Report for Worksheet 2: Properties of water from quantum mechanical and atomistic simulation

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Contents

1 Short Questions –Short Answers

- **A1**: Water molecules consist of one oxygen atom (O) and two hydrogen atoms (H). Because oxygen has a much higher electronegativity (i.e a tendency to attract bond electrons towards itself) than hydrogen, water molecules exhibit positive partial charges at the hydrogen atoms and negative partial charges at the oxygen atoms. A dipole moment arises (i.e the molecules are polar) because of the non-linear (bent) molecular structure.

- **A2**: A hydrogen bond is a weak bond (compared to covalent or ionic bonds) which arises between a (partially positively charged) hydrogen atom (as part of a molecule) and partially negatively charged atom like oxygen (e.g. in water, i.e also part of a molecule). Hydrogen bonds can be intermolecular (e.g. in water) or intramolecular (e.g. in DNA or proteins).

- **A3**: The H–O–H angle in water molecules is about $104.45°$.[1] Hydrogen bonds in water have a typical length of $1.97Å$.[2]

- **A4**: SPC, SPC/E and TIP3P are all 3-site water models, meaning that they include partial charges at three sites in the molecule. SPC and SPC/E have a bond length of 1.0 Å and an angle of $109.47°$ (tetrahedral) while TIP33P has a bond length of 0.9572 Å and an angle of $104.52°$. The partial charges and strength of the Lennard-Jones interaction also vary between the models. The difference between SPC and SPC/E is that SPC/E also includes an average polarization energy.

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[1]https://en.wikipedia.org/wiki/Properties_of_water, accessed on May 8 2020, 20:00
[2]http://chemistry.elmhurst.edu/vchembook/161Ahydrogenbond.html, accessed on May 8 2020, 20:00

2 Quantum Mechanical Calculation of Water

2.1 Quantum Mechanical Calculation of Water

We performed simulations of the water dimer using the PBE functional and the LDA functional, both with and without a van der Waals interaction. A visualization of the water dimer is shown in Figure 1. The obtained bond lengths are shown in Table 1. To calculate these bond lengths, we used the output data in the position file and wrote the python script bond_lengths.py. The OH-bond lengths which are shown in the table were averaged over all four bonds. The van der Waals interaction seems to have no influence on the length of the covalent O-H bond, while it seems to vary with the used functional. Both PBE and LDA overestimate the length of the covalent O-H bond (the experimental value is about 0.95 Å). For the hydrogen bond, the used exchange correlation functional also seems to be much more important than the van der Waals interaction. LDA heavily underestimates the length of the hydrogen bond (experimental value 1.97 Å) while PBE is quite close to the experimental value.
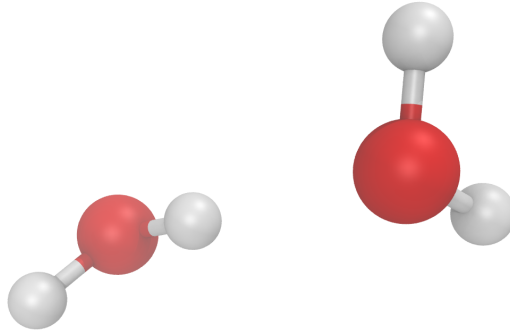

Figure 1: Visualization of the water dimer, it has a hydrogen bond.

Table 1: Bond lengths for different functionals.

functional	length of O-H bond $\left[\text{Å}\right]$	length of hydrogen bond $\left[\text{Å}\right]$
PBE with vdW	0.9745	1.9379
PBE without vdW	0.9745	1.9380
LDA with vdW	0.9777	1.7470
LDA without vdW	0.9777	1.7429

We performed simulations of the water monomer using the PBE functional and the LDA functional, both with and without a van der Waals interaction. The obtained Hirshfeld charges of O and H are shown in Table 2. Again, there is a difference between the two different functionals.

