambda$ in simulations not obeying the ‘dogma’ and using the λ scaling. In general, leaving the ‘dogma’ requires rewriting the simulation program to implement two different subroutines, one providing the PES and another one providing the DMS. However, in case the λ scaling approximation is used for the DMS, then there is no need to write the new program. Results obtained with the standard program with E'_{el} correspond to those obtained with $E_{\text{el}} = E'_{\text{el}}/\lambda$, when using the λ scaling.

6.2. Electric fields and phase transitions

Many computer simulation programs permit the incorporation of a static electric field (or even a dynamical one having a certain frequency). No doubt many research groups will start to apply electric fields to a number of problems and

there will be dozens of papers dealing with that. This means that now we should not only care about E^0 , but we should seriously consider how well we represent the changes in the energy of the system with the external field (i.e. the hyper-surface). The dielectric constant is related to the magnitude of the change in energy with the field, and for this reason it matters. Leaving the 'dogma' will provide a better description of the hyper-surface so that predictions will be more reliable.

Another interesting issue to consider in the future is the effect of electric fields on phase transitions. This is even more complex and challenging. Now what matters is the difference in the value of the dielectric constant between the two phases. In the particular case of the fluid–solid transition, the most common scenario in the case of molecular polar systems is that of a solid with a low dielectric constant (the constraints imposed by the lattice will not allow large fluctuations of the total polarisation of the solid, so that the dielectric constant will be small) and a liquid with a moderate dielectric constant. If the prediction of the model for the dielectric constant of the liquid phase is good, then the simulations will predict (correctly) a decrease in the melting point due to the presence of the electric field. However, there is an important exception to this common scenario: the ice Ih–water transition. Experimentally, the dielectric constant of ice Ih at the melting point is slightly larger than that of water (the existence of proton disorder in the solid [134] allows ice Ih to respond efficiently to an electric field). According to this, when applying an electric field the melting point will increase as the polarisation of ice Ih is larger than that of water and becomes further stabilised by the electric field. What will happen in simulations? Although the interest in the dielectric constant of ice Ih has been rather small, recently, it has become clear that within the formalism of the 'dogma', the dielectric constant of ice Ih is lower than that of liquid water (by about 15% for TIP4P models, and by about 50% for models such as TIP3P, SPC/E or TIP5P). Therefore, these models, within the formalism of the 'dogma', will predict (incorrectly) that the melting point of ice Ih decreases by a small amount (TIP4P like models) and significantly (TIP3P, SPC/E and TIP5P). For huge electric fields (of about 1 V/nm), a ferroelectric Ih (or Ic) phase [135,136] will be stabilised and one should expect a huge increase in the melting point with the field, as has been observed recently by Yan, Overduin and Patey [137]. This is interesting and probably relevant for water under confinement, but not so important for bulk water because the intensity of the electric field required to stabilise the ferroelectric field is huge and is beyond the electric breakdown point of water [138] (which is of about 0.01 V/nm). Therefore, for experimental studies of bulk water, the key variable to understand the impact of an electric field on the ice Ih–water phase transition is the difference between the dielectric constant of these two phases [26]. If the λ scaling is used for TIP4P/2005 (with the same value of λ for ice Ih

and for the liquid phase), the description of the dielectric constant of both phases improves but the dielectric constant of ice Ih is still slightly lower than that of water. In order to make predictions that can be compared to experiments, it is necessary to use different values of λ for ice Ih and for the liquid phase as we did in the previous work [26]. A similar problem was faced by Skinner and co-workers to describe the dielectric constants of ice Ih and water. These authors use the E3B model as the PES for both the liquid and the solid phases. However, to describe the DMS, they use a polarisable model with different parameters for the solid and liquid phases; therefore, the experimental values of ϵ_r were reproduced for both phases. If one does that, the predictions for the effect of the electric field on the phase transition would make sense and could be compared to experimental results. Now that interest in the effect of electric fields in phase transitions is growing, the issue of the dielectric constant of the two phases involved matters and the idea of using different charges (or even empirical expressions) to describe the PES and the DMS may be useful.

