# Entropy of Liquid Water from Ab Initio Molecular Dynamics

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ABSTRACT: We have computed the entropy of liquid water using a two-phase thermodynamic model and trajectories generated by ab initio molecular dynamics simulations. We present the results obtained with semilocal, hybrid, and van der Waals density functionals. We show that in all cases, at the experimental equilibrium density and at temperatures in the vicinity of 300 K, the computed entropies are underestimated, with respect to experiment, and the liquid exhibits a degree of tetrahedral order higher than in experiments. The underestimate is more severe for the PBE and PBE0 functionals than for several van der Waals functionals.
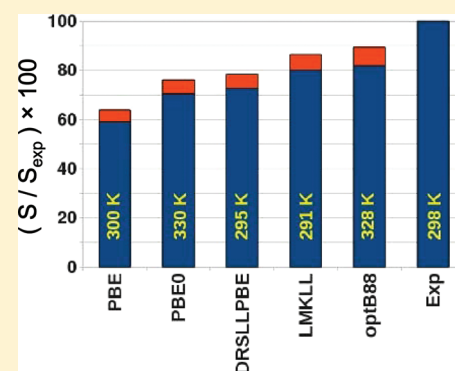
1. INTRODUCTION

The description of liquid water from first principles is an ongoing challenge. Accounting for the properties of this liquid requires the ability to describe, with the same level of accuracy, different bonds: intramolecular covalent bonds, intermolecular hydrogen bonds, the interaction between non-hydrogen bonded first neighbors molecules, and van der Waals interactions. None of the known density functionals or hybrid functionals are capable of giving a consistent, highly accurate description of all these bonds.[1] Therefore, the calculation of energy differences between the various configurations explored as molecules diffuse does not benefit from error cancellations as much as in simpler systems, where similar bonds are present during time evolution. As a consequence, even the simplest properties of water, e.g., structure and self-diffusion, have proved difficult to compute accurately with ab initio molecular dynamics (MD). In addition, efficient ways to account for proton quantum effects are in principle required to accurately simulate liquid water.[2]

The simulation cells affordable at present in ab initio MD simulations of water with semilocal functionals contain at most $\simeq 128-150$ molecules (often $\simeq 32-64$ molecules), and sampling is done up to at most $\simeq 100-150$ ps (often over $10-50$ ps). The computational cost increases when using nonlocal van der Waals functionals and even more so when employing hybrid functionals (that require the calculation of the Fock exchange operator), and thus affordable cell sizes and simulation times decrease. Therefore, many first-principle studies of the pure liquid have concentrated on structural, vibrational, and electronic properties and self-diffusion. Very few investigations of thermodynamic and transport properties have been reported in literature,[3,4] as they require the use of a relatively large cell and long simulation times. Hence, the debate on the structural properties of water has been mostly based on the calculation of pair correlation functions.

In an attempt to better understand the performance of several density functionals in describing the properties of liquid water, we have computed the total entropy of the liquid, the tetrahedral component of the entropy,[5] and a tetrahedral order parameter,[6] using semilocal, hybrid,[1] and van der Waals density functionals (vdW-DFs).[7] Although our results have been obtained with small supercells (containing 32 and 96 molecules) and thus are not highly accurate, the comparison between the values obtained with different functionals is significant and interesting, as is the comparison with experiment. We find that at the experimental equilibrium density and close to 300 K the total entropy of liquid water is substantially underestimated with all functionals considered here. The total entropy remains moderately underestimated also above room temperature ($\simeq 400$ K), at conditions under which the agreement with experiment for pair correlation functions is good. All functionals overestimate the tetrahedral order in the liquid, although some vdW-DFs appear to give results in better agreement with experiment than semilocal and hybrid functionals.

