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***Ab initio* molecular dynamics simulation of liquid water and water–vapor interface**

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The results of *ab initio* molecular dynamics simulations of liquid water and liquid water–vapor interface using the Perdew-Wang 91 (PW91) exchange-correlation functional are presented. The structural and transport properties of liquid water are comparable to the previous results using Becke-Lee-Yang-Parr (BLYP) functional and experimental data. The shape and the position of the first peak in the oxygen–oxygen radial distribution function is in good agreement with the most recent neutron diffraction data. The *ab initio* molecular dynamics simulation of liquid water–vapor interface, which is the first of its kind, suggests a preferred orientation of the surface water dipole towards the bulk region. © 2001 American Institute of Physics. [DOI: 10.1063/1.1413515]

I. INTRODUCTION

The structure and dynamics of liquid water have been the subject of many theoretical and experimental investigations.^{1–13} Still there is a continued interest in the interpretation of the experimental results and in using various simulation methods at different levels of theory. Most of the empirical potentials used in “classical” molecular dynamics (MD) simulations are essentially optimized to reproduce the experimentally observed bulk properties. However, the interpretation of the experimental results (see Ref. 2 and references therein) may lead to quite distinct pair radial distribution functions (RDF).

An alternative to the MD simulations using classical interaction potentials are *ab initio* molecular dynamics methods, which do not require any input from experiments or previous theoretical calculations. Recent publications of *ab initio* MD simulations have shown a good prediction of the structural and dynamical properties of bulk liquid water (Refs. 9–13 and references therein). One of the main conclusions⁹ is that the BLYP exchange-correlation (XC) functional^{14,15} gives the best description for bulk water. In another work¹³ the results for HCTH/120 exchange-correlation functional were also reported to well estimate the experimental observations. The comparison between the density functionals reported by Sprik *et al.*⁹ and Boese *et al.*¹³ does not include the PW91 density functional.¹⁶ Furthermore, recent work of Hamman¹⁷ showed that both PW91 and PBE¹⁸ density functionals give a good agreement with experiment for the sublimation energy and the volume of hexagonal ice Ih. The PW91 exchange-correlation functional is commonly used for modeling adsorption processes on transition metal surfaces. Since our interest is in the application of density functional theory methods for description of metal–liquid water interfaces, the purpose of the present

work is to assess the accuracy of the PW91 functional for simulation of liquid water.

In this work density functional theory (DFT) simulations of single water molecule, water dimer and bulk water are presented. The water monomer and dimer have been studied by means of geometry optimizations, whereas molecular dynamics simulations have been performed to model liquid water at ambient conditions.

We present also the first results of a self-consistent *ab initio* molecular dynamics simulation of a thin water layer as a model for liquid water–vapor interface. The structure of liquid water–vapor interface has been studied quite intensively using experimental¹⁹ or theoretical^{20–26} methods. These studies, however, lead to different conclusions regarding the orientational distributions of the surface water dipole moments. In this work we study the orientational distribution at the water/vapor interface using *ab initio* MD methods.

II. COMPUTATIONAL METHOD

The *ab initio* MD simulations in this paper have been carried out using Vienna *Ab Initio* Simulation Package^{27,28} (VASP) which is a DFT-based code for systems with periodic boundary conditions. The forces acting on the atomic nuclei are computed from a self-consistent solution of the Kohn-Sham equations.²⁹ The interactions between the ions and the electrons are described using Vanderbilt-type³⁰ ultrasoft pseudopotentials provided by Kresse and Hafner.³¹ The code uses a plane-wave (PW) basis set and for the exchange-correlation part of the energy functional, we used the generalized gradient approximation proposed by Perdew and Wang¹⁶ (PW91). An essential difference of the molecular dynamics method implemented in VASP with the Car-Parrinello MD³² is that the electronic wave functions are not included in the equations of motion of the system. The electronic ground state is computed self-consistently at each MD step.

