

MSE 760 project Final report

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1 Water Model candidates-Pros and cons

The definition of a water model generally contains (i) the geometry within a water molecule, i.e. the angle between two H–O bonds and the length of H–O bonds, (ii) parameters for atomic charges and Lennard-Jones (LJ) potential. Several trade-offs exist when considering the choice of an appropriate water model.

First comes with the computational complexity. While simple empirical models with less fitting parameters can be used/perform fine in large system size (usually larger than 10,000 molecules) or long simulation time (larger than 10 ns), complex models, especially *ab initio* models would provide accurate results even with a much smaller system size (smaller than 1000 molecules).

Second is the rivalry between electrostatic forces and LJ interaction. At short distance range, LJ force is adding strong repulsion such that atoms would not collapse owing to electrostatic attractions. While at an intermediate distance, according to its nondirectional nature, LJ interactions will compete with the directional attractive electrostatic forces in order to hold up the structure. A hint of the interaction between electrostatic forces and LJ forces can be seen in Eq. (1).

$$E_{ab} = \sum_i^{ona} \sum_j^{onb} \frac{k_C q_i q_j}{r_{ij}} + \frac{A}{r_{OO}^{12}} - \frac{B}{r_{OO}^6} \quad (1)$$

Table. 1 shows the parameters of 4 selected water models. SPC, SPC/E and TIP3P-Ew models are all 3-site planar models, where three interaction points coincide with the three atoms of water molecule. Every site is associated with a point charge with slightly differed values, while the site corresponding to oxygen atom has the contribution from LJ forces as well. Within the 3-site models, SPC model simplifies the structure of water molecule using the *H-O-H* angle of an ideal tetrahedral, as 109.47° , instead of the observed value as 104.52° .

2 Previous problems and corresponding findings

- Create a bulk of H₂O with associated potentials (SPC, SPC/E, TIP3P, TIP4P, TIP4P-Ew). It is known that different water models are developed to fit well with some specific parameters (i.e., the radial distribution function, the density anomaly or other critical

Parameters	SPC	SPC/E	TIP3P-Ew	TIP4P-Ew
$\epsilon_{O-O}/(kcalmol^{-1})$	0.15535	0.15535	0.102	0.16275
$\sigma_{O-O}/\text{\AA}$	3.166	3.166	3.188	3.16435
q_H/e	0.41	0.4238	0.415	0.52422
q_O/e	-0.82	-0.8476	-0.83	
q_M/e				-1.04844
$l_{O-H}/\text{\AA}$	1.0	1.0	0.9572	0.9572
$l_{O-M}/\text{\AA}$				0.125
θ_{H-O-H}	109.47°	109.47°	104.52°	104.52°
$r_c/\text{\AA}$	10.0	10.0	13.0	10.0

Table 1: Parameters of different water models

parameters) [1], thus it requires some tests on which model provides a better fit for surface tension forces. A preliminary test has been run with a flexible SPC/E model developed by Zhang et al. [2], and the $g(r)$ after running for 60,000 steps with step size 0.5fs is shown in Fig. 1. The reference LAMMPS input file comes from [3] with 6400 atoms with a setting to melt ice and equilibrate at 298K.

The data file passed to `read.data` command in the preliminary tests includes the position information of all the atoms converged from crystalmaker, right now only one molecule is defined in the data file and replicated as needed. It becomes much easier to switch water models.