The idea of using different charges and/or methodologies in different phases to obtain the DMS is fine for determining the properties of each phase, or the effect of an electric field on a phase transition. However, this approach cannot deal with problems like interfacial properties or nucleation phenomena since it is not clear how to incorporate interfacial molecules (which are not neither fully liquid nor fully solid) into the treatment. Polarizable models (and/or *ab initio* calculations), in principle, do not have this problem as these methods provide a DMS that can be used for both phases. Whether these treatments are able to describe quantitatively, the dielectric constant of both phases need to be analysed in more detail although recent results suggest that this may indeed be the case [74,139]. In any case, the possibility of using a non-polarizable model for the PES and a polarizable model for the DMS is also open.

This paper does not pretend to be a heroic defense of non-polarizable models. These models have limitations, as it is clear from the water test. Rather this paper advocates that the discussion about the quality of water models to describe the dielectric constant was probably wrong, because it was based on the assumption that the same charges should be used to describe the PES and the DMS. This is not necessary. Probably, it is not in the prediction of the dielectric constant where polarizable models defeat clearly non-polarizable models. It is rather for properties like the vapour pressure, cluster properties, critical pressure, second virial coefficient and vapourisation enthalpy, where polarizable models show their superiority over non-polarizable ones [73–75]. Certainly, everything suggests that models with parameters depending on the local environment (i.e. polarizable) provide a better PES (especially when the model is used to describe the properties of the gas and of condensed phases simultaneously).

6.3. Classical electrostatics is not quantum mechanics

The dipole moment of a configuration can be easily obtained, once the positions of the nuclei are provided and the electron density is known. The formula used in quantum mechanics to obtain the dipole moment of a certain configuration is identical to the formula used in classical electrostatics to obtain the dipole moment of a certain distribution of point charges and a continuous charge distribution. Thus, concerning the DMS, classical electrostatics and quantum mechanics get along very well. What about the energy, i.e. the PES? It is instructive to write the expression of the energy as obtained from DFT [140] (in the absence of an electric field):

$$\begin{aligned}
 E^0(\mathbf{R}^{3N}) = E[\rho^0(\mathbf{r}; \mathbf{R}^{3N})] = & \frac{1}{2} \iint \frac{\rho^0(\mathbf{r}_1)\rho^0(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
 & - \sum_{\gamma=1}^{3N} \int \frac{Z_{\gamma}}{|\mathbf{r} - \mathbf{R}_{\gamma}|} \rho^0(\mathbf{r}) d\mathbf{r} + \sum_{\gamma} \sum_{\eta>\gamma} \frac{Z_{\gamma}Z_{\eta}}{R_{\gamma\eta}} \\
 & - \frac{1}{2} \sum_{i=1}^{n_e} \int \Psi_i(\mathbf{r}) \nabla^2 \Psi_i(\mathbf{r}) d\mathbf{r} + E_{XC}[\rho^0(\mathbf{r})] \quad (31)
 \end{aligned}$$

where the electronic density at point \mathbf{r} has been approximated by the sum of the contributions of different orbitals Ψ_i , i.e. $\rho^0(\mathbf{r}) = \sum_{i=1}^{n_e} |\Psi_i(\mathbf{r})|^2$ and we used atomic units. For each configuration of the nuclei, the electron density will be obtained by minimising the energy of the system with respect to the electron density. In the functional, the first three terms have a simple electrostatic origin, namely the repulsion energy between the electronic clouds, the attractive energy between the nuclei and the electronic cloud, and the repulsion energy between the nuclei. These terms can be easily understood from pure electrostatics. Let us now analyse the last two terms. One is the kinetic energy of the electrons, and the last one, E_{XC} , represents the exchange correlation functional. These two terms cannot be derived from classical electrostatics. Empirical potentials recognise that and this is the reason why LJ centres are often included to incorporate long-range dispersive forces and short-range repulsive forces as an implicit way of including part of the contribution of the E_{XC} and kinetic energy terms. One should not forget that the exact energy of a configuration cannot be obtained from simple formulas from electrostatics and/or from any treatment based on an analogous electrostatic problem. The presence of the exchange correlation and kinetic energy terms is the reason why the quantum world cannot be mapped into a problem of classical electrostatics. Thus, concerning the energy (and the electron density, which will be obtained from minimisation of the functional), the classical electrostatics and the quantum chemistry are divorced. They simply predict different things, because they are using different functionals.