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The initial configuration for the *ab initio* simulation was taken from an equilibrated run performed with the MD package MOLLY.³³

A number of input parameters of the VASP program, such as the energy cutoff for the PW basis set, the size of periodic unit cell, the number of *k*-points sampled in the Brillouin zone, are of importance for the accuracy of the calculation. In the next section we will first present several tests of the accuracy using simple systems containing one water molecule and a water dimer in a cubic box. Sections III B. and III C. concern *ab initio* MD simulations of bulk liquid water and a thin water layer which are discussed in relation to previous MD results. For comparison, additional classical MD simulations were performed for systems containing 32, 64 and 128 water molecules using the SPC/E potential.³⁴

III. RESULTS AND DISCUSSIONS

A. Water molecule and dimer in a cubic box

Water Molecule in a Cubic Box: Computational Parameters. To estimate the proper computational setup, we performed a series of calculations concerning the dependence of the total energy and the optimized geometry of a water molecule on the cell dimensions, the number of *k*-points, and the quality of the plane-wave basis set. First the unit cell size was varied in the range of 8.0 to 15.5 Å, while keeping the energy cutoff of the PW basis set constant at 500 eV. Only the Γ -point was used for the integration of the band energies. In this range of box sizes there was only a small (<0.01 eV) increase in the computed total energy. The final geometries of the molecule were practically the same — we found differences of less than 0.002 Å and 0.3° for the O–H bond length and H–O–H bond angle, respectively. The convergence with respect to the number of *k*-points in the Brillouin zone was tested using the same cutoff and a unit cell of side length $L=9.861$ Å. (This unit cell size was also used for the simulation of bulk liquid water and will be referred to as the MD unit cell.) Switching from the Γ -point—only to a $3\times3\times3$ Monkhorst-Pack-type mesh³⁵ (corresponding to 8 irreducible *k*-points) — resulted in a difference in the computed total energy of less than 1×10^{-5} eV. The basis set dependence was evaluated by varying the energy cutoff E_{cut} from 300 to 600 eV. The total energy converged to within 0.01 eV for E_{cut} greater than 400 eV with no significant changes in the optimized geometry of the molecule for cutoffs above 325 eV.

To conclude, the MD unit cell size, a Γ -point-only sampling of the Brillouin zone, and a cutoff of 400 eV are sufficient for an *accurate* description of a water molecule. The estimated O–H bond length of 0.973 Å and H–O–H angle of 104° are the same as the results obtained⁹ using the BLYP functional and are in a reasonable agreement with the experimental values of 0.958 Å and 104°, respectively.³⁶ Except for the cutoff of the plane-wave basis set, which was varied, the simulations of the water dimer were therefore performed using the above-mentioned settings.

Water Dimer in a Cubic Box. To obtain the water dimer equilibrium geometry and dissociation energy and their dependence on the computational parameters, two series of cal-

TABLE I. Calculated O–O distance and binding energy of water dimer compared to the results using CCSD(T)³⁸ and BLYP⁹ and experiment.^{37,41}

	$r(\text{O}-\text{O})/\text{\AA}$	$E_{\text{dimer}}/\text{kJ}\cdot\text{mol}^{-1}$
$E_{\text{cut}}=325$ eV	2.88	23.5
$E_{\text{cut}}=400$ eV	2.89	23.9
CCSD(T)	2.91	21.0
BLYP	2.95	18
Experiment	2.98	22

culations were performed using the “accurate” cutoff of 400 eV and a reduced cutoff of 325 eV. The configuration under study corresponds to the *trans*-configuration with a plane of symmetry, which has been determined experimentally.³⁷ The dissociation energy of the dimer (Table I) was computed as the difference in the total energy of the dimer and the sum of the total energies of two single water molecules in the same unit cell size using the same cutoff. The energies were corrected for dipole–dipole interactions between periodic images in the neighboring cells as implemented in VASP. The O–O distance (Table I) in the water dimer is shifted to a smaller value compared to experiment³⁷ or the BLYP result,⁹ but compares well to high-level *ab initio* coupled-cluster results.³⁸

From the presented results for the water monomer and dimer we conclude that, already for a cutoff of 325 eV, the predicted equilibrium geometries and dissociation energy are in a reasonable agreement with the experimental and other theoretical results. The simulation of bulk liquid water was nevertheless performed using the “accurate” cutoff of 400 eV. The molecular dynamics of the water slab was performed using a reduced cutoff of 325 eV, to improve the computational speed.

B. Molecular dynamics simulation of liquid water

An *ab initio* MD simulation of liquid water was carried out using a model of 32 molecules placed in a cubic box of size 9.861 Å, corresponding to the density $\rho=0.998$ g·cm^{−3} at ambient conditions. All atoms, including the hydrogens, were treated classically with no quantum effects taken into account. The Verlet integration scheme was used with a time step of 0.5 fs and no constraints to the molecular geometries were applied. The starting configuration was obtained from an equilibrated “classical” simulation performed with MOLLY. The system was equilibrated for 1 ps, after which statistical data were collected for 3.5 ps. The average temperature during the microcanonical *NVE* ensemble simulation was 307 K.