Accurate calculations of the total entropy (S) of water using MD or Monte Carlo and empirical potentials have been reported, e.g., by Wang et al.[8] and by Shirts and Pande.[9] The former use suitable expansions of correlation functions, and the latter employ free-energy perturbation methods. Shah et al.[10] computed the excess entropy (S_{ex}) of water using the TIP3P empirical potential and a quasichemical theory framework based on the potential distribution theorem.[11] Their computed value is in satisfactory agreement with experiment.[12] The excess entropy

is defined as $S_{ex} = S - S_{ig}$, where S_{ig} is the entropy of an ideal gas. Quasichemical theory[10] was also applied to trajectories obtained using ab initio MD[3] at the BLYP-D level of theory. However, the authors of ref 3 reported only the excess free energy not the excess entropy.

Recently, Lin et al.[13] have suggested a two-phase thermodynamic model[14] based on the calculation of densities of translational, rotational, and vibrational states. Although exact only in the dilute limit, this approach has been shown to give results for the total entropy of water in satisfactory agreement with those obtained with the more accurate techniques of ref 8 and ref 9. The model of Lin et al.[13] underestimates the results of refs 8 and 9 by ~5%. The great advantage of the method of ref 13 is that it requires short simulation times (from 10 to 20 ps), and it appears to give converged results also for small cells, as discussed below in the Methods section. It is therefore a suitable technique to be combined with ab initio MD simulations.

The rest of the paper is organized as follows: In section 2 we present the approach used to compute the total entropy of liquid water. Our results are discussed in section 3, and our conclusions are given in section 4.

2. METHODS

The total entropy of a condensed system may be expressed as

$$S = k_B \int_0^\infty d\omega S(\omega) W(\omega) \tag{1}$$
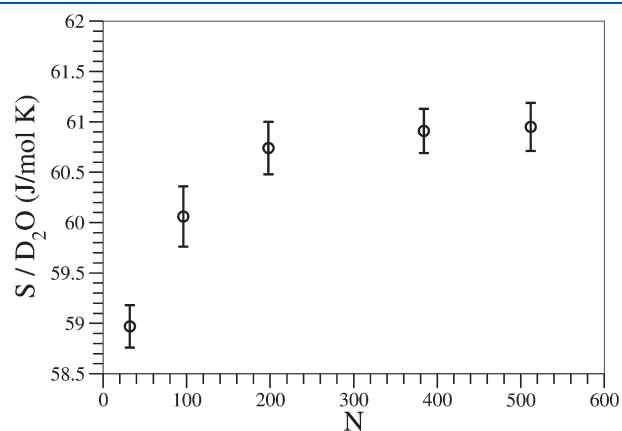
Figure 1. Size effects. Total entropy of liquid water computed with classical molecular dynamics and a flexible potential (SPC/Fd), as a function of the number of molecules (N = 32, 96, 192, 384, and 512) in the simulation cell, at ~300 K and the experimental equilibrium density.

where k_B is the Boltzmann constant; $S(\omega)$ is the density of normal modes at frequency ω; and in the case of a harmonic system, the weighting function $W(\omega)$ is

$$W(\omega) = \frac{\beta h \omega}{\exp(\beta h \omega) - 1} - \ln[1 - \exp(-\beta h \omega)] \tag{2}$$

where h is the Plank constant and $\beta = 1/k_B T$. For a liquid or a gas, low-frequency diffusive modes yield the largest contribution to the entropy, and the harmonic approximation (eq 2) is not valid. Li et al.[14] suggested to write S as a sum of two contributions $S = S^{gas} + S^{solid}$, where the gaslike component S^{gas} is approximated by that of hard spheres at a given density and temperature. For the solid-like part S^{solid}, eq 2 may be used. For a molecular liquid, the density of states $S(\omega)$ is decomposed into translational (S_{tra}), rotational (S_{rot}), and vibrational (S_{vib}) components

$$S(\omega) = S_{tra}(\omega) + S_{rot}(\omega) + S_{vib}(\omega) \tag{3}$$

The translational and rotational parts contain both a gaslike and a solid-like component, while $S_{vib}(\omega)$ has only a solid-like component. The solid-like part of the translational density of states (DOS) is obtained from the center of mass velocities of the molecules; the rotational DOS is calculated from the molecule angular velocities; and the vibrational part is determined from the velocities, as obtained from MD trajectories, once the translational and rotational components have been subtracted.