Table 2: Hirshfeld charges of O and H for different functionals.

functional	Hirshfeld charge of O $[e]$	Hirshfeld charge of H $[e]$
PBE with vdW	-1.108	0.560
PBE without vdW	-1.108	0.560
LDA with vdW	-1.127	0.570
LDA without vdW	-1.127	0.570

2.2 Ab Initio Molecular Dynamics Simulation of Water Dimer

We performed ab initio molecular dynamics simulations of the water monomer and dimer using the PBE functional at temperatures $T \in \{100\,\text{K}, 200\,\text{K}, 300\,\text{K}\}$. The time step was set to $0.5\,\text{fs}$. Due to timing reasons we could run the simulation for only ≈ 600 time steps.

To calculate the mean potential energy of the hydrogen bond of the water dimer, we have to subtract the mean energy of two water monomers from the mean energy of the water dimer:

$$\langle E_{\text{pot,H-bond}} \rangle = \langle E_{\text{pot,dimer}} \rangle - 2 \cdot \langle E_{\text{pot,monomer}} \rangle. \tag{1}$$

In order to calculate the mean potential energy for a given trajectory, we wrote the python script energies.py. The calculated mean potential energies for the hydrogen bonds are shown in Table 3.

Table 3: Mean potential energy of the hydrogen bond $\langle E_{\text{pot,H-bond}} \rangle$ in eV.

temperature T [K]	$\langle E_{\text{pot,H-bond}} \rangle$ [eV]
100	-0.256
200	-0.269
300	-0.288

In order to calculate the mean length of the hydrogen bond, we wrote the python script mean_bond_lengths.py. The calculated mean lengths of the hydrogen bonds are shown in Table 4. As expected, the bond length increases with temperature.

Table 4: Length of the hydrogen bond for different temperatures.

temperature T [K]	mean length of hydrogen bond $\left[\text{Å}\right]$
100	2.0044
200	2.3560
300	2.7168
input structure	1.9758

3 Atomistic Simulation of Water

3.1 Running the Simulations

We performed atomistic simulations of 216 water molecules using GROMACS and three different water models (SPCE, SPCE/E and TIP3P). The temperature was set to $T = 300\,\mathrm{K}$ and the simulations were run for 250000 time steps of size $\Delta t = 2\,\mathrm{fs}$.

3.2 Analysis

Radial Distribution Function

Figure 3 – Figure 5 show the calculated radial distribution functions for the different water models. On a qualitative level, they all look like we would expect the RDF of a fluid to look like: for small radii, the RDF is zero because two water molecules can never occupy the same place. Then comes the highest peak due to the water molecules in the immediate neighbourhood. For even larger radii there are (damped) oscillations of the RDF because of particles in even larger "shells", the damping is due to the fact that a fluid exhibits no long-range order. In the limit $r \to \infty$, the RDF approaches the value 1.0, because there are no long-range correlations in fluids. Figure 2 shows how particles arrange around a particle in a fluid, leading to this characteristic behaviour.

While the different RDFs agree on a qualitative level, the peaks for SPC and SPCE are damped much weaker than for TIP3P, this suggest that the fluid phase for the former two is somehow more ordered than for TIP3P.
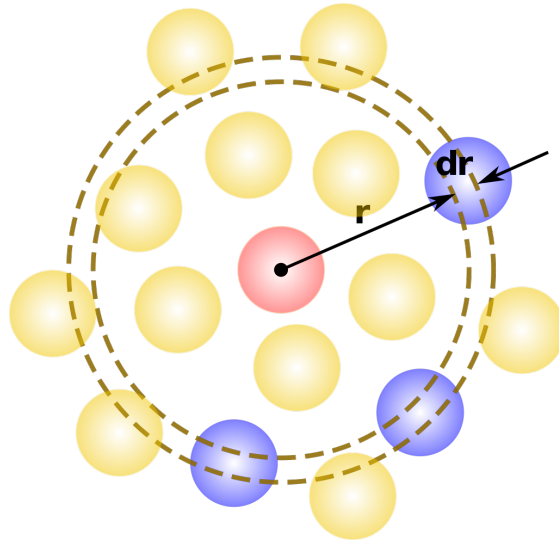

Figure 2: Schematic explanation of the RDF. (Taken from `https://commons.wikimedia.org/wiki/File:Rdf_schematic.svg`, accessed on May 18, 2020 at 8:00 pm.)