The laws of quantum chemistry cannot be mapped exactly into an analogous electrostatic problem. One may think that using the same electrostatics entities (partial charges, diffusive charges, fixed dipoles, induced dipoles, quadrupoles, etc.) to describe the PES, and the DMS is a sign of consistency. Using the same charges for the PES and DMS is consistent in an imaginary world where the interaction between molecules is given by LJ centres and charges and/or multi-poles that obey a certain simple model derived from classical electrostatics. However, nature follows the laws of quantum chemistry. Once one recognises that classical electrostatics cannot describe the PES and DMS simultaneously, the step to use different models to describe the PES and DMS follows naturally. In fact, we have already mentioned that within team D (i.e. analytical potentials), there are two groups: analytical *ab initio* potentials and empirical potentials. Interestingly, the community developing *ab initio* analytical potentials is open to the use of different fits for the PES and DMS [51,53,54], and they regard charges, or partial charges, as merely fitting parameters to surfaces that were obtained from high-level *ab initio* calculations. They simply want to reproduce the high-level results for the two surfaces with high accuracy and they do not attach so much physical significance to the fitting parameters. However, in the community developing empirical potentials, we replaced the quantum problem by a simple electrostatic problem, and then implicitly assumed that ‘for consistency’ the same charges should be used for the PES and DMS. Using simple classical electrostatic models for the energy is fully inconsistent with the laws of the microscopic world. For this reason, we do not see any reason when developing empirical potentials (with parameters obtained to reproduce experimental properties) why we could not use different models/treatments for the PES and DMS.

6.4. Coarse-grained models of water and the dielectric constant

In 1990, Tomas Boublik, on a sabbatical leave in Madrid, taught me (among many other things) the perturbation theory proposed by Wertheim [59] for associating fluids, that was further extended by Chapman, Jackson and Gubbins [60], and which is nowadays known as SAFT [141]. He figured out that the theory could be very useful to implement an equation of state for fused hard-sphere chains [142], extending his classical work on the equation of state of hard-convex bodies [143] and hard-sphere mixtures [144]. In Wertheim’s/SAFT theory, the molecules are described by strong short-range associating sites (emulating the hydrogen bond), and the properties can be computed by using well-defined approximations. The theory is becoming quite successful for practical applications. Quite often, no dipoles or partial charges are used to define the interactions between molecules. Probably, it is fair to say that it is one of the most popular perturbation theories of liquids after

van der Waals [145]. In this theory, water is described as a spherical molecule, with four short-range association sites, two hydrogens and two 'lone pair electron' sites located in a tetrahedral arrangement. A very successful model within this framework is the Kolafa–Nezbeda model of water [56,57,146] that is composed by just a hard sphere and four association sites. The contribution of dispersive forces to the properties can be obtained either using a mean field approach, or eventually modifying the Kolafa–Nezbeda model, so that one has an LJ centre plus four associating sites [64,65]. This is a reasonable model of water, and has been shown that when used in combination with SAFT, it can describe many properties of water. Thus, SAFT provides a good description of water because the potential used to describe water (i.e. the PES) is simple but still reasonable. Probably, in a water test like that one presented in Table 2, these models will obtain a score lower than TIP4P/2005 but probably not worse than TIP3P (i.e. 2.7). The same is true for the mW model of water of Molinero and co-workers. In this case, the tetrahedral coordination of water is induced, not by using associating sites as in SAFT's approach, but by introducing three body forces [147]. This model has no charges. Molinero and co-workers have implemented the water test (not for all the properties considered in our initial test but for some of them) and showed that mW describes reasonably well water [148]. The score was lower (6.1) than TIP4P/2005 (7.8 for the properties selected by Molinero and co-workers) but still reasonable. Thus, mW is a reasonable PES of water. Let us emphasise again that both the SAFT and the mW PES do not use partial charges and still provide a reasonable description of water. Partial charges are certainly a possibility to induce tetrahedral order in water, but it is clear that it is not the only one. It is clear that the PES of water should indeed favour tetrahedral coordination of the molecules.

