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Liquid Water from First Principles:
Validation of Different Sampling Approaches

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Abstract

A series of first principles molecular dynamics and Monte Carlo simulations were carried out for liquid water to assess the validity and reproducibility of different sampling approaches. These simulations include Car-Parrinello molecular dynamics simulations using the program `CPMD` with different values of the fictitious electron mass in the microcanonical and canonical ensembles, Born-Oppenheimer molecular dynamics using the programs `CPMD` and `CP2K` in the microcanonical ensemble, and Metropolis Monte Carlo using `CP2K` in the canonical ensemble. With the exception of one simulation for 128 water molecules, all other simulations were carried out for systems consisting of 64 molecules. It is found that the structural and thermodynamic properties of these simulations are in excellent agreement with each other as long as adiabatic sampling is maintained in the Car-Parrinello molecular dynamics simulations either by choosing a sufficiently small fictitious mass in the microcanonical ensemble or by Nosé-Hoover thermostats in the canonical ensemble. Using the Becke-Lee-Yang-Parr exchange and correlation energy functionals and norm-conserving Troullier-Martins or Goedecker-Teter-Hutter pseudopotentials, simulations at a fixed density of 1.0 g/cm^3 and a temperature close to 315 K yield a height of the first peak in the oxygen–oxygen radial distribution function of about 3.0, a classical constant-volume heat capacity of about 70 J K^{-1} mol^{-1}, and a self-diffusion constant of about 0.1 Å^2/ps.

I. INTRODUCTION

Water holds a unique role among liquids, not only because of its ubiquity and importance on earth, but more so because of its anomalous liquid properties. Thus, understanding its properties has been a grand challenge for liquid state theory[1] and molecular simulation.[2] The first particle-based simulations of liquid water using pairwise empirical potentials were carried out almost 40 years ago.[3] However, the strong dipole moment and large polarizability of water and its participation in many chemical processes, particularly its self-dissociation, pose a challenge for empirical potentials. Although great strides have been made in the development of empirical force fields for water, none of these has yet succeeded to yield a quantitative description of the thermodynamic, structural, and dynamic properties of water over its entire liquid range.[4] In contrast, an *ab initio* representation of water affords the opportunity to study both physical and chemical properties of water.

The first Car-Parrinello molecular dynamics (CPMD) simulation[5] for liquid water employing a quantum-mechanical description of the molecular interactions was performed in the early nineties,[6] but available computer resources limited this CPMD simulations to a small system size (32 molecules) and short simulation length (1.5 and 2 ps for equilibration and production, respectively). However, it should be emphasized that without the gains in efficiency afforded by the CPMD approach,[5] which propagates the electron density using classical dynamics using a fictitious electron mass, μ, first principles simulations for liquid water would not have been possible in the early nineties.

Large increases in the available computer power and in the efficiency of the simulation approaches are now enabling more systematic studies of the liquid properties of water using first principles approaches. In particular, using the CPMD approach it is now possible to follow the trajectories of 64 water molecules for more than 10 ps[7–9] or of 216 water molecules for about 5 ps.[10] Thus, one should expect that the field of first principles simulations of water has matured in the 10 years following the initial simulation.[6] However, two independent reports by Asthagiri *et al.*[11] and Grossman *et al.*[12] have recently questioned the reproducibility and validity of CPMD simulations for liquid water. Asthagiri *et al.* suggested that different analysis procedures, different choices of the fictitious electron masses, or different thermostatting procedures "could play a role ... in the prevailing nonuniform agreement of the simulation results".[11] Grossman *et al.*[12] evaluated among other parameters explicitly the dependence of structural and dynamic properties on the fictitious electron mass and for a relatively small value of $\mu = 340$ a.u. obtained a liquid phase that is significantly more structured than seen in previous simulations.[7–9]

In light of the recent criticism, the goal of this research is to further assess the reproducibility and validity of first principles simulations of liquid water using different approaches to sample the trajectories (e.g, different electronic structure methods, different fictitious electron masses, and different statistical mechanical ensembles), but maintaining the other simulation parameters (density functional, pseudopotential, and to the extent possible temperature). The next section provides a brief description of the simulation details and analysis parameters, and in the following section the results are presented and discussed.

II. SIMULATION METHODS AND DETAILS

The first principle simulations of this work were performed using the computer programs `CPMD` and `CP2K` that are developed by a large group of researchers and are publicly available.[13,14] Car-Parrinello molecular dynamics[5] combines density functional theory with extended systems molecular dynamics[15] via the introduction of a fictitious electronic kinetic energy term into the Lagrangian. This classical treatment of the electronic degrees of freedom allows for a very efficient sampling of the Kohn-Sham energy functional[16] for soft-condensed matter systems, but requires the use of a fictitious electron mass, μ, as a parameter of the Lagrangian that needs to be chosen judiciously to allow for the adiabatic separation of nuclear and electronic degrees of freedom.[17] Furthermore, the use of separate Nosé-Hoover thermostats[18] for the ionic and electronic degrees of freedom enables `CPMD` to control the adiabatic separation for first principles simulations in the canonical ensemble.[19] The computer program `CPMD` also allows one to sample molecular dynamics trajectories using Born-Oppenheimer dynamics, i.e. quenching the electronic structure at every time step.[20]