Hydrogen Bond Analysis

The number of hydrogen bonds per water molecule for the three different water models is shown in Table 5.

Mean Square Displacement and Diffusion Coefficient

Figure 6–Figure 8 show plots of the mean square displacement which was computed for the different water models. For larger values of t, the MSD begins to oscillate stronger and stronger due to the fact that there are less samples available. We can clearly see that the slope (i.e. the diffusion coefficient) for TIP3P is by far the largest while for SPC/E it is the smallest.

Table 5: Average number of hydrogen bonds per water molecule for different water models.

water model	avg. number of H-bonds
SPC	1.73
SPCE	1.80
TIP3P	1.67

To identify the ballistic regime, we plot the MSD on log-log plot (Figure 9–Figure 11). For all three models there is a change in the slope which points to change in the power law t^n. To investigate the behaviour for $t \to 0$, we fitted a power law $a \cdot t^n$ to the first few data points of each model. The obtained fits are also shown in the respective figures. Table 6 shows the exponents which were extracted from the fits. While they are all larger than 1, they are still smaller than the value we would expect for purely ballistic motion ($n = 2$).

Table 6: Computed power law exponents in the short time limit for the different water models

water model	power law exponent n
SPC	1.240
SPCE	1.253
TIP3P	1.255

GROMACS uses a fitting range of $[50\,\mathrm{ps}, 450\,\mathrm{ps}]$ which seems sensible given the fact that there is a ballistic regime for small t and larger fluctutations for large t. The computed diffusion coefficients are given in Table 7, while they are not exactly equal, they are of the same order of magnitude.

Table 7: Computed diffusion coefficients for the different water models

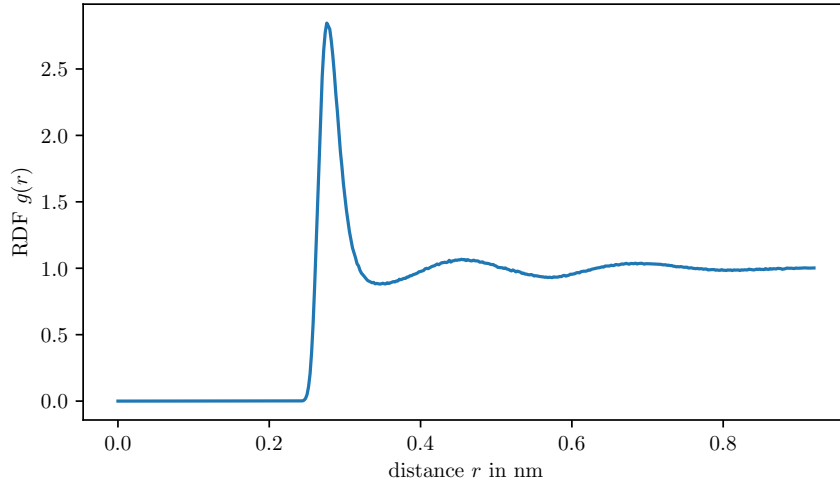| water model	diffusion coefficient D in $10^{-5}\,\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
SPC	3.7948 ± 0.1089
SPCE	2.2704 ± 0.1190
TIP3P	5.0608 ± 0.3821