Enthalpy of Vaporization. A thermodynamic property of a molecular liquid that is relatively easy to estimate from our simulations is the enthalpy of vaporization. The enthalpy H of a thermodynamic system is given by the expression $H=U+pV$, where U is the internal energy of the system and p and V are the pressure and the volume, respectively. The evaluation of U from a MD run is straightforward by averaging the total energy of the system. The internal energy of the model liquid state (32 molecules in a box) was calculated in this way. Considering a system of classical particles, the

internal energy U can be expressed as a sum of the potential energy of the optimized (equilibrium) geometry and the averaged kinetic energy of the thermal movement E_k . For the purpose of evaluating the enthalpy of vaporization, the gas phase water is considered a gas of noninteracting molecules with $N=9$ degrees of freedom (including translations). Thus, the total average kinetic energy of a molecule at a temperature T is $E_k = NkT/2$ and the gas occupies a molar volume V_m as an ideal gas. Following this scheme and taking the pressure $p=1$ atm, the computed enthalpy of vaporization of liquid water is $39 \text{ kJ}\cdot\text{mol}^{-1}$ (307 K) in satisfactory agreement with the experimental value of $43.9 \text{ kJ}\cdot\text{mol}^{-1}$ (298 K).³⁶

Radial Distribution Functions. We have evaluated the radial distribution functions (RDF) of the three atom pairs, i.e., O–O, O–H, and H–H. The comparison with the results from neutron diffraction data is shown on Fig. 1. The determination of the O–O pair distribution function based on neutron diffraction has been subject to a number of revisions due to experimental uncertainties.² Most noticeable is the fact that, the position and the shape of the first peak of the O–O RDF at $2.7\text{\AA}$ are in good agreement with the most recent experimental result² giving a peak at around $2.75\text{\AA}$. The pair radial distribution functions using BLYP and HCTH/120 density functionals were found^{9,13} to compare very well with the older experimental data,¹ which are also shown on Fig. 1. It should be noted that the molecular structure in our simulation is more ordered compared to the experiment, resulting in a lower value of the first minimum in the RDF. The computed RDF is in fact quite sensitive to the size of the unit cell. In a recent work Silvestrelli *et al.*¹¹ reported a significant improvement in the RDF's compared to experiment with the increase of the size of the system from 32 to 64 deuterated water molecules. The shape of the O–H distribution function is also influenced by quantum effects of the hydrogen atoms, which are not taken into account in our model (for a quantum mechanical study and the extent of quantum effects on the RDF's, see for example Ref. 7). In conclusion, accounting for the limitations of the model, the radial distribution functions for the PW91 density functional compare well with the experimental neutron diffraction data, and are not notably inferior to those obtained with the BLYP functional.

Self-Diffusion Coefficient. An important dynamic characteristic of a liquid is the self-diffusion coefficient D . As the oxygen atoms are much heavier than the hydrogen atoms, we considered the movement of the oxygen atoms to be representative for the movement of the center-of-mass of the molecules. The self-diffusion coefficient can be computed using the mean-square displacement (MSD) or the velocity autocorrelation function.³⁹ The value for the self-diffusion coefficient is $0.8 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ using the MSD of the oxygen atoms (Fig. 2, $N=3$ directional degrees of freedom) and $1.2 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ from the integration the oxygen velocity autocorrelation function. The difference in the results for D , using the two definitions, is due to the relatively short MD simulation time. It is, however, more important to notice that the value of D and the shape of the MSD function implies a liquid-like behavior of a bulk water. Compared with the ex-

FIG. 1. (a) O–O, (b) O–H and (c) H–H radial distribution functions: the computed RDF's are given by solid lines; dotted and dashed lines represent Soper's experimental data from 2000² and 1997,¹ respectively.

perimental result of $2.30 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, the computed value confirms the reduced mobility of the molecules, which is related to the small size of the unit cell. The result for BLYP for a system of the same size, but using 32 deuterated water molecules, was reported as $1.0 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ ¹¹ and $1.3 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$.¹⁹ The influence of the size of the unit cell was demonstrated by Silvestrelli *et al.*,¹¹ who reported an increase of D by a factor of around 2.5 for a system of 64 deuterated water molecules compared to 32. This result also agrees with the classical MD simulations that we carried out for models containing 32, 64, and 128 water molecules. The computed self-diffusion coefficients are 1.8, 2.7 and $2.7 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$, respectively.