The program `CP2K`[14] is a general purpose program that builds upon the success of `CPMD`. The electronic structure part of `CP2K` uses the Gaussian plane wave (GPW) method[21] for the calculation of forces and energies. The GPW method is based on the Kohn-Sham formulation[16] of density functional theory and employs a hybrid scheme of Gaussian and plane wave functions. Here the Kohn-Sham orbitals are expanded using a linear combination of atom-centered Gaussian-type orbital functions, and an auxiliary basis set of plane waves describes the electronic charge density.[21] This combination is chemically more intuitive and computationally more efficient than sole use of a plane wave basis set. First principles simulations with `CP2K` sample directly from the Born-Oppenheimer surface.

The computational efficiency of the GPW energy routine is exploited in `CP2K`-MC, a module of `CP2K` that allows for Monte Carlo sampling from various statistical-mechanical ensembles,[2] including those with fluctuating particle numbers. Use of a Monte Carlo framework is advantageous because temperature, pressure, and chemical potential are explicitly accounted for in the acceptance rules,[2] and the momentum part of the Hamiltonian can be removed by integration,[22] i.e. the configurational properties are independent of any choice of mass. Our Monte Carlo implementation for water in the canonical ensemble employs three different types of trial moves: (i) translations of rigid molecules, (ii) rigid-body rotations around the molecular center of mass, and (iii) conformational moves altering either bond length or angle. The type of move is selected at random and the separate move types ensure equipartition of the translational, rotational, and vibrational degrees of freedom of the system. Pre-sampling of trajectories[23,24] with an inexpensive approximate potential[25] for a short sequence of moves is carried out to reduce the number of expensive *ab initio* energy evaluations, thereby enhancing the computational efficiency. The current implementation uses a sequence of 16 pre-sampling moves per GPW energy calculation resulting in about two accepted trial displacements (with maximum displacements that yield a 50% acceptance rate for the pre-sampling moves). The length of the Monte Carlo simulations is measured in MC cycles, where one cycle consists of N GPW calculations, but it should be noted that one of these cycles encompasses about $2N$ accepted trial displacements, that is four times more than in a conventional simulation without pre-sampling.

Table I summarizes the details for the nine simulation runs for liquid water carried out for this work. The choices of BLYP density functional with generalized gradient approximation,[26] norm-conserving Troullier-Martins pseudopotential[27] with Kleinman-Bylander transformation to fully non-local form,[28] and plane wave cut-off for the Kohn-Sham orbitals follow those used in previous CPMD simulations for water.[7,8] Two different choices for the fictitious electron mass were employed in some of the runs: a relatively low value of $\mu = 400$ a.u. and a high value of $\mu = 800$ a.u. that is at the upper end of values used previously for liquid H_2O (μ can be increased by a factor of $\sqrt{2}$ for simulations of D_2O). In the `CP2K` simulations, the norm-conserving pseudopotentials of Goedecker, Teter, and

Hutter (GTH)[29] were applied to remove the core electrons, a triple-zeta valence basis set augmented with two sets of *d*-type or *p*-type polarization functions (TZV2P) optimized for the use with the GTH pseudopotentials was employed for O and H, and a charge density cut-off of 280 Ry was used for the auxiliary plane wave basis set.

To reduce the risk that our simulations fall outside the liquid phase range for the BLYP density functional, a slightly elevated target temperature of 315 K was used. The molecular dynamics simulations were equilibrated for about 3 to 5 ps prior to the production runs, and about 200 Monte Carlo cycles were used to equilibrate the two `CP2K`-MC-NVT runs. In the two simulations using Born-Oppenheimer dynamics, `CPMD`-NVE-BO and `CP2K`-MD-NVE, the energy is converged to 1 part in 10^7 at every step and the total energy is conserved over 10 ps to about 2 parts in 10^6.

The radial distribution functions (RDFs) were calculated using a bin width of 0.005 Å for separations smaller than 1.2 Å (only including the intramolecular oxygen–hydrogen bond) and a bin width of 0.02 Å for larger separations. The coordination numbers were evaluated from the value of the oxygen–oxygen number integral at the position of the first minimum in the corresponding RDF. The classical constant-volume heat capacities were calculated from the fluctuations[22,30] either of the kinetic energy for microcanonical simulations, the total energy for molecular dynamics runs in the canonical ensemble, or of the potential energy for the Monte Carlo simulations to which the classical contribution of the momentum part was added. Finally, the self-diffusion constants were computed via the Einstein relation from linear fits to the diffusive regime (using a range from 3–6 ps) of the center-of-mass mean square displacements that were averaged by shifting the time origin by 1 ps.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the oxygen–oxygen and oxygen–hydrogen RDFs for four different simulations in the microcanonical ensemble. The most important result is the striking uniformity of the structural results for the four simulations. Neither switching computer programs for Born-Oppenheimer dynamics, nor switching from Born-Oppenheimer dynamics to CP dynamics with $\mu = 400$ a.u., nor increasing the system size from 64 to 128 molecules leads to the nonuniformity observed in previous first principles simulations for water.[11,12] Here it should be noted that some scatter is unavoidable because of (i) statistical uncertainties (a variance of about 0.1 was estimated for the RDFs) arising from "short" simulation length and "small" system size compared to simulations using empirical potentials, and (ii) unavoidable variations in the ionic temperature (see Table I) for simulations in the microcanonical ensemble. The simulation results for run `CPMD`-NVE-800 are not reported because an adiabatic separation of nuclear and electronic degrees of freedom was not achieved in this simulation (see below).

