Report 1 - Simulation of water and methanol

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1 Introduction

The aim of this report is the study of the behaviour of water and methanol molecules. Both substances are extremely important in science and their behaviour model creation is crucial for the development of the liquid investigation. Water molecules are known to be not linear, polar with an electrical dipole moment and ability of creating up to 4 hydrogen bonds with neighbouring molecules in the liquid state. At the same time methanol is the simplest alcohol whose major difference from the water occurs at the structural level in the condensed phase. Specifically, it may be observed that four water molecules form a tetrahedral coordinate with the 104:5° angle between the hydrogen atoms whereas the methanol molecules form clusters consisting of chains or small rings [6]. Methanol molecules are polar as well and have lower boiling and melting temperature than water [1].

The molecular dynamics methodology turns out to be a good approach for the examination of the various substance models since it allows us to create the system and observe its evolution in time. The simulation methodology is based on the initialization of the molecules positions and then its transformation according to the proper laws of motion of the atoms. This approach is a numerical one and in consequence not exact. Nevertheless, on this basis the characteristics of the liquids such us its radial distribution function, diffusion coefficient and others may be calculated. The obtained results shall be compared with the experimental ones in order to verify the accuracy of the used simulation model. However, it is known that the power of the molecular dynamics simulation is limited by the system complexity which highly influences on the needed computational time. As a result, mostly the time of the system observation is short or the model not complex what can lead to the misleading conclusions and the obtained results shall be treated with caution. It was also observed in the studies on this topic that the usage of the cut offs, as in this report, can also produce artifacts [6].

The obtained up to date results on the study of water and methanol are summed up below. In this report I'm to check and analyse if the used models in my simulation are consistent with the current knowledge and observations.

1.1 Water models investigation

Before discussing water model properties it's first worth to introduce 3 basic criteria that define them: the number of included sites (points), inclusion of polarization effect and whether molecule is flexible or rigid [1]. In [5] 46 distinct models were presented with the site range from 3 to 6 and none of them gave the perfect results in prediction of all the substance properties. In fact, the models tend to be created to fit one particular property such as radial distribution function, density anomaly or critical parameters. One of the most popular due to its computational efficiency is the three site SPC water model, used in this report, that assumes that:

- the angle between to hydrogen bonds is 109.47° [1], the value that differs from the true one

- the molecules are rigid (flex.SPC eliminates this assumption)

- the polarization effect is included.

The SPC's disadvantage is that it tends to exhibit the disagreement with the melting point value and predicts significantly faster diffusion comparing to the experimental one. On the other hand, it's known to properly estimate the density and the dielectric permittivity of water [12]. Its improvement - SPC/E gives especially better results when estimating the diffusion coefficient (though still the value is overestimated) and is also considered to be accurate for capturing other experimental properties of water such as dielectric constant. Nevertheless, it fails to estimate well critical data, vapor pressure or second virial coefficients and the radial distribution function of the oxygen atoms [2]. Another popular model is the TIP3P, also the 3 site one with the high computational efficiency, capable of reproducing the enthalpy of vaporization and dielectric constant reasonably but underestimating the density and overestimating the self-diffusion constant [8]. To deal with this problematic issue some 4, 5 and 6

site more complex models were developed but again none of the analysed 40 rigid, flexible, polarizable and ab initio models was capable of agreeing with both the experimental internal energy and the experimental radial distribution [5]. Having all this in mind, although water molecules appear to be very simple at the first sight, they are extremely difficult to model at the computational level. The probable reason for the appearing discrepancies between the simulation data and the experimental one is that the known models tend to consider water to be a collection of almost independent molecules that are kept together by weak electrostatic bonds while they are rather " 'flickering' clusters and microdomains" [1].

Notwithstanding, the conducted studies have revealed many important features and the progress have been made. It was noted that the size of the system, the box length, and the use of a reaction field have comparable impact on the results for all water models [6]. Moreover, scientists observed that the fluctuations in thermodynamic properties are proportional to the square root of the system size. Similarly, it was concluded that differences between large and small systems exist indeed. Particularly, when calculating the dielectric constant or diffusion constant for which the obtained values are higher for all systems with a large number of molecules [16].