The excess entropy of a system, often used to characterize the properties of water, is related to the total entropy by a simple relationship: $S_{ex} = S - S_{ig}$. S_{ex} may be expressed as an infinite sum of n-point density correlations $S_{ex} = \Sigma_{n=2}^\infty S_n$. For liquid water, it has been shown that the dominant contribution to S_{ex} comes from the two body term S_2 (known as "pair entropy"),[15] that in turn can be approximated by the sum of a translational and rotational term $S_2 = S_2^{tra} + S_2^{rot}$. In our calculations, we obtained S_2^{tra} from the two-point translational correlations, defined as

$$S_2^{tra} = -2\pi \rho k_B \int [g(r)\ln(g(r)) - (g(r) - 1)]r^2 dr \tag{4}$$

where ρ is density and $g(r)$ is the oxygen–oxygen radial distribution function.

We also computed the tetrahedral entropy S_Q as defined in ref 5

$$S_Q = S_0 + \frac{3}{2} k_B \sum_{k=1}^N \ln(1 - Q_k) \tag{5}$$

Table 1. Total Entropy (S) of Heavy Liquid Water and Its Translational (S_{tra}), Rotational (S_{rot}), and Vibrational (S_{vib}) Components and Excess Entropy (S_{ex}), Translational Pair Entropy (S_2^{tra}), Tetrahedral Entropy (S_Q), and the Average of the Tetrahedral Order Parameter $\langle Q_k \rangle$, as Computed with Classical MD and the Flexible Model SPC/Fd[30] [a]

N	T (K)	S_{tra}	S_{rot}	S_{vib}	S	$S_{ex} = S - S_{ig}$	$S_2^{tra} \approx S_{ex}^{tra}$	$S_Q - S_0$	$\langle Q_k \rangle$
32	298 ± 19	47.93 ± 0.20	10.85 ± 0.008	0.10 ± 0.00	58.97 ± 0.21	−71.45	−13.25	−15.44	0.65 ± 0.18
96	302 ± 11	49.00 ± 0.29	10.86 ± 0.010	0.20 ± 0.00	60.06 ± 0.30	−70.36	−13.41	−14.33	0.63 ± 0.18
192	301 ± 8	49.57 ± 0.25	10.96 ± 0.008	0.21 ± 0.00	60.74 ± 0.26	−69.68	−13.44	−14.09	0.62 ± 0.18
384	296 ± 5	49.93 ± 0.22	10.79 ± 0.007	0.19 ± 0.00	60.91 ± 0.22	−69.51	−13.39	−14.33	0.63 ± 0.18
512	299 ± 5	50.33 ± 0.24	10.42 ± 0.004	0.20 ± 0.00	60.95 ± 0.24	−69.47	−13.39	−14.21	0.62 ± 0.18

[a] All values of entropy are in J/(mol K). S_{ig} is the entropy of an ideal gas of water molecules.[43] Results are presented as a function of the number of molecules N included in the simulation cell and the temperature T. S^{D_2O}[expt.] = 71.77[34] and 72.25 J/(mol K)[35] at 298 K; S_{ex}[expt.] = −58.99 J/(mol K);[43] $\langle q \rangle^{D_2O}$[expt.] = 0.593[36] at 298 K.

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Table 2. Total Entropy (S) of Heavy Liquid Water and Its Translational (S_{tra}), Rotational (S_{rot}), and Vibrational (S_{vib}) Components and Excess Entropy (S_{ex}), Translational Pair Entropy (S_2^{tra}), Tetrahedral Entropy (S_Q), and the Average of the Tetrahedral Order Parameter $\langle Q_k \rangle$, As Computed with Ab Initio MD and the PBE Functional[17,18] ^{a}

ρ	T (K)	S_{tra}	S_{rot}	S_{vib}	S	$S_{ex} = S - S_{ig}$	$S_2^{tra} \approx S_{ex}^{tra}$	$S_Q - S_0$	$\langle Q_k \rangle$
ρ_0 (96)	407 ± 16	51.49 ± 0.44	12.51 ± 0.03	0.87 ± 0.00	64.90 ± 0.47	-65.52	-14.45	-18.94	0.72 ± 0.18
ρ_0 (32)	408 ± 27	51.79 ± 0.88	12.67 ± 0.03	0.86 ± 0.00	65.31 ± 0.91	-65.11	-13.19	-18.43	0.71 ± 0.18
ρ_L (32)	404 ± 27	57.07 ± 0.39	13.64 ± 0.02	0.80 ± 0.00	71.51 ± 0.41	-58.91	-12.59	-16.88	0.65 ± 0.24