The oxygen–oxygen and oxygen–hydrogen RDFs for the two molecular dynamics and two Monte Carlo simulations in the canonical ensemble ($T_{\text{ion}} = 315$ K) are shown in Figures 3 and 4. Again, the agreement in these structural data is very satisfactory and the small differences between these simulations appear to be well within the statistical uncertainties. It should be emphasized that a value of $\mu = 800$ a.u. yields stable CPMD trajectories for simulations in the canonical ensemble when massive thermostatting of the nuclear and electronic degrees of freedom is employed.

The numerical values for the height, $g_{\text{OO,max}}$, and location, $r_{\text{OO,max}}$, of the first maximum in the oxygen–oxygen RDFs and the corresponding coordination numbers for all simulations are listed in Table II. The average values for $g_{\text{OO,max}}$ and $r_{\text{OO,max}}$ are 3.0 ± 0.1 and 2.75 ± 0.02 Å, respectively, and the coordination numbers are all close to the tetrahedral value of 4.

To assess the temperature dependence of the RDFs at fixed density and to provide pseudo-experimental results close to the temperature of our first principles simulations, some adiabatic nuclear-electronic sampling Monte Carlo simulations[31] were carried out for the polarizable TIP4-pol2 model[32] that is known to yield an excellent real space representation[33] of the experimentally obtained x-ray structure factor over a temperature range from 275 to 350 K at a constant pressure of 101 kPa.[33,34] As can be seen from Figure 5, increasing the temperature by 10 K at a constant density of 1.0 g/cm^3 leads to a decreased height of the first peak in the oxygen–oxygen RDF by about 0.09. Thus, the temperature spread of the microcanonical simulations can be responsible for variations in $g_{\text{OO,max}}$ of about 0.1.

Compared to the RDFs obtained for the TIP4P-pol2 model, the RDFs for the BLYP representation of water (for 64- and 128-molecule systems) appear to be somewhat overstructured, i.e. at $T \simeq 315$ K the value of $g_{\text{OO,max}}$ is shifted upward by 0.2 and the depth of the first minimum in the oxygen–oxygen RDF is overestimated by a similar amount. Even considering the difference in temperature the degree of overstructuring is somewhat smaller in the present simulations than for the results reported by Grossman *et al.*[12] with their peak heights ranging from 3.5 to 4.1 for simulations of 32-molecule systems (H_2O or D_2O with $\mu = 340$ a.u.) and $g_{\mathrm{OO,max}} = 3.3$ for a 54-molecule system at $T \simeq 295$ K. However, it should be noted that Grossman *et al.*[12] use a different pseudopotential for all and a different density functional for some of their simulations. The agreement between the structural results of the present work and earlier simulations by Chen *et al.*[8] is excellent (adjusting for the temperature difference), e.g. Chen *et al.* reported a value of 3.1 for $g_{\mathrm{OO,max}}$ at $T = 300$ K. The structural parameters obtained recently by Izvekov and Voth[9] ($g_{\mathrm{OO,max}} = 2.7$ at $T = 307$ K and $g_{\mathrm{OO,max}} = 2.8$ at $T = 305$ K) fall outside of the range of the present work.

In addition to the purely structural properties discussed above, the classical constant-volume heat capacity, C_V^{class}, and the self-diffusion constant, D_{self}, were calculated. In particular, the former property should very sensitive to the quality of the adiabatic sampling, i.e. one might expect that the heat capacity increases when simulations deviate from the adiabatic limit and heat is pumped into the fictitious electronic degrees of freedom.[31] As can be seen from the numerical data for C_V^{class} listed in Table II, the calculated values albeit plagued by large statistical uncertainties for these short simulations do not appear to be affected by switching from BO sampling to CPMD sampling with $\mu = 400$ a.u. to Monte Carlo sampling in the microcanonical or canonical ensemble. Here it should be emphasized that we report the values for the *classical* constant heat capacity in Table II that can be computed directly from the classical trajectories and allow for a direct comparison of simulations for H_2O and D_2O and an immediate assessment of whether the fictitious electronic degrees of freedom make a substantial contribution to the heat capacity. Quantum effects play a significant role for the heat capacity of water, and including appropriate quantum corrections for all degrees of freedom[35] leads to a reduction of C_V^{class} of H_2O by about 25 J K^{-1} mol^{-1}.