1.2 Methanol investigation

Without no doubt, less articles and simulation studies have been conducted for the methanol than for the water. The main focus in this matter is rather on the study of the mixture of this substance than on the pure methanol as it happens it this report. The methanol models that were created until now share a lot with the water ones. Firstly, they can also can be distinguished by the rigidness, polarisation and site criteria. Secondly, the same problem of the creation of the one perfect model arises also for this substance - none is perfect and the vast majority of them is specialized to correctly estimate only some properties.

The good computational efficiency is obtained again for the three site models which were analysed in [4]. The simulation of the methanol in this study was performed using J2 and H1 that assume a molecule to be rigid and non-polarisable. It was observed that the resulting dipole moments for both models are larger than the experimental one. On the other hand, the estimated of configurational energy U, the diffusion coefficient and radial distribution function were good. Nevertheless, authors stressed that the nature of the experimental data does not permit the evaluation of the model's potential at the rdf level and should be always done at the partial distribution one. Another group of scientists analysed the mixture of water and methanol using SPC and GROMOS96 models respectively and demonstrated that the diffusion coefficient of methanol in water is well estimated with the error around 10% as well as the density of the mixture (1% error) [14]. In [10] pure methanol was investigated and the models J1, J2, H1, H2, B3, L1, GROMOS96, TraPPE-UA andOPLS-AA were compared. It was observed that TraPPE-UA, B3, and L1 are the best one for the calculation of the density and that OPLS-AA and GROMOS96 models fit well the surface tension at high temperatures and L1 and TraPPE-UA at low. When dealing with the diffusion coefficient the most convenient option is to use J2 or GROMOS96. It was finally concluded that the TraPPE-UA is the best model for thermodynamic and dynamical properties, while OPLS-AA is the best model for structural properties.

2 Methodology

The simulation is performed using GROMACS software. The first step is the setting of the initial simulation parameters. In the considered cases the temperature is equal 298.15 K, the pressure 1 bar and the number of molecules is 216. It's assumed that the liquid molecules' configuration is limited to the certain box space. The initial configurations of both systems are shown on the Figure 1. The length of the simulation is 200 ps. In the next steps atoms of the water move according to OPLS type force field and atoms of the methanol according to the GROMOS96 type force field. In each iteration all the atoms are moved and the system parameters are stored. In this way it's possible to observe and analyse their time evolution.

3 Analysis of the results

In this section the obtained graphs that describe the systems evolution are presented and analysed.

3.1 Radial distribution function

The radial distribution function tells us what is the probability of observing two atoms in the specific distance r. It's worth to notice that the radial distribution function is relative to the uniform probability distribution that is, the one observed for the ideal gas. In the simulation it is calculated by taking in each iteration all possible distances r between the atoms and recording how many pairs of the atoms have r distance between each
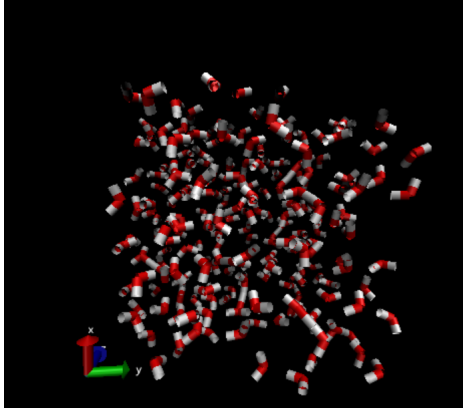
(a) Water visualization
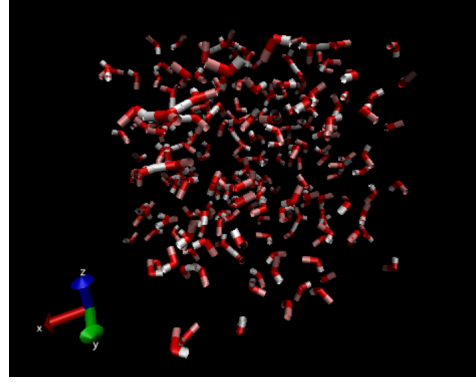
(b) Methanol visualization