Now let us state a common criticism received by these models: 'they are not real models of water since they have no partial charges and therefore their dielectric constant is 1'. At this point, I hope to have succeeded in convincing the reader that this statement is absolutely wrong. It is based on the 'dogma', i.e. on the implicit assumption that the charges used to describe the PES should also be used in the description of the DMS. In this case, there are no charges in the PES, but you could certainly use charges to describe the DMS. I do not see any reason, why these type of 'coarse-grained' models could not be used for modelling salt solutions. In fact, some attempts to do that have been undertaken in the past [149–151] by introducing a short-range attraction to describe the interaction between the ions and water, and by using a Yukawa-like potential to describe the ion–ion interactions.

7. Conclusions

The main conclusion of this work is simple. For water, there are two surfaces, the PES and the DMS (strictly speaking,

three if one includes in the treatment the PS). Empirical potentials are aimed at describing the PES (i.e. the energy of the system in the absence of the field). It is also possible to use empirical expressions to describe the DMS. In the case you use partial charges/multi-poles to describe the PES, this is fine but there is no reason to use the same partial charges/multi-poles to describe the DMS. If you do not use partial charges/multi-poles in the description of the PES, as in coarse-grained models, there is no reason why you could not use partial charges/multi-poles in the description of the DMS. The implicit assumption that the same charges should be used in the description of the PES and of the DMS is a 'dogma'. This 'dogma' has contaminated all our analyses about the ability of water models to describe the dielectric constant. We need to revise our thinking about this property. There is nothing wrong (neither physically nor from a practical point of view) in using different charges for the PES and for the DMS. Therefore, the charges used for the PES are not necessarily the best to describe the DMS. The error also goes the other way around. In cases where the charges to be used in the description of the DMS seems more or less obvious (as when you have ions), these charges may not necessarily be the best to describe the PES. The idea also extends to the PS. The charges used to describe the PES and/or the DMS do not provide any information about how the polarisation of the system changes with an electric field. For this reason, it is also possible to include an approximate empirical expression to describe the PS.

Since we are not solving the Schrödinger equation, let us be practical when describing the PES and DMS. Empirical potentials should provide a good PES, thus describing all properties of water in the absence of an electric field. Once you have a good PES, then you need a good DMS to describe the dielectric constant of water. If the descriptions of the PES and DMS are correct, then you will correctly describe all the experimental properties of water, including the dielectric constant. Thus, the conclusion is that water is one molecule, with two surfaces (three when the PS is included), and that we have been doing during years of water simulations, one mistake.

Of course, although we used water for the discussion, since this is the molecule we have studied in more detail during these years (and it is probably the molecule that has been studied by more people); the central idea of this paper can also be extended to other molecules. The PES, DMS and PS are the three surfaces that should be fitted using different parameters. Now that the work aimed to study the effect of electric fields on matter is appearing in the literature, a good PES, a good DMS and (to lesser extent) a good PS are needed. If we continue using the 'dogma' to describe the PES, DMS and PS, then the predictions from computer simulations on the impact of electric fields on the properties and on the phase transitions of water (particularly on the ice Ih–water transition) may be incorrect.

It is time to depart from the path initiated by Bernal and Fowler [10].

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