The mean square displacements of the `CPMD` and `CP2K`-MD runs and the corresponding self-diffusion constants are shown in Figure 6 and Table II, respectively. Since the average displacement over the course of a 10 ps run is similar in magnitude to the molecular diameter, these simulations are not yet accessing the long time scales required for an unambiguous determination of the self-diffusion constant via the Einstein relation.[2] In addition, the “short” simulation length and “small” system size and unavoidable variations in the ionic temperature for simulations in the microcanonical ensemble are responsible for a large scatter of these data. The average value of 0.1 $\mathrm{\AA}^2$/ps for the six simulations presented here is about a factor of three smaller than its experimental counterpart.[36] Thus, with our current computational resources, it is impossible to assess whether the observations that D_{self} for the two runs with BO dynamics are close and about a factor of two smaller or of two larger than the Car-Parrinello dynamics runs in the microcanonical or canonical ensemble, respectively, are significant or fortuitous. The results reported by Grossman *et al.*[12] for CPMD simulations with $\mu = 340$ a.u. in the microcanonical ensemble show a similar degree of scatter and range from 0.006 to 0.04 Å^2/ps at $T \simeq 295$ K.

As mentioned above, run `CPMD`-NVE-800 was aborted because this microcanonical simulation with the large fictitious electron mass did not result in adiabatic sampling. Figure 7 shows a comparison of the energetics of runs `CPMD`-NVE-800 and `CPMD`-NVE-400-128. It should be emphasized that monitoring the conservation of the total energy is not a very good diagnostic of whether a CPMD simulation achieves adiabatic sampling, e.g. the total energy of run `CPMD`-NVE-800 changed only by 3 parts in 10^7 over the 5.0 ps length of the simulation. A much better measure is the stability of the kinetic energy of the fictitious electronic degrees of freedom, and it shows the problems of run `CPMD`-NVE-800 very clearly (see Figure 7). Thus, any CPMD simulation for H_2O using an electron mass of about 800 a.u. (or 1100 a.u. for D_2O) should be suspect without an explicit demonstration that the electronic kinetic energy does not drift significantly throughout the run. Furthermore, the limit of what constitutes a sufficiently small electronic mass for a simulation in the microcanonical ensemble depends on system size and length of the run, i.e. the suggested value of $\mu = 400$ a.u. will require re-evaluation once CPMD simulations will be able to access hundreds of water molecules for hundreds of picoseconds.

IV. CONCLUSIONS

The excellent agreement observed here for the simulations of liquid water demonstrates that the CPMD approach enables valid sampling of structural and thermodynamic properties (which depend only on the generalized position coordinates of the Hamiltonian for a classical trajectory[22]) provided that adiabatic sampling is maintained over the full length of the simulation. Adiabatic sampling of CPMD trajectories requires a sufficiently small electron mass for simulations in the microcanonical ensemble. In addition, a slightly larger fictitious electron mass can be used when massive thermostatting of nuclear and electronic degrees of freedom is employed in the canonical ensemble. When a consistent description of the physical system is used (density functional and pseudopotential), then the results of first principles simulations using CPMD sampling in the microcanonical and canonical ensembles, using Born-Oppenheimer dynamics in the microcanonical ensemble, and Metropolis Monte Carlo sampling in the canonical ensemble appear to be very reproducible (as they should be). These simulations also constitute a good test of the `CPMD` and `CP2K` computer programs.

The computational benefits of CPMD sampling over Born-Oppenheimer sampling for structural and thermodynamic properties are appreciable for liquid water and arise from the substantial reduction in computer time per step (by about a factor of 20) that is only partially compensated by the requirement for a smaller timestep (by about a factor of 5). The drawback is that the use of fictitious electronic degrees of freedom and thermostats can potentially alter dynamical properties,[37,38] albeit the statistics of the present work do not allow for an unambiguous assessment of the influence of the different dynamics approaches on transport properties.

The simulations show that the BLYP-TM and BLYP-GTH descriptions of water (at $T \simeq 315$ K and $\rho = 1.0$ g/cm^3) yield an overstructured liquid, an underestimated heat capacity, and an underestimated self-diffusion constant. Additional simulations are currently underway to explore the effects of temperature, system size, and changes of density functional and plane wave cut-off on first principles simulations of liquid water.

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[1] Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed. (Academic Press: New York, 1986).

[2] Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids* (Oxford University Press: Oxford, 1987).

[3] Barker, J. P.; Watts, R. O. *Chem. Phys. Lett.* **1969**, *3*, 144.

[4] Chen, B.; Potoff, J. J.; Siepmann, J. I. *J. Phys. Chem. B* **2000**, *104*, 2378.

[5] Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

[6] Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1993**, *99*, 9080.

[7] Silvestrelli, P. L., Parrinello, M. *J. Chem. Phys.* **1999**, *111*, 3572.