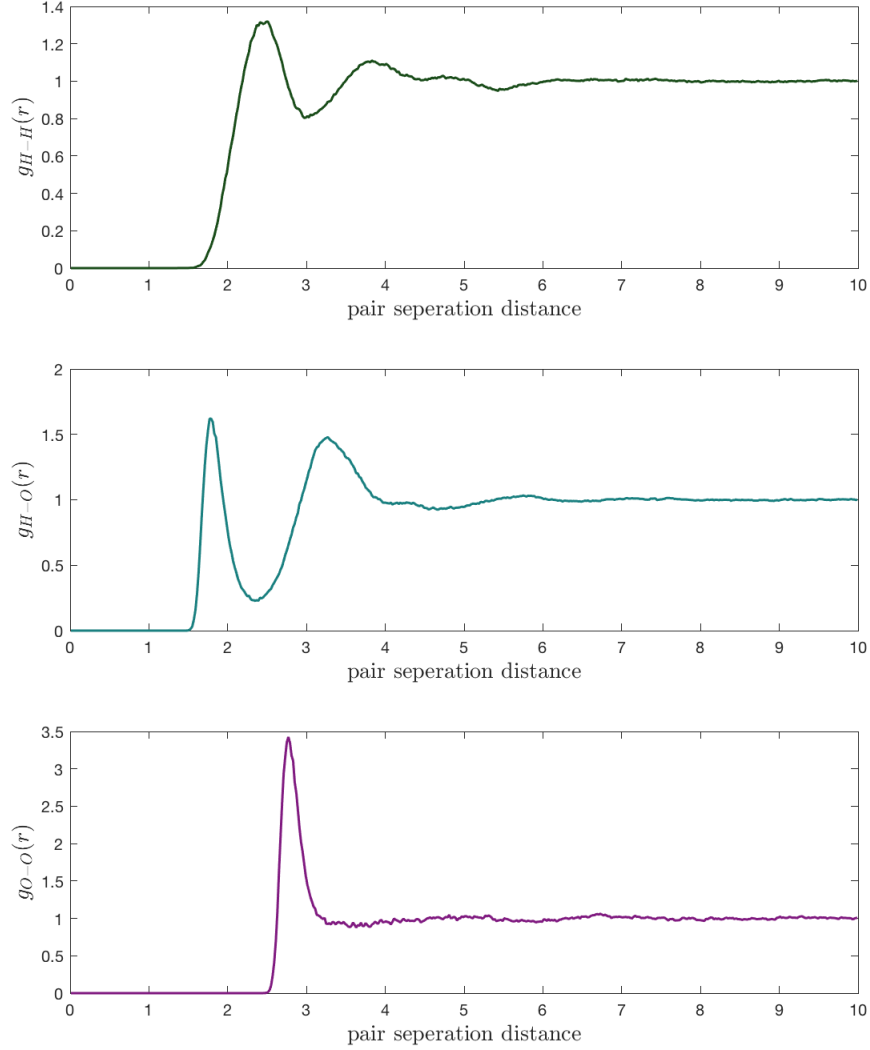


Figure 1: Radial distribution function $g(r)$ with flexible SPC/E model developed by Zhang et al. [2] after running for 60,000 steps with step size 0.5fs at 298K

- Based on the preliminary results, tests can be run with PBC, and I'm currently in the progress of finding an indicator to confirm the relaxation of the system, then compare if `nvt` or `npt` works better for the system. I noticed in the previous lab that we could have equilibration stage and production stage written in the input file, but still need to understand which condition (`nvt`/`npt`) might be proper for which stage and why.

It turned out that `npt` works well for system with PBC in all 3 directions, whereas `nvt` works better for elongated dimension in z direction when trying to equilibrate the system with vacancy. One interesting test could be run to find a better Q , as the time span allowed to reach the target temperature, in order to relax the system within a

proper amount of time and to achieve comparatively small fluctuation. Together with `fix shake` command in LAMMPS, which will preserve the bond and angle parameters to form a rigid model. The way that `fix shake` works is that it will set constraints for the site positions as shown in Eq. (2)

$$\mathbf{r}_{ij}^{n+1} = \mathbf{r}_j^n - \mathbf{r}_i^n \quad (2)$$

$$\mathbf{r}_{ij}^{n+1} \cdot \mathbf{r}_{ij}^{n+1} = d_{ij}^2 \quad (3)$$

- After being comfortable with the single phase water model, a vacuum phase needs to be added with a small volume to allow atoms close to surface some space to relieve their energy. At this point, the main challenge would be how to remove the PBC while still being able to stabilize the system (need to start with some examples on liquid/vacuum interface or liquid/vapor interface and look at how boundary conditions are treated).

The vacancy has been created, although the surface tension results will fluctuate a lot at current stage, as shown in Fig.2