Figure 1: Visualization of the initial state of the system

other. Next, the results are averaged and the function may be plotted. In this report the radial distribution functions of the oxygen atoms for both methanol and water is presented on the Figure 2. The experimental radial distribution function that the simulation results are compared to was obtained using neutron scattering data. It
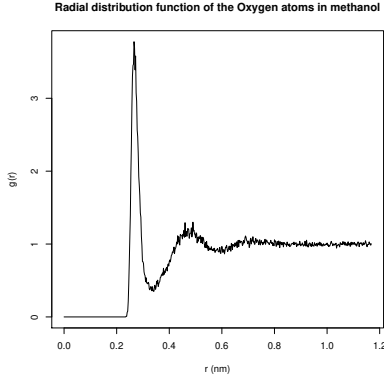
(a) Methanol simulation data
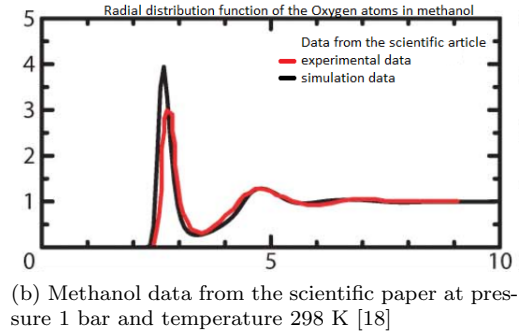
(b) Methanol data from the scientific paper at pressure 1 bar and temperature 298 K [18]
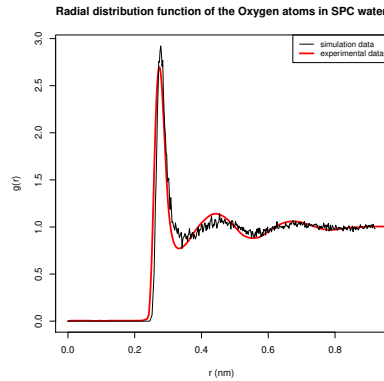
(c) Water simulation data compared with the experimental one at pressure 1 bar and temperature 298.15K [17]

Figure 2: Radial distribution function

may be observed that the overall shape of the simulation radial distribution function for the water and methanol exhibits the typical liquid pattern. It's noted that there is 0 probability of finding other oxygen atoms at the distances below 0.246 nm for water and 0.236 nm for methanol what means that below this value the repulsive forces block the appearance of other oxygen atoms. The peaks are observed on both plots and correspond to the

distances that are the most frequently occupied. The highest appears at 0.278 nm for the water and at 0.266 nm for the methanol. Each peak is lower than the previous one and finally the curve tends to 1. It is caused by the attractive nature of the interaction between atoms which is strong for short distances and gets weaker along with the r raising. Moreover, it can be said that the radial distribution functions obtained from the simulation present a satisfactory agreement with the experimental data. The observed curves are generally similar though slightly overestimated as it happened for SPC model in [15] and for GROMOS96 model in [7]. There's still room for improvement in this matter.