^{a} All values of entropy are in J/(mol K). S_{ig} is the entropy of an ideal gas of water molecules.[43] Results are presented as a function of the density of the liquid (ρ_0 is the experimental equilibrium density, and $\rho_L = 0.85$ g/cm^{-3}) and the temperature T, for different cell sizes (the number of water molecules used in the MD cell is given within brackets in the first column). S^{D_2O}[expt.] = 71.77[34] and 72.25 J/(mol K)[35] at 298 K; S_{ex}[expt.] = -58.99 J/(mol K);[42] $\langle q \rangle^{D_2O}$[expt.] = 0.593[36] at 298 K.

Table 3. Total Entropy (S) of Heavy Liquid Water and Its Translational (S_{tra}), Rotational (S_{rot}), and Vibrational (S_{vib}) Components and Excess Entropy (S_{ex}), Translational Pair Entropy (S_2^{tra}), Tetrahedral Entropy (S_Q), and the Average of the Tetrahedral Order Parameter $\langle Q_k \rangle$, As Computed with Ab Initio MD and Various Functionals (See Text)^a

functional	T (K)	S_{tra}	S_{rot}	S_{vib}	S	$S_{ex} = S - S_{ig}$	$S_2^{tra} \approx S_{ex}^{tra}$	$S_Q - S_0$	$\langle Q_k \rangle$
PBE	300 ± 20	34.84 ± 0.25	7.60 ± 0.08	0.30 ± 0.00	42.74 ± 0.33	-86.68	-19.13	-24.48	0.82 ± 0.13
PBE0	330 ± 24	41.87 ± 0.70	8.79 ± 0.05	0.24 ± 0.00	50.90 ± 0.75	-79.52	-14.86	-19.71	0.73 ± 0.17
DRSLLPBE	295 ± 20	42.18 ± 0.45	10.05 ± 0.05	0.24 ± 0.00	52.47 ± 0.50	-77.95	-13.29	-18.42	0.72 ± 0.16
LMKLL	291 ± 20	47.09 ± 0.34	10.47 ± 0.02	0.23 ± 0.00	57.79 ± 0.36	-72.63	-13.01	-16.14	0.67 ± 0.17
optB88	328 ± 24	47.96 ± 0.75	10.85 ± 0.04	0.40 ± 0.00	59.21 ± 0.81	-71.21	-12.75	-17.72	0.70 ± 0.17

^{a} All values of entropy are in J/(mol K). S_{ig} is the entropy of an ideal gas of water molecules.[43] The density was fixed at the experimental equilibrium density in all cases. S^{D_2O}[expt.] = 71.77[34] and 72.25 J/(mol K)[35] at 298 K; S_{ex}[expt.] = -58.99 J/(mol K);[42] $\langle q \rangle^{D_2O}$[expt.] = 0.593[36] at 298 K.

where $S_0 = N k_B[\ln \Omega_0 + (3/2)\ln(8/3)]$; Ω_0 is the volume of the cell; N is the number of molecules in the cell; and

$$Q_k = 1 - \frac{3}{8} \sum_{i=1}^{3} \sum_{j=i+1}^{4} \left(\cos \theta_{ikj} + \frac{1}{3} \right)^2 \quad (6)$$

is the tetrahedral order parameter as defined in ref 6. θ_{ikj} is the angle formed by the kth molecule and its nearest neighbors i and j. Perfect tetrahedral order yields $\langle Q_k \rangle = 1$, while in the absence of any correlation (i.e., for an ideal gas) $\langle Q_k \rangle = 0$.