Assuming transferability of the results concerning the size of the system, the estimated value for PW91 is not only

FIG. 2. Mean-square displacement (MSD) of the O atoms normalized to the number of directional degrees of freedom N . The solid line represents the three-dimensional MSD of bulk water; dashed and dotted lines correspond to two-dimensional xy and one-dimensional z MSD of the water slab, respectively.

comparable to the BLYP, but both density functionals are in a reasonable agreement with the experiment. Boese *et al.*¹³ computed a self-diffusion coefficient of $2.7 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for a system of 32 molecules using the HCTH/120 density functional. This result therefore appears to point to a mobility of the water molecules, which is too high compared to experiment.

Vibrational Power Spectrum. We also examined the vibrational properties of the system in terms of the vibrational power spectrum, which is defined as the Fourier transformation of the velocity autocorrelation function.³⁹ The power spectrum (Fig. 3) was computed using the hydrogen velocity autocorrelation. The broad peak at $2900\text{--}3800 \text{ cm}^{-1}$ corresponds to the intramolecular stretching; the bending vibrations are recognized at around 1600 cm^{-1} . The broad peak in the region $400\text{--}1000 \text{ cm}^{-1}$ represents intermolecular modes. These results agree well with the experimental infrared and Raman spectral data.^{3–5}

C. Molecular dynamics simulation of water–vapor interface

Our model for water–vapor interface is based on a system containing a thin water slab. The model was constructed by taking a configuration from the equilibrated *ab initio* simulation of bulk water and placing it in a rectangular box obtained by doubling the original size in the z -direction. The resulting simulation unit cell is $9.861 \times 9.861 \times 19.723 \text{ Å}$ and contains 32 water molecules in a slab of a thickness 9.861 Å and a vacuum region of the same size. For this simulation we

FIG. 3. Computed power spectrum of bulk liquid water (dotted line) and liquid water slab (solid line).

FIG. 4. Density distributions along the z -axis. The solid and dotted line correspond to the oxygen and the hydrogen distributions from a 4 ps *ab initio* MD simulation. The dashed line (zero shifted to 1) corresponds to the oxygen distribution from a 250 ps classical MD simulation. All distribution functions are normalized to the bulk density. The preferred orientation of the water dipoles concluded from the *ab initio* MD is shown on the right.

reduced the accuracy of the computation in favor of speed by lowering the energy cutoff for the plane-wave basis set from 400 to 325 eV. As shown previously (Table I), the accuracy of the calculation should be still reasonable.

The equilibration of the system was performed in two stages: (i) a MD simulation run at 335 K for 1.4 ps, followed by (ii) a simulation at 300 K with Nosé thermostat for 1.5 ps. During these runs we observed a rearrangement of the water molecules, particularly at the surface and the thickness of the water layer slightly expanded to about 10 Å . Next, data collection was performed for a period of 4 ps. The time step for all these simulations was 0.5 fs.

Density profile along the surface normal. The limited size of our system does not allow a “real” bulk region in the middle of the slab. Therefore, it is not possible to produce realistic data for the water density distribution along the surface normal (Fig. 4). The result is also strongly influenced by the reduced mobility of the molecules, as discussed below in connection to the MSD and self-diffusion. It should be pointed out, however, that the *ab initio* O-distribution along the z -axis agrees qualitatively with the result from a much longer classical MD simulation. Indeed, the classical MD result, obtained using the same number of molecules, clearly shows the existence of a layering in the model with two outer layers L1 and L3 and one inner layer L2. The observed maxima in the density profile correspond to the maxima obtained from the *ab initio* simulation. The presence of “gaps” in the *ab initio* O-distribution function is due to the limited simulation time. However, as seen from the H-distribution, the water molecules still interact via hydrogen bonds. It should be mentioned here that a classical molecular simulation of 4 ps, which is the length of the *ab initio* simulation, produces a similar density profile along the surface normal as the *ab initio* simulation.

Mean-Square Displacement and Self-Diffusion. As can be seen from Fig. 2, which shows the computed xy ($N=2$) and z ($N=1$) components of the MSD of the O atoms, only “cage movement” effects are observed, resulting in the small slope of the curve at longer times. This picture contradicts the findings in earlier (classical) MD simulations,^{22,25} where an increase of the self-diffusion coefficient in the surface

transition zone compared to the bulk region was reported. These simulations were performed using much bigger systems containing 350 or more water molecules. The differences in the transport properties are a result of the combined effect of the small size of the MD unit cell and the number of molecules. Under these conditions the mobility of the molecules is highly reduced due to geometrical constraints and space confinement. This effect is much stronger for the two-dimensional slab system compared to the three-dimensional simulation of 32 bulk water molecules as the number of translational degrees of freedom is reduced.