Figure 3: Radial distribution function for the SPC water model.
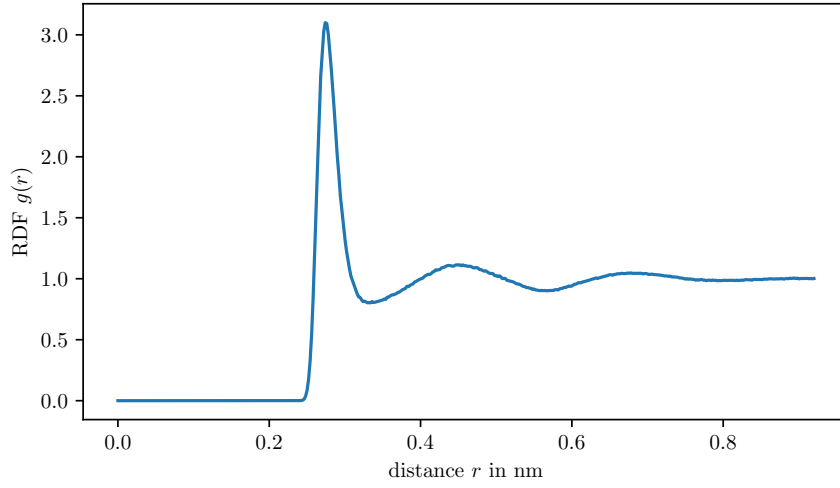

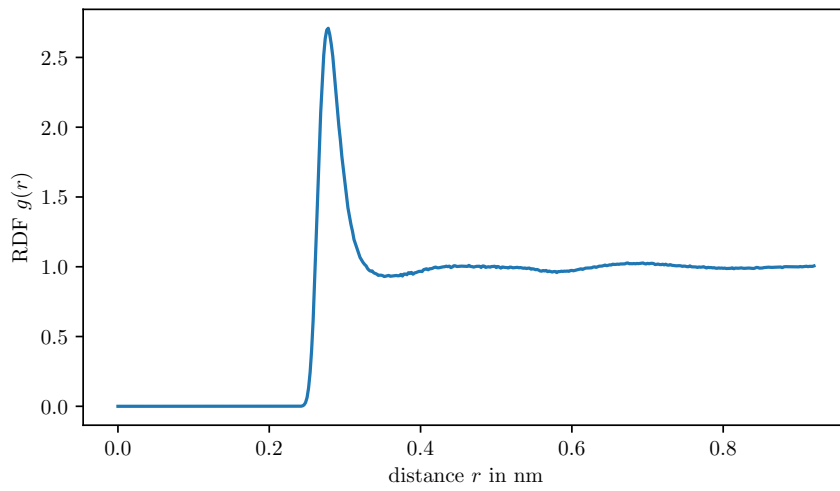Figure 4: Radial distribution function for the SPCE water model.

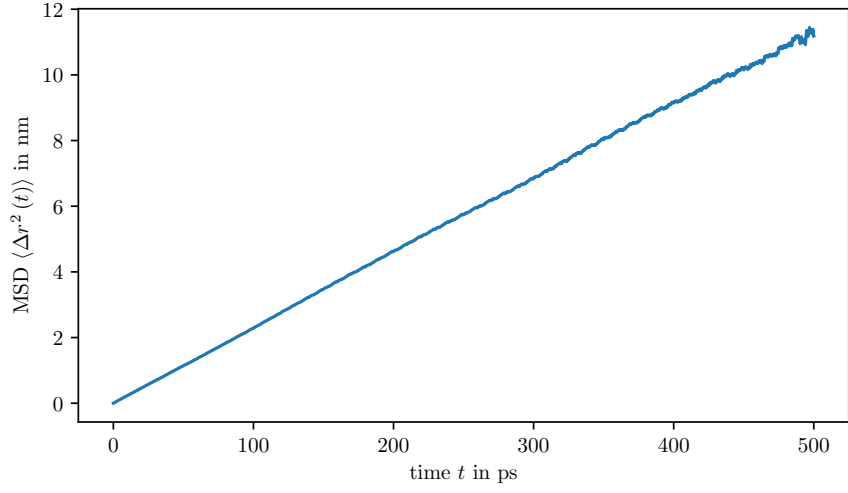Figure 5: Radial distribution function for the TIP3P water model.