[8] Chen, B.; Ivanov, I.; Park, J. M.; Parrinello, M.; Klein, M. L. *J. Phys. Chem. B* **2002**, *106*, 12006.

[9] Izvekov, S.; Voth, G. A. *J. Chem. Phys.* **2002**, *116*, 10372.

[10] Kuo, I.-F. W.; Mundy, C. J. *Science* **2004**, *303*, 658.

[11] Asthagiri, D.; Pratt, L. R.; Kress, J. D. *Phys. Rev. E* **2003**, *68*, 041505.

[12] Grossman, J. C.; Schwegler, E.; Draeger, E. W.; Gygi, F.; Galli, G. *J. Chem. Phys.* **2004**, *120*, 300.

[13] CPMD, Version 3.7; copyright IBM Corp., 1990-2003, copyright MPI für Festköperforschung Stuttgart, 1997-2001; www.cpmd.org.

[14] CP2K, Version 0.0, cp2k.berlios.de

[15] Anderson, H. C. *J. Chem. Phys.* **1980**, *72*, 2384.

[16] Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

[17] Pastore, G.; Smargassi, E.; Buda, F. *Phys. Rev. A* **1991**, *44*, 6334.

[18] Nosé, S. *Mol. Phys.* **1984**, *52*, 255; Hoover, W. G. *Phys. Rev. A* **1985**, *31*, 1695.

[19] Tuckerman, M. E.; Parrinello, M. *J. Chem. Phys.* **1994**, *101*, 1302.

[20] Hutter, J.; Lüthi, H. P.; Parrinello, M. *Comp. Mat. Sci.* **1994**, *2*, 244.

[21] Lippert, G.; Hutter, J.; Parrinello, M. *Mol. Phys.* **1997**, *92*, 477.

[22] McQuarrie, D. A. *Statistical Mechanics* (Harper and Row: New York, 1996).

[23] Iftimie, R.; Salahub, D.; Wei, D.; Schofield, J. *J. Chem. Phys.* **2000**, *113*, 4852.

[24] Gelb, L. D. *J. Phys. Chem.* **2003**, *118*, 7747.

[25] Izvekov, S.; Parrinello, M. C.; Burnham, C. J.; Voth, G. A. *J. Chem. Phys.* **2004**, in press.

[26] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098; Lee, C.; Yang, W.; Parr, R. C. *Phys. Rev. B* **1988**, *37*, 785.

[27] Troullier, N.; Martins, J. *Phys. Rev. B* **1991**, *43*, 1993.

[28] Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425.

[29] Goedecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703; Hartwigsen, C.; Goedecker, S.; Hutter, J. *Phys. Rev. B* **1998**, *58*, 3641.

[30] Frenkel, D.; Smit, B. *Understanding Molecular Simulation* (Academic Press: San Diego, 1996).

[31] Chen, B.; Siepmann, J. I. *Theo. Chem. Acc.* **1999**, *103*, 87.

[32] Chen, B.; Xing, J.; Siepmann, J. I. *J. Phys. Chem. B* **2000**, *104*, 2391.

[33] Hura, G.; Russo, D.; Glaeser, R. M.; Head-Gordon, T.; Krack, M.; Parrinello, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1981.

[34] Hura, G.; Sorenson, J. M.; Glaeser, R. M.; Head-Gordon, T. *J. Chem. Phys.* **2000**, *113*, 9140; Sorenson, J. M.; Hura, G.; Glaeser, R. M.; Head-Gordon, T. *J. Chem. Phys.* **2000**, *113*, 9149.

[35] Owicki, J. C.; Scheraga, H. A. *J. Am. Chem. Soc.* **1977**, *99*, 7403.

[36] Mills, R. *J. Phys. Chem.* **1973**, *77*, 685.

[37] Sprik, M. *J. Phys. Chem.* **1991**, *95*, 2283.

[38] Tangney, P.; Scandolo, S. *J. Chem. Phys.* **2002**, *116*, 14.