4 Mean square displacement (MSD)

The mean square displacement informs us how much on average the molecule moved during the simulation. It's calculated in each iteration as the average squared difference between the current and the initial position. At the end of the simulation it's possible to plot the MSD in the function of time what is shown on the Figure 3.
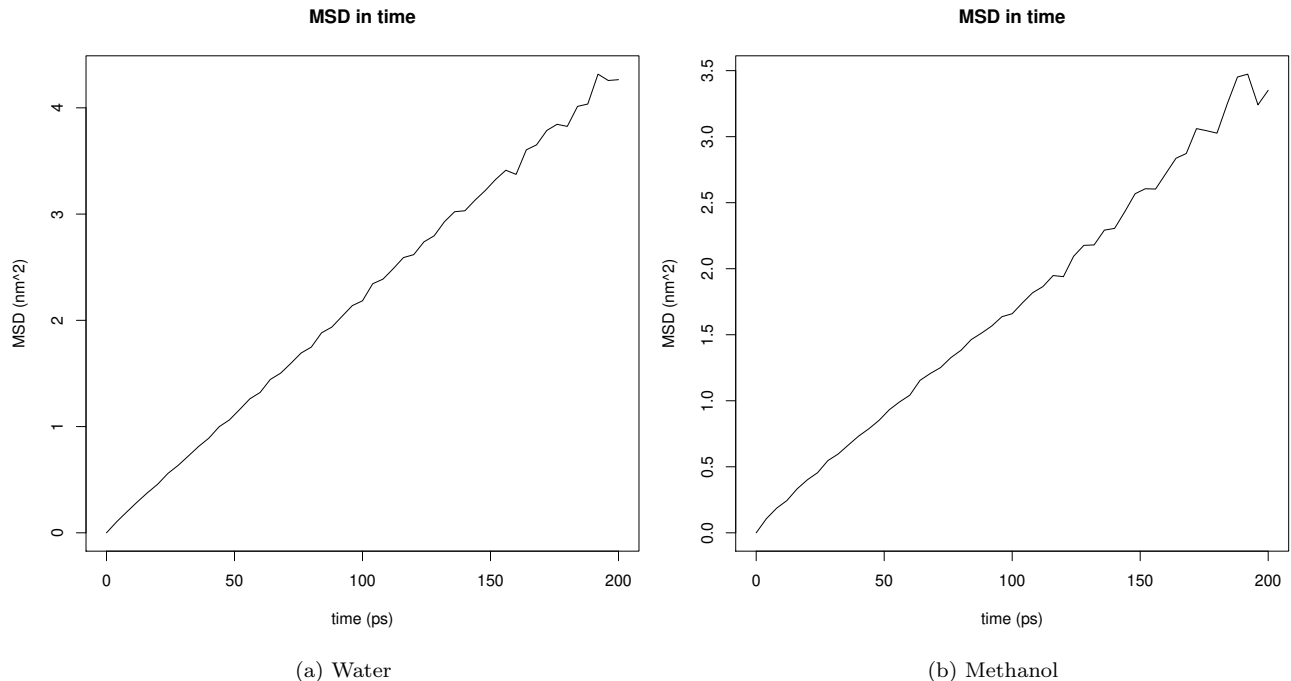

(a) Water

(b) Methanol

Figure 3: MSD plot in the function of time

Both resulting graphs are roughly linear what permits the calculation of the diffusion coefficient using the least square method for the data points (Table 1).

Table 1: Diffusion constants

Simulation	Simulation diffusion constant $\frac{cm^2}{s}$	Error estimation $\frac{cm^2}{s}$	Experimental value $\frac{cm^2}{s}$ at 1 atm and 298.15 K
water	$3.5852 \cdot 10^{-5}$	$0.1309 \cdot 10^{-5}$	2.299 [11]
methanol	$2.7733 \cdot 10^{-5}$	$0.3420 \cdot 10^{-5}$	2.42 [7]

It's noted that the calculated value for the methanol rather oscillates around the experimental one though the estimation error is slightly higher than for the wate. Generally, the performed simulation confirms, what was already stated in the introduction, that GROMOS96 model manages to predict well the diffusion coefficient. In contrary the coefficient for the water differs a lot from the experimental value what is consistent with the knowledge about SPC water model. As it was already mentioned the modification of SPC - SPC/E is capable of

reproducing the correct constant value though shares the identical geometry parameters. The difference between these models that has a significant impact on the diffusion calculation lies in the atomic charges assigned to oxygen and hydrogen atoms which are slightly higher for SPC/E [1] [13].

5   Hydrogen bonds

The next step of the analysis is the study of the hydrogen bonding that plays an important role in physico-chemical properties of the substance. The hydrogen bonds are know as intermolecular forces of attraction. Their appearance is calculated in the simulation on the basis of the positions of the atoms using the appropriate geometric criterion. The plots on the Figure 4 present how the number of hydrogen bonds per molecule changes during the simulation. It may observed on the figures that the number of bonds is constantly changing in time for