We carried out first-principles MD simulations with several functionals, using the *Qbox* code:[16] the semilocal functional PBE,[17,18] the hybrid functional PBE0,[19] and the vdW-DFs DRSLLPBE,[20] LMKLL,[21] and optB88.[22] In vdW-DFs, the exchange correlation energy is defined as

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl} \quad (7)$$

where E_x^{GGA} is the exchange energy as defined for generalized gradient approximations (GGA) functionals; E_c^{LDA} is the local correlation energy obtained within the local density approximation (LDA); and E_c^{nl} is the nonlocal correlation energy, expressed as

$$E_c^{nl} = \frac{1}{2} \int d^3 \vec{r} \int d^3 \vec{r}\,' n(\vec{r}) \phi(\vec{r}, \vec{r}\,') n(\vec{r}\,') \quad (8)$$

The kernel ϕ is a universal function,[23] and it must be evaluated numerically. In DRSLLPBE,[20] $E_x^{GGA} = E_x^{PBE}$, and the kernel ϕ is the one originally proposed in ref 23. In the optB88 functional,[22] $E_x^{GGA} = E_x^{opt-B88}$, where B88 stands for the Becke exchange functional[24] and opt indicates that some of the parameters entering the B88 functional have been optimized to reproduce the binding energies of the molecules of the S22 data set, as obtained within CCSD(T); ϕ is the same as in ref 23. In LMKLL,[21] $E_x^{GGA} = E_x^{PW86}$,[25] and a modified screening factor is adopted in the definition
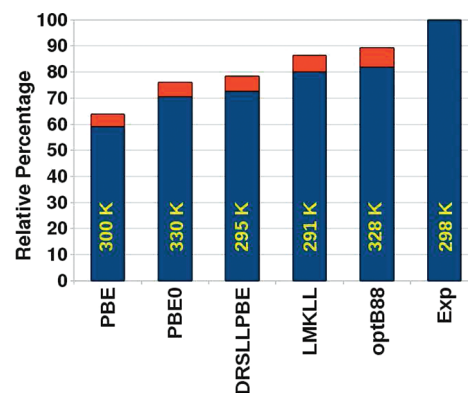
Figure 2. Relative percentage of the computed total entropy of heavy liquid water, with respect to experiment, as obtained with different density functionals (PBE, PBE0, DRSLLPBE, LMKLL, and optB88, see text) at a temperature (specified in the bars) close to 300 K. The experimental value of the total entropy is 72.25 J/(mol K)[35] (71.77 J/(mol K)[34]). All the simulations were performed within the NVE ensemble, at the experimental equilibrium density. The red bars indicate the estimated, combined error ($\simeq 8\%$) of size effects (see Figure 1) and the approximation contained in the two-phase thermodynamic model used here.[13]

of the kernel function ϕ. The PBE0 exchange-correlation functional is defined as $E_{xc}^{PBE0} = E_{xc}^{PBE} + (1/4)(E_x^{HF} - E_x^{PBE})$, where E_{xc}^{PBE} and E_x^{PBE} are the PBE exchange-correlation and exchange functionals, respectively, and E_x^{HF} is the Hartree–Fock exchange energy. The structural and vibrational properties of water obtained with PBE, PBE0, and vdW-DFs have been reported and discussed elsewhere.[7,26,27]

We performed simulations with cubic cells of 32 deuterated water molecules at a fixed density of 1.1 g/cm^3. In the case of the PBE functional, we compared our results with those obtained with a cell of 96 molecules at a density of 1.1 g/cm^3 and with a cell
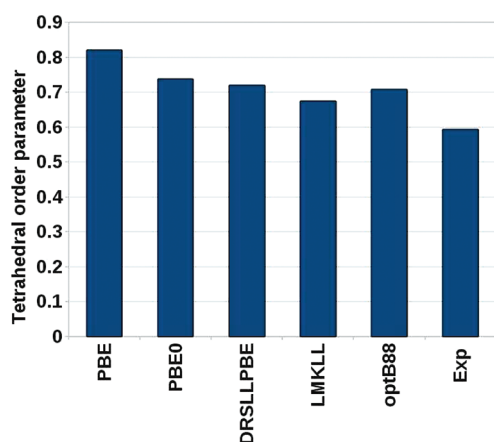
Figure 3. Average values of the tetrahedral order parameter $\langle Q_k \rangle$ for heavy liquid water from ab initio molecular dynamics, with respect to the one estimated from experimental data, 0.593[36] at 298 K. The conditions of the simulations and the functionals are the same as in Figure 2.