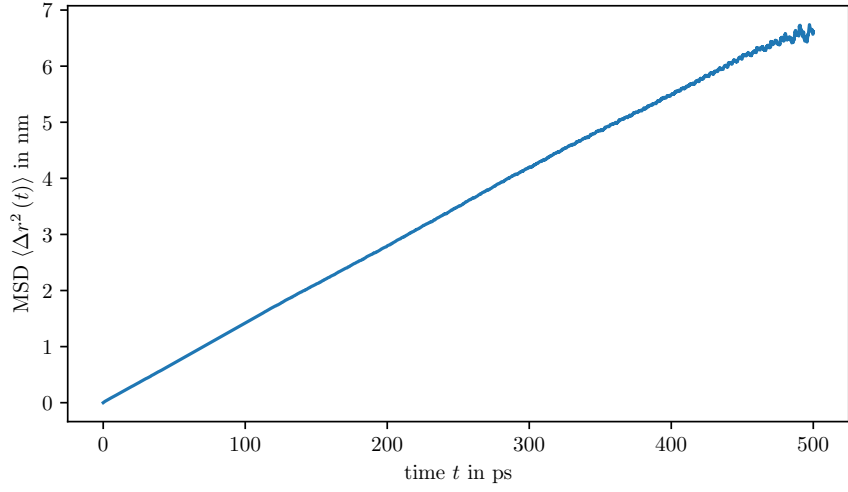Figure 6: Mean square displacement for the SPC water model.

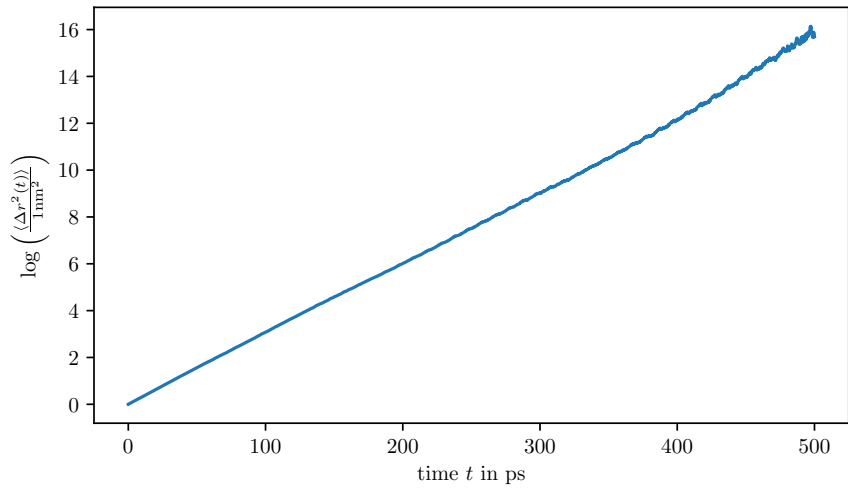Figure 7: Mean square displacement for the SPCE water model.