Figures

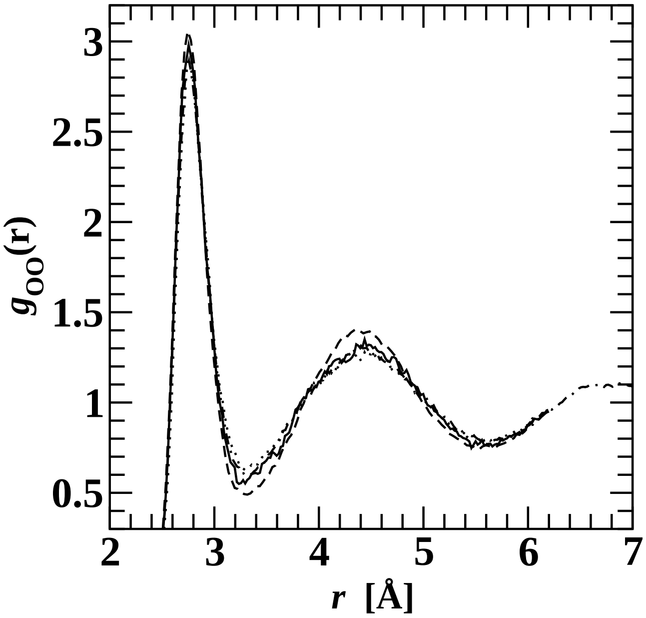

FIG. 1: Comparison of the oxygen–oxygen radial distribution functions obtained from first principles simulations in the microcanonical ensemble. The results for the runs `CPMD`-NVE-BO, `CP2K`-MD-NVE, `CPMD`-NVE-400, and `CPMD`-NVE-400-128 are shown as solid, dashed, dotted, and dash-dotted lines, respectively.

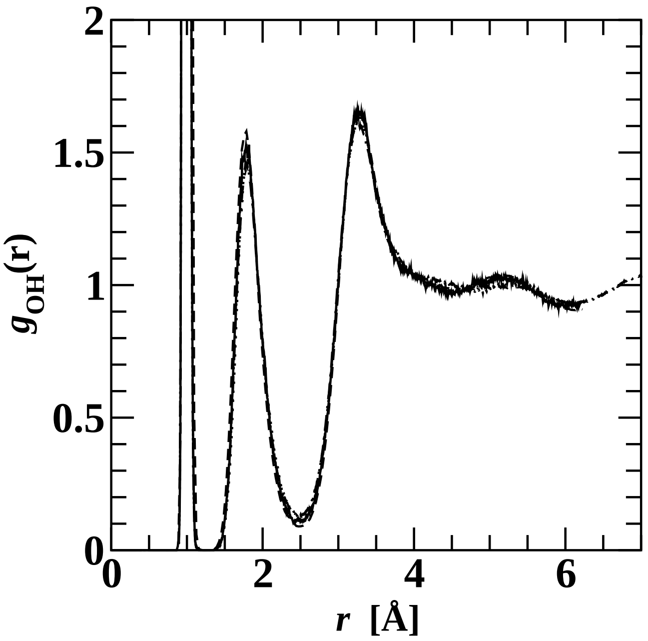

FIG. 2: Comparison of the oxygen–hydrogen radial distribution functions obtained from first principles simulations in the microcanonical ensemble. Line styles are the same as in Figure 1.

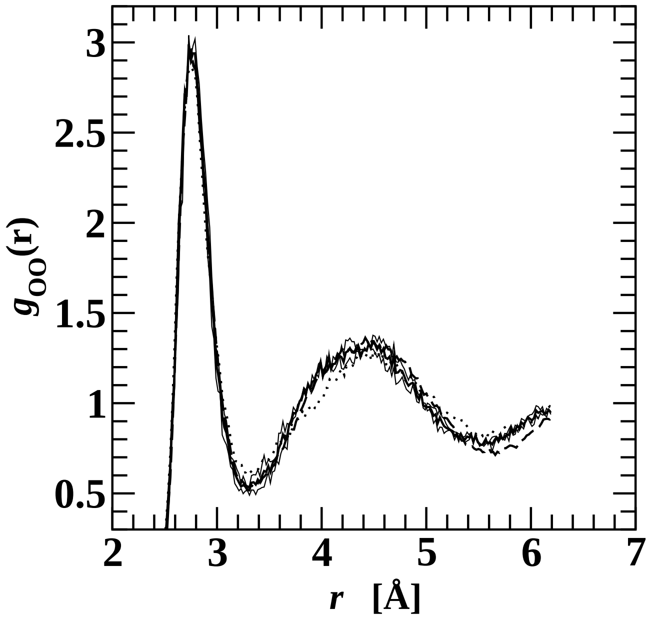

FIG. 3: Comparison of the oxygen–oxygen radial distribution functions obtained from first principles simulations in the canonical ensemble. The results for the runs `CP2K`-MC-NVT, `CPMD`-NVT-i-400, and `CPMD`-NVT-ie-800 are shown as solid (thick line for the average and thin lines for the two independent simulations), dashed, and dotted lines, respectively.

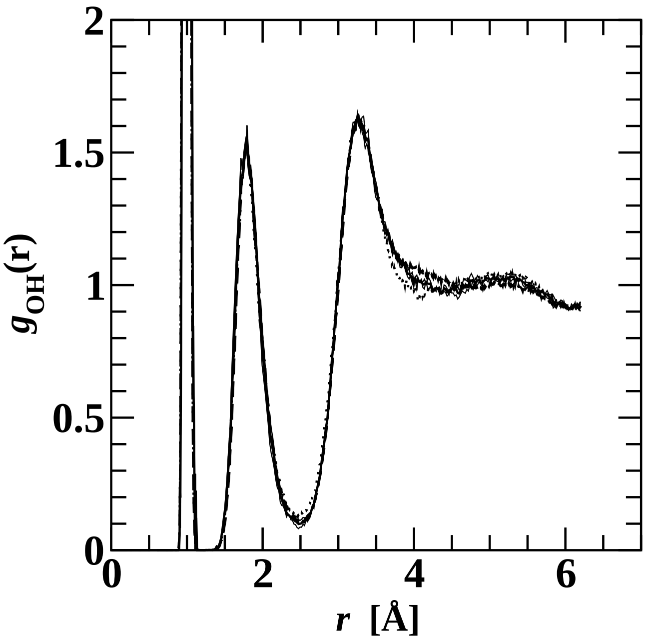

FIG. 4: Comparison of the oxygen–hydrogen radial distribution functions obtained from first principles simulations in the canonical ensemble. Line styles are the same as in Figure 3.