of 32 molecules at a density of 0.85 g/cm^3. We used plane wave basis sets and norm-conserving pseudopotentials of the HSCV type[28,29] with a kinetic energy cutoff of 85 Ry. Simulations were carried out with a time step of 10 au in the NVE ensemble, within the Born—Oppenheimer approximation, and trajectories were collected for 20—30 ps for each run. We used deuterium instead of hydrogen for computational convenience, so as to use a larger MD time step.

Since we employed small supercells in our ab initio simulations, we first tested size effects using a flexible, classical potential SPC/Fd.[30] Classical simulations of heavy water (N = 32, 96, 192, 384, 512) were carried out within the NVE ensemble at 300 K, using the DL_POLY_2 simulation package.[31] Each simulation was run for 50 ps, with an Ewald sum precision of 10^{-6} and a time step of 0.5 fs. Our results are shown in Figure 1 and Table 1 for several deuterated water samples. Although the SPC/Fd potential has been fitted to describe hydrogenated water, here we carried out calculations for deuterated water for consistency with our ab initio results that are focused on the heavy liquid. Figure 1 shows that entropy values are reasonably well converged for simulation cells with $N > \sim 100$, and even for the smallest cell size of 32 molecules, the underestimate of converged results is modest, about 3%. We also tested convergence as a function of the simulation time and found that after 10—20 ps results are well converged at $T \geq$ 300 K, as reported by Lin et al.[13] Table 1 shows that the vibrational contribution to the total entropy is small compared to the rotational and translational ones, the latter being the most important. As expected, the computed values of the total entropy are very sensitive to small temperature variations.

We now turn to the discussion of results obtained with ab initio MD. When comparing with experiment, to assess the accuracy of the electronic structure theory, we will take into account that an estimated $\simeq$8% error on our results comes from the combined effect of small cell sizes (3%) and the use of the thermodynamical model of ref 13 (5%).