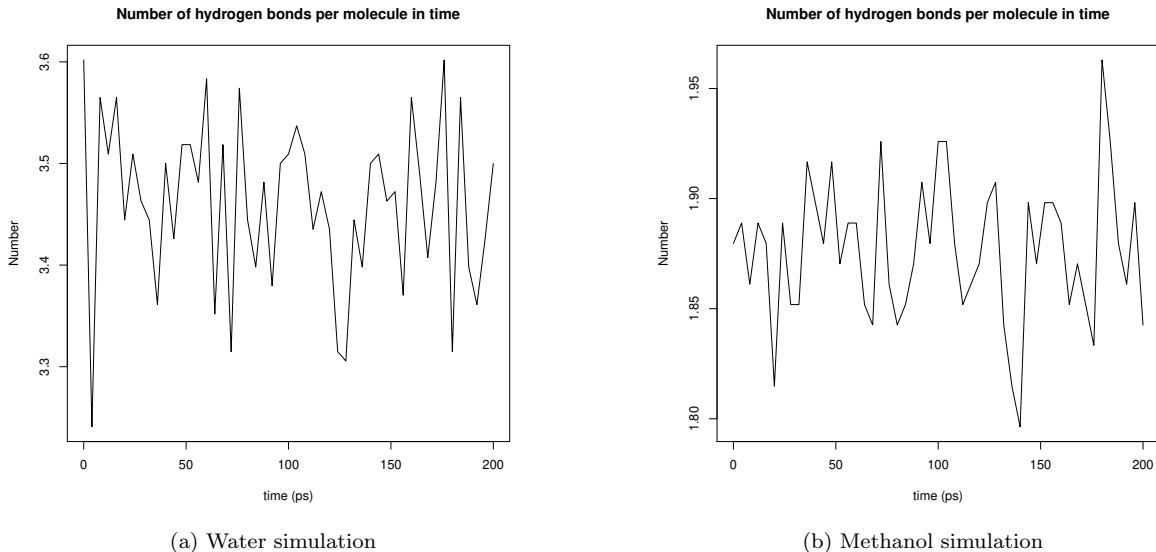(a) Water simulation   (b) Methanol simulation

Figure 4: Number of hydrogen bonds per molecule in time

both water and methanol. The characteristic oscillations appear because the hydrogen bonds lifetime is limited, thus in each iteration new bonds appear and other are broken according to changes in atoms positions. In the Table 2 some other important statistics on this topic are presented. One may note that the average number of hydrogen bonds per molecule is much higher for the water than for methanol what means that more energy would be needed to break all the intermolecular attractions for this substance.

To correctly compare the experimental and simulation results it's first worth to highlight some important features. Each water molecule possesses two proton donors and two proton acceptors (lone pairs of electrons) and is capable of having up to 4 hydrogen bonds. The mean number is known to depend on the assumed charges in the model thus its value varies depending on the chosen system [3]. Having this in mind as well as the difference in the definition interpretation and experimental methodology, there's no agreement among the scientists what is the accurate number of hydrogen bonds per water molecule. It's estimated to be between 2 and 4 depending on the taken approach. The experimental techniques such as for example oxygen K-edge X-ray absorption technique results in 3.3 value at 298 K and 1 bar pressure while theoretical analysis of XAS and XRS spectra, based on density functional theory (DFT) with a small model cluster of 11 molecules, revealed that each molecule has on average 2.2 ± 0.5 H-bonds at 25°C. What is known for sure is that the mean value decreases with the increasing temperature [3]. The resulting simulation value seems to be reasonable and consistent with the current knowledge since many studies have obtained the similar number [3]. Nevertheless, it was shown in [14] that MD simulations give more accurate results at higher temperatures [14] thus some discrepancy has the right to appear at 298 K.

Regarding the methanol, it can form up to three hydrogen bonds, one donated and two accepted. Various MD simulation demonstrated that a methanol molecule in overwhelming majority of cases forms only 2 - one donated and one accepted [9]. The simulation observation is consistent with this fact. The mean value does not exceed 2 and oscillates around 1.9. Moreover, it may be noticed that it is lower than for the water what is caused by the lower polarity of the methanol molecules [14].

Table 2: Analysis of the number of hydrogen bonds

Simulation	Total average number	Average number per molecule	Maximum number per molecule	Experimental number per molecule
water	373.7	3.46	3.6	between 2 and 4
methanol	202.667	1.88	1.96	around 2

6 Density

The last step in this simulation analysis is the study of how the density of the substances changes in time what is presented on the Figure 5.