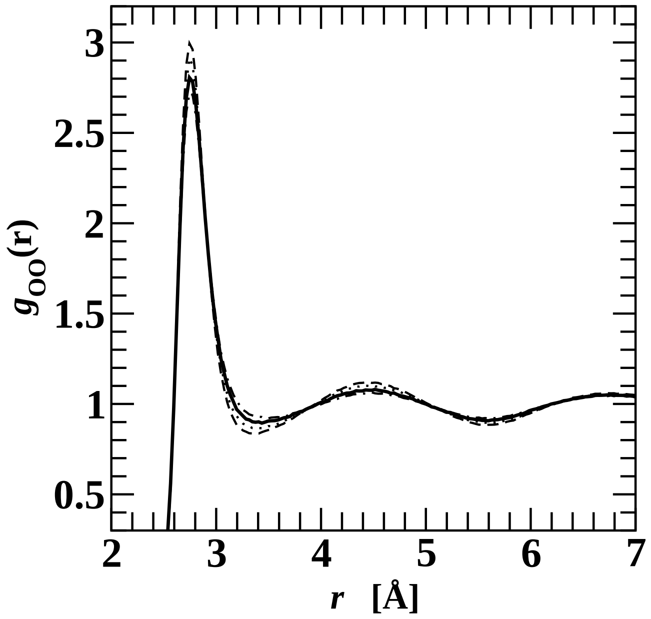

FIG. 5: Temperature dependence of the oxygen–oxygen radial distribution functions from classical Monte Carlo simulations in the canonical ensemble ($\rho = 1.0$ g/cm^3) for the polarizable TIP4P-pol2 model.[32] The results at T = 298, 308, 318, and 328 K are shown as dashed, dotted, solid, and dash-dotted lines, respectively, and the corresponding values for $g_{\rm OO,max}$ are 3.00, 2.92, 2.81, and 2.73, respectively.

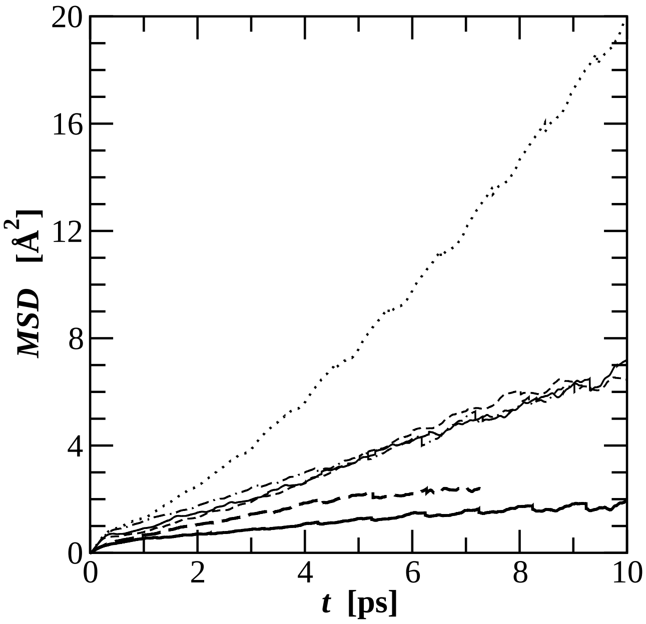

FIG. 6: Center-of-mass mean square displacement obtained from first principles simulations. The results for the microcanonical runs `CPMD`-NVE-BO, `CP2K`-MD-NVE, `CPMD`-NVE-400, and `CPMD`-NVE-400-128, are shown as thin solid, dashed, dotted, and dash-dotted lines, respectively, and for the canonical runs `CPMD`-NVT-i-400, and `CPMD`-NVT-ie-800 thick solid and dashed lines, respectively.