3. RESULTS AND DISCUSSION

In the past decade, the PBE functional has been used in many simulations of water at different temperatures (T) and densities (ρ);[2,32,33] therefore, we first considered the effect of T and ρ on the value of the total entropy obtained within PBE. The results
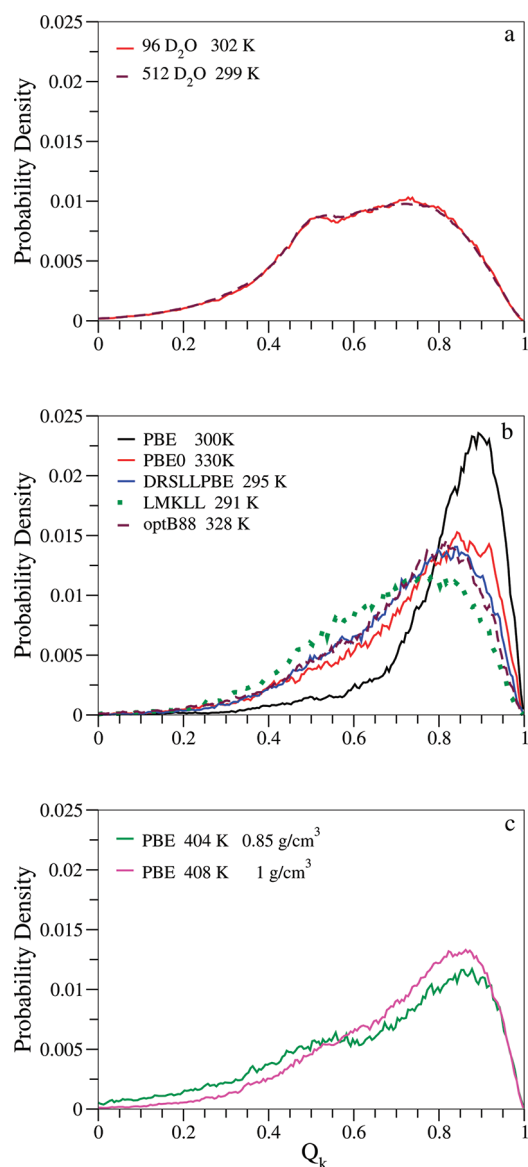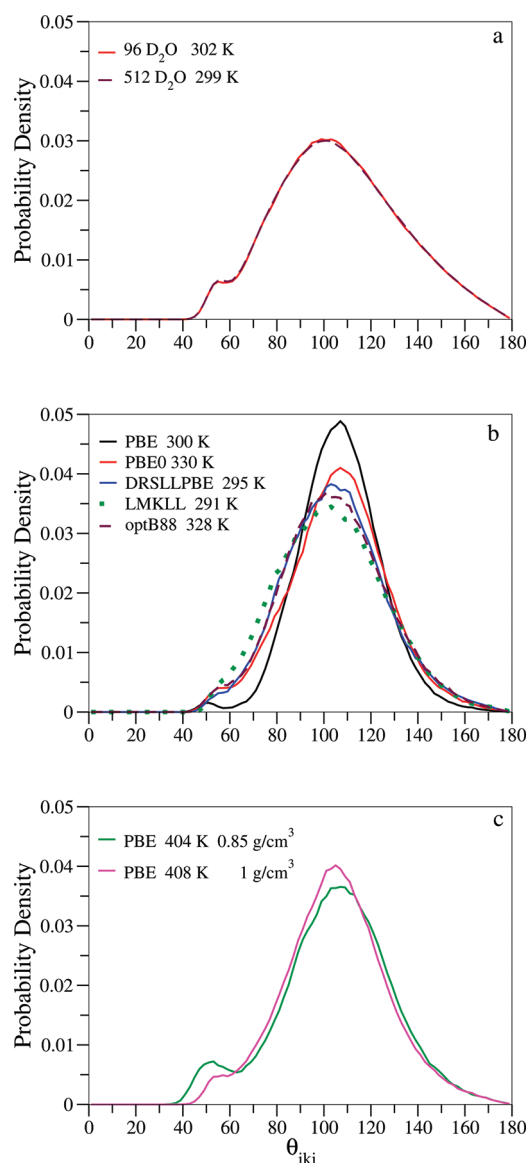

Figure 4. Distribution of the tetrahedral order parameter Q_k. Results are presented for (a) classical simulations with the SPC/Fd potential; (b) several density functionals at temperatures close to 300 K; and (c) the PBE functional at $\sim$400 K and two different densities.

are reported in Table 2. Within computational error bars, the calculated entropy of 96 and 32 water molecule samples is identical at $\sim$400 K and the experimental equilibrium density (ρ_0). As discussed, e.g. in ref 33, these simulation conditions yield structural and diffusion properties of the liquid in good agreement with experimental results obtained at 298 K. Taking into account the 8% error discussed in section 2, the error of the PBE functional for the total entropy is estimated to be 1—2% compared to the experimental values (71.77[34] and 72.25 J/(mol K)[35]). Therefore, even at 400 K, the liquid appears to exhibit a slightly higher degree of order with respect to experiments. Consistent with these results, we find that the tetrahedral order parameter (see Table 2) is larger than the one estimated from measured correlation functions.[36]

The equilibrium density of water using PBE has been predicted to be lower than experiment, namely, 0.85—0.90 g/cm^3,[20,37] for

Figure 5. Distribution of angles θ_{ikj}. Results are presented for (a) classical simulations with the SPC/Fd potential; (b) several density functionals at temperatures close to 300 K; and (c) the PBE functional at ~400 K and two different densities.

light and heavy water, respectively. These results are consistent with our calculations of pressure at the fixed experimental density, yielding a value of ~1 GPa.[38] We have repeated calculations of the entropy for a water sample at ~400 K and ρ = 0.85 g/cm³, and we find a value of the entropy that overestimates experiment by approximately 8%. We note that the oxygen—oxygen pair correlation function ($g_{OO}(r)$) calculated with a 32 water molecule cell at ~400 K and a density of 0.85 g/cm³ is more structured than that obtained at ρ_0 and in worse agreement with neutron diffraction data at 298 K than the $g_{OO}(r)$ computed at ρ_0.[27] As expected, if T is lowered from 400 to 300 K, at the experimental equilibrium density, the total entropy of the liquid within PBE turns out to be severely underestimated (see Table 3).