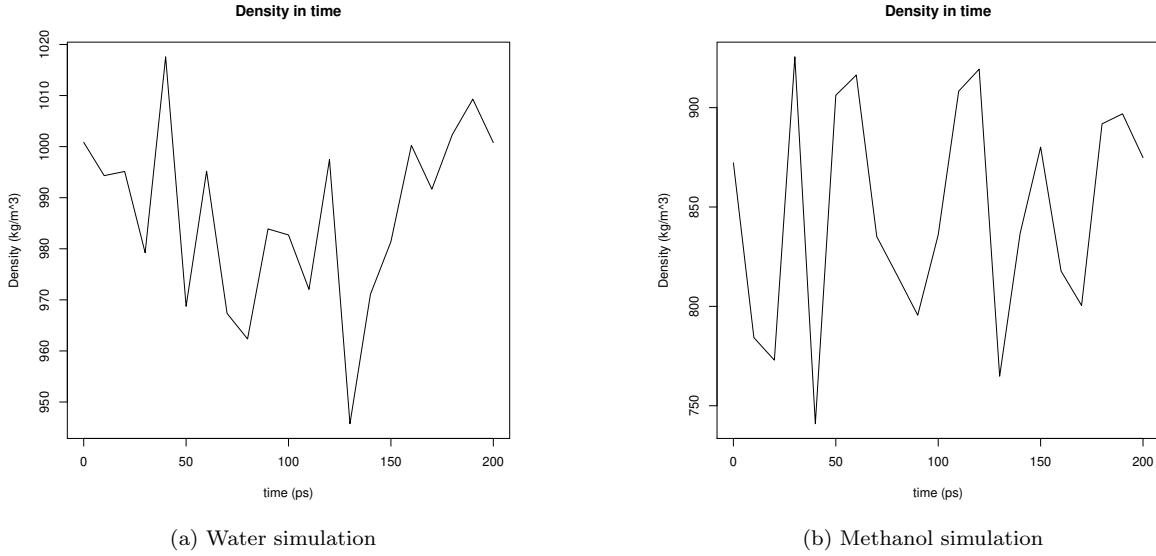(a) Water simulation

(b) Methanol simulation

Figure 5: Substance density in time

It's noted that the density value doesn't seem to raise nor decrease but rather oscillates around some average value as it happened in the previous sections. This behaviour is caused by the microscopic changes in the system in each simulation iteration. In the Table 3 the estimated density and the experimental one are compared.

Table 3: Analysis of the density

Simulation	Average simulation density $\frac{kg}{m^3}$	Estimation error	Experimental density $\frac{kg}{m^3}$ at 1 atm and 298.15 K
water	975.01	1	997.04 [19]
methanol	845.2	6	786.9 [7]

It is confirmed in the simulation that SPC water model approximates really well the density. In case of the methanol the result is worse and less precise (larger estimation error) though still acceptable (error around 7%).

7 Conclusion

In this report I have performed the molecular dynamics simulation of both water and methanol and tried to compare the results with the experimental ones and those from other papers. It seems that the used models are a decent approximation of the reality and rather consistent with the up to date observations.

As it was predicted by the scientists SPC water model deals quite well with the approximation of the majority of the considered here substance properties though fails to calculate well the diffusion coefficient due to the assumed model charges. The best result was obtained for the water density that approximated the experimental value in 97%. Similarly, the radial distribution was well estimated though there is still room for improvement. The matter of the correct calculation of the hydrogen bonds is slightly obscure since no strict number is considered the best one in the science society. Nevertheless, the value does not exceed the maximum one and belongs to the range obtained in other studies. The inclusion of the polarization effect without no doubt has a generally positive impact on the simulation accuracy. However, the assumed charges in the model influence on the incorrect diffusion coefficient calculation. The other disadvantages of the SPC are that the angle between the atoms is a bit higher than the real one and the molecule is considered rigid. All these factors may result in some differences between the simulation and experimental data.