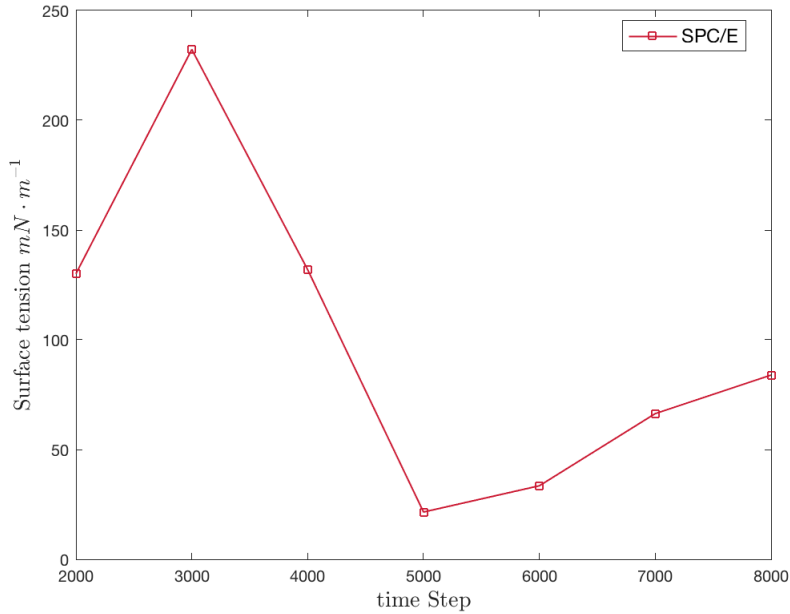


Figure 2: Preliminary results for surface tension with SPC/E model

- When the water model is constructed with proper boundary conditions to stabilize the system, surface tension force will be obtained from pressure following the equations in [4], then compared with their results.

It's hard to tell where the surface tension result lands at current stage. A longer simulation time might help, but as an observation from the visualized system, some water molecules are escaping the bulk even at temperature 300K, which might make the result questionable.

- Subsequently, different water models (SPC, SPC/E, TIP3P, TIP4P, TIP4P-Ew) will be tested to explore their advantages, mostly as a verification of what has been proposed in the literatures, but would be helpful in getting more insight for the physical concept behind different models, rather than simply taking the parameters themselves.

This can be elaborated more in the following weeks.

3 Plots and visualization of molecules

1. Create a bulk of water molecules with PBC

LAMMPS code for creating the water models and input file scripts are referenced from [5].

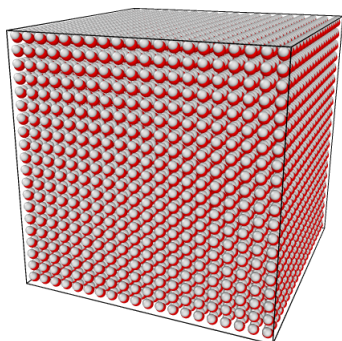


Figure 3: Initial structure with $20 \times 20 \times 20$ molecules

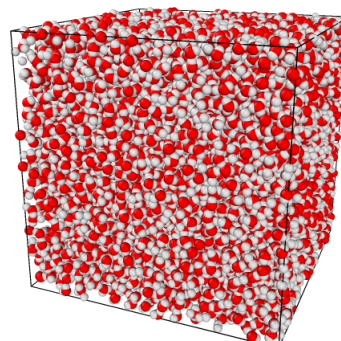


Figure 4: After equilibrated at 298K with 8,000 molecules

2. Check the relaxation of system using Radial Distribution Function $g(r)$

The Radial Distribution Function $g(r)$ for the distance between oxygen atoms $O-O$ can be seen from Fig.5, very similar results can be found for 4 different water models, which confirms the relaxation of system.

The other evidence can be seen from the convergence of potential energy shown in Fig.6

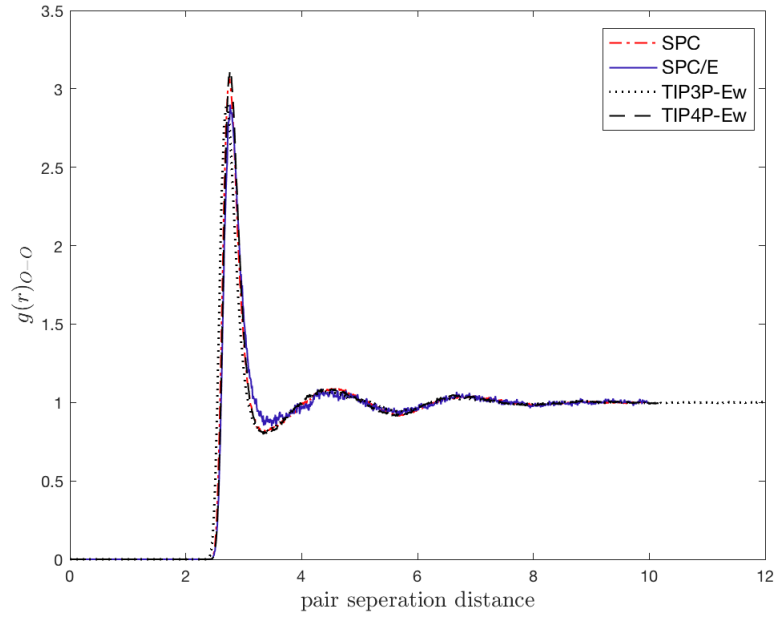


Figure 5: Radial distribution function $g(r)$ SPC, SPC/E, TIP3P-Ew and TIP4P-Ew models after running for 4,000 steps with step size 2.0fs at 298K