Next, we investigated the effect of different descriptions of the exchange correlation energy on the computed value of the total

entropy. Our findings are reported in Table 3, and the relative percentage of computed entropy with respect to the experimental value is shown in Figure 2. In the vicinity of 300 K, at the experimental equilibrium density all functionals severely underestimate (10—30%) the total entropy of liquid water.[39] van der Waals functionals appear to perform better than PBE0 (in particular optB88), although underestimates persist, the lowest one being of the order of 10%. If T is raised, e.g., to 368 K, the entropy obtained with PBE0 is still underestimated by 10% with respect to the measured value. These findings, together with the data obtained for the tetrahedral order parameter (see Figure 3) and for the tetrahedral and pair entropy, indicate that the degree of order in the liquid, as described by semilocal, hybrid, and van der Waals functionals, is too high, with respect to experiment. Also our results for the excess entropy are all consistent with a high tetrahedral order in the liquid. Most likely, with all these functionals, although to different extents, hydrogen bonded configurations are too energetically favored, compared to non-hydrogen bonded ones, and thus the liquid turns out to be more ordered (icelike) than in reality. Therefore, at least qualitatively, the major error of the density functional theory used to describe water appears to be in the energy difference between hydrogen bonded and non-hydrogen bonded configurations occurring within the first (and perhaps also second) solvation shell.

Another indicator of the order in the liquid is the distribution of the tetrahedral order parameter, shown in Figure 4. The distribution obtained with a classical model (Figure 4a) shows two peaks (~0.5 and ~0.75), but all ab initio results in the vicinity of 300 K (Figure 4b) show only one peak, similar to what is found with classical models in a regime where the liquid is supercooled.[5] At 400 K, the PBE results show a peak or a shoulder, at lower values of the tetrahedral parameter (Figure 4c), depending on the chosen density. Similar information is obtained from the distribution of angles θ_{ikj} (Figure 5), where it is seen that the probability of sampling angles below 70° becomes significant only at 400 K when using the PBE functional.

4. CONCLUSIONS

We have presented ab initio calculations of the entropy of liquid water using semilocal,[17,18] hybrid,[19] and vdW-DFs.[20−22] In the vicinity of 300 K and at the experimental equilibrium density, we have found that all functionals underestimate the total entropy of the liquid by factors ranging from 10% to 30%, after taking into account underestimates coming from the use of a two-phase thermodynamic model and by size effects. These results, consistent with our computed values for a tetrahedral order parameter and the tetrahedral entropy, indicate that all functionals considered here provide a description of the liquid with a degree of tetrahedral order that is too high, compared to experiment. At higher T (for example, 400 K for PBE), the agreement with experiment is instead satisfactory, although a modest underestimate of the total entropy remains. Most likely the major error of all density functionals comes from an overestimate of the energy difference between hydrogen bonded and non-hydrogen bonded configurations explored by the liquid. This hypothesis is consistent with the results available for ice[40] and for the water dimer.[7] At ambient conditions the structural properties of ice are in better agreement with experiment when using PBE and vdW-DFs than those of liquid water, indicating that hydrogen bonds are reasonably well described by these functionals (although some discrepancies with measurements are

present; these will be discussed elsewhere[41]). Likewise, the potential energy curve of the hydrogen bonded dimer is relatively well described by all the functionals considered here, when compared with high level CCSD(T) quantum chemistry calculations.[7]

Our findings contribute to assess the accuracy of various functionals for the description of water. However, important data are still missing, namely, the equilibrium density and the melting point of the liquid for the various functionals. These results are available (although with relatively large error bars) only for the PBE functional, among those considered in this paper.

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