Regarding the methanol, it was shown that the used model manages to estimate rather well all considered properties. Obviously, the discrepancies appear. Although the overall shape of the radial distribution function is reproduced, the first peak is significantly higher than for the experimental data. The very encouraging results were obtained for the estimation of the diffusion coefficient with 87% of the accuracy and the density with 93%. Similarly, the number of hydrogen bonds has a reasonable value. To sum up the methanol simulation, the GROMOS96 model seems to predict all the investigated properties at the similar level. The inconsistencies appear for each one of them but for none they are large enough to state that it fails to reproduce some characteristic.

The conducted computer experiment has demonstrated that the simple basic simulations are capable of reproducing the liquid properties at the acceptable level. Surely, the larger systems and more complex models would estimate better all the characteristics though it is already possible to conclude the general substance behaviour and observe the influence of the microscopic behaviour on the macroscopic state for small and not complex systems. Nevertheless, to diagnose perfectly the accuracy and correctness of the used models further investigation with longer simulation time and bigger number of molecules is needed.

References

[1] Water structure and science by Martin Chaplin, howpublished = `http://www1.lsbu.ac.uk/water/water_models.html`,.

[2] A. Bartók A. Baranyai and A. A. Chialvo. On the performance of simple planar models of water in the vapor and the ice phases, in physics and chemistry of ice, ed. w. kuhs, pp. 109-115.

[3] Amit K. Ghosh Abhishek Rastogi and SJ Suresh. Hydrogen bond interactions between water molecules in bulk liquid, near electrode surfaces and around ions.

[4] L Bianchi C J Wormald Ashok Adya, Oleg N. Kalugin. The structure of liquid methanol: A molecular dynamics study using three-site models.

[5] B.Guillot. A reappraisal of what we have learnt during three decades of computer simulations on water. *Journal of Molecular Liquids*, 2002.

[6] Paul J. van Maaren David van der Spoel and Herman J. C. Berendsenb). A systematic study of water models for molecular simulation: The derivation of water models optimized for use with reaction field.

[7] HAIYAN LIU WILFRED F. VAN GUNSTEREN HAIBO YU, DAAN P. GEERKE. Molecular dynamics simulations of liquid methanol and methanol–water mixtures with polarizable models. *Wiley InterScience*, 2006.

[8] Saeed Izadi1 and Alexey V. Onufriev. Accuracy limit of rigid 3-point water models.

[9] Tobias Steinel John B. Asbury and M. D. Fayer. Hydrogen bond networks: Structure and evolution after hydrogen bond breaking.

[10] Hind Abu-Ghazleh Rakan Al-Salmanb Manal Al-Alia Khitam Khasawneha, Abdalla Obeidatb. Evaluation test of the most popular models of methanol using selected thermodynamic, dynamic and structural properties.

[11] A. Sacco M. Holz, S.R. Heil. Temperature-dependent self-diffusion coefficients of water and six selected molecular liquids for calibration in accurate 1h nmr pfg measurements. *Physical Chemistry Chemical Physics*, 2000.

[12] J. Mavri M. Praprotnik, D. Janezic. Temperature dependence of water vibrational spectrum: A molecular dynamics simulation study.

[13] Denys E. S. Santos Thereza A. Soares Manoela P. M. Lima, Manuela Nader. Compatibility of gromos-derived atomic parameters for lipopolysaccharide membranes with the spc/e water model and alternative long-range electrostatic treatments using single nonbonded cutoff and atom-based charge schemes.

[14] Mara Cantoni Palazzo Mancini. Molecular dynamics simulation of methanol-water mixture.

[15] A. Pullman. Intermolecular forces.

[16] C. R. Groom T. van Mourika R. E. Skyner, J. L. McDonagh and J. B. O. Mitchell. A review of methods for the calculation of solution free energies and the modelling of systems in solution.

[17] A.K. Soper. The radial distribution functions of water and ice from 220 to 673 k and at pressures up to 400 mpa. *Chemical Physics*, (121±137), 2000.

[18] Akihiro Morita Tatsuya Ishiyama, Vladimir Vyacheslavovich Sokolov. Molecular dynamics simulation of liquid methanol. i. molecular modeling including c-h vibration and fermi resonance. *The journal of chemical physics*, (24046076), 2011.

[19] Berndt Wischnewski. Richard-wagner-str. 49.