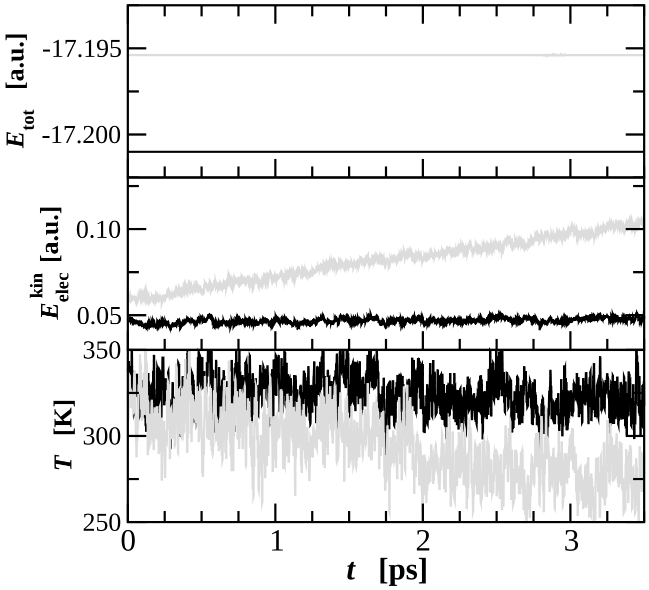

FIG. 7: Comparison of the total energy per molecule (top panel), electronic kinetic energy (middle panel), and kinetic temperature of the ions (bottom panel). The results for runs `CPMD`-NVE-800 and `CPMD`-NVE-400-128 are shown as grey and black lines, respectively.

Tables

TABLE I: Simulation details for the different runs. `CPMD` and `CP2K` denote the computer programs. MD, MC, NVE, and NVT refer to simulations using molecular dynamics or Monte Carlo in the microcanonical or canonical ensemble, respectively. The labels "i" and "ie" stand for the use of massive thermostats for only the ionic degrees of freedom or separately for ionic and electronic degrees of freedom ($T_{\mathrm{elec}} = 0.03$ K), respectively. BO, the first, and the second number denote Born-Oppenheimer dynamics, the value of μ for CPMD dynamics, and the number of molecules when different from $N = 64$, respectively. BLYP, PW, TZV2P, TM, and GTH stand for Becke exchange plus Lee-Yang-Parr correlation functional,[26] a plane wave basis set, a triple-zeta valence basis set augmented with two sets of *d*-type or *p*-type polarization functions, and norm-conserving Troullier-Martins and Goedecker-Teter–Hutter pseudopotentials,[27,29] respectively. Δt, t_{prod} and T_{ion} are the timestep, length of the production period, and the average temperature of the ionic translational degrees of freedom, respectively.

	functional	basis set	pseudo-potential	cut-off [Ry]	μ [a.u.]	N	molecule	Δt [fs]	t_{prod} [ps]	T_{ion} [K]
`CPMD`-NVE-BO	BLYP	PW	TM	85	n/a	64	D_2O	0.48	11.4	328
`CPMD`-NVE-400	BLYP	PW	TM	85	400	64	H_2O	0.097	25.7	313
`CPMD`-NVE-400-128	BLYP	PW	TM	85	400	128	H_2O	0.097	9.0	324
`CPMD`-NVE-800	BLYP	PW	TM	85	800	64	H_2O	0.097	5.0	n/a
`CP2K`-MD-NVE	BLYP	TZV2P	GTH	280	n/a	64	H_2O	0.5	12.0	328
`CPMD`-NVT-i-400	BLYP	PW	TM	85	400	64	H_2O	0.097	11.1	315
`CPMD`-NVT-ie-800	BLYP	PW	TM	85	800	64	H_2O	0.097	7.2	315
`CP2K`-MC-NVT[a]	BLYP	TZV2P	GTH	280	n/a	64	H_2O	n/a	n/a	315

[a] Two independent simulation runs using 500 MC cycles for production were carried out.

TABLE II: Comparison of the simulation results. The ensemble averages of the height and position of the first maximum in the oxygen–oxygen radial distribution function, the oxygen–oxygen coordination number, the OO bond length, the HOH bond angle, the classical constant-volume heat capacity, and the self-diffusion constant are listed.

	$g_{\mathrm{OO,max}}$	$r_{\mathrm{OO,max}}$	coordination	d_{OH}	α_{HOH}	C_V^{class}	D_{self}
		[Å]		[Å]	[deg]	[J mol^{-1} K^{-1}]	[Å^2/ps]
CPMD-NVE-BO	3.0	2.76	4.0	0.990	105.9	70	0.1
CPMD-NVE-400	2.9	2.75	4.0	0.990	105.8	67	0.3
CPMD-NVE-400-128	2.9	2.75	4.0	0.989	105.8	75	0.1
CP2K-MD-NVE	3.1	2.75	4.0	1.001	105.6	64	0.1
CPMD-NVT-i-400	3.0	2.75	4.0	0.990	105.9	54	0.03
CPMD-NVT-ie-800	2.9	2.75	4.0	0.990	105.9	74	0.05
CP2K-MC-NVT[a]	3.0	2.77	4.1	0.997	105.6	89	n/a
CP2K-MC-NVT[b]	3.0	2.73	3.9	0.997	104.3	69	n/a
⟨CP2K-MC-NVT⟩[c]	3.0	2.75	4.0	0.997	105.0	79	n/a

[a] Independent MC run A.

[b] Independent MC run B.

[c] Average of two independent MC runs.