Oriental Distribution of the Molecules. It is generally accepted in the literature that the coupling between the translational and rotational motions of water molecules in liquid water is weak. With this assumption, the molecular orientational distributions should not be affected by the limitations of the model to such an extent as the transport properties. To test the validity of this assertion, we performed classical MD simulations of water slabs containing 32 and 128 molecules. Even for a system of 32 molecules and simulation time of 4 ps, the result qualitatively reproduces the molecular orientation computed for a system of 128 molecules with a 5 ns simulation time, with an uncertainty in the maximum of the angular distribution of around 10° . This suggests that in spite of the relatively poor density profile obtained from a 4 ps simulation with 32 water molecules, the qualitative conclusions regarding the dipole orientation should still be valid.

To describe the orientation of the molecules, one can define an angle variable θ between the dipole moment of a water molecule and the z -axis of the unit cell, which is also the axis perpendicular to the surface (Fig. 4). An angle of $\theta = 90^\circ$ corresponds to an orientation of the dipole parallel to the surface plane. We divided the water layer along the z -axis into three sublayers each of a thickness of around 3.5 Å. The choice of the positions of the dividing planes corresponds to the sublayers as observed from the density profiles of both the classical and the *ab initio* MD simulations. As mentioned before, we refer to the middle sublayer as L2, and to the two outer sublayers as L1 and L3. L1 is the outer layer from the negative side of z , and L3 that from the positive z . In this definition a molecule's dipole moment points directly to the vacuum region if θ is 180° for the sublayer L1 and 0° for the sublayer L3. As can be seen from Fig. 5a, the results for L1 and L3 are quite symmetric and the preferred orientation of the dipoles is towards the "bulk" region. (N.B. The probability plot has been normalized to unity; in this representation random orientational distribution corresponds to the line at $y = 1$.) The maximum probability is at an angle of 120° with the *outward* surface normal, which qualitatively agrees with the experimental second-harmonic generation results.¹⁹ Most of the "classical" simulations studies also agree with our result,^{21–23,25} although two studies reported a water dipole orientation parallel to the surface.^{20,24}

The intramolecular O–H bond orientation can be described by an angle variable ϕ between the bond and the surface normal in analogy to the dipole moment orientation angle θ . The evaluation of ϕ (Fig. 5b) showed that about 20% of the bonds point towards the bulk at an angle of

FIG. 5. Angular distributions of the water dipole (a) and the O–H bond (b). Solid, dotted and dashed lines correspond to sublayers L1, L2 and L3, respectively.

160 – 180° with the outward surface normal. Compared to the result for the dipole moment, the O–H orientational distribution is not that symmetric. It should be noted that the used normalization has the effect of over-accentuating the deviations from the homogeneous distribution at angles ϕ around 0° and 180° . This results in a much higher peak in the curve for L1 around $\phi = 0^\circ$, which only corresponds to a fraction of the O–H bonds. The corresponding peak in the L3-curve is slightly shifted and is around $\phi = 160^\circ$.

Vibrational Power Spectrum. As in the case of bulk liquid water, the vibrational power spectrum was computed using the hydrogen velocity autocorrelation function (Fig. 3). Compared to the bulk water, the peak at 3750 – 3800 cm^{-1} is strongly enhanced due to free O–H groups at the surface. This peak is indeed expected on the basis of the preferred orientation illustrated on Fig. 4 and is in agreement with the experimentally observed peak at 3690 cm^{-1} .⁴⁰

IV. SUMMARY AND CONCLUSIONS

We presented an investigation of (non-deuterated) aqueous systems using DFT-based methods with a self-consistent treatment of the electrons. The Perdew-Wang 91 exchange-correlation functional used in this work gives an acceptable description of the properties of a water molecule, a water dimer, and liquid water. The computed enthalpy of vaporization of $39\text{ kJ}\cdot\text{mol}^{-1}$ is in satisfactory agreement with the experimental value of $43.9\text{ kJ}\cdot\text{mol}^{-1}$. Taking into account the small system size, the structural results in terms of radial

distribution functions show a reasonable agreement with the most recent neutron diffraction data. The simulated O–O separation is comparable to the result using the BLYP functional and gives a better description of the shape and the position of the first peak than BLYP. The estimated value for the self-diffusion coefficient is also in reasonable agreement with the BLYP results and experiment. The *ab initio* simulation of the liquid water–vapor interface shows a preferred orientation of the water molecule dipole towards the bulk region at an angle of 120° with the outward surface normal. This result agrees qualitatively with most of the previous classical MD simulation results and experimental data.

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