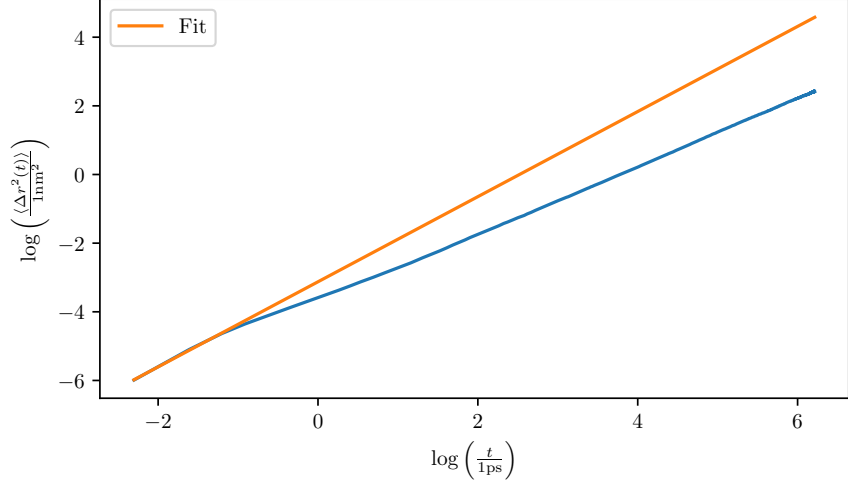Figure 8: Mean square displacement for the TIP3P water model.

Figure 9: Log-log plot of the mean square displacement for the SPC water model.
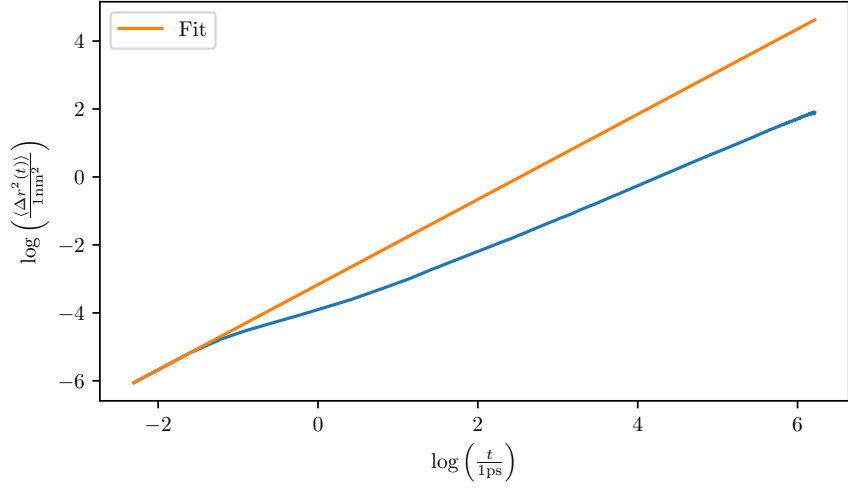

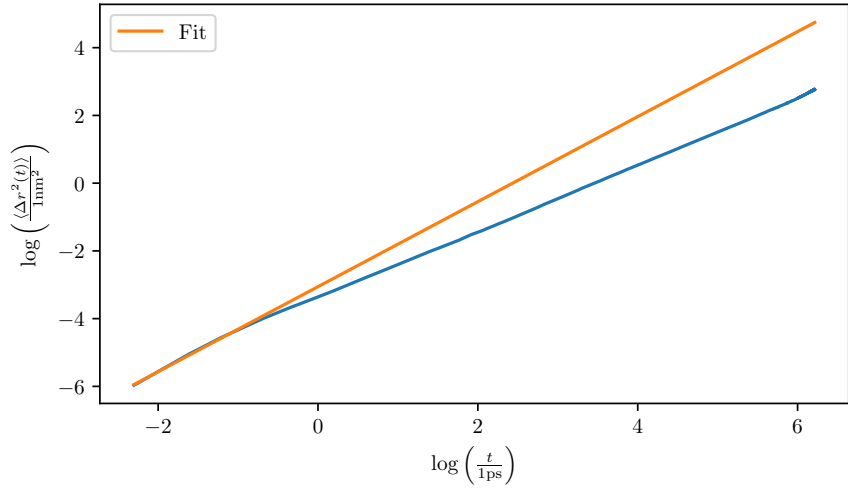Figure 10: Log-log plot of the mean square displacement for the SPCE water model.

Figure 11: Log-log plot of the mean square displacement for the TIP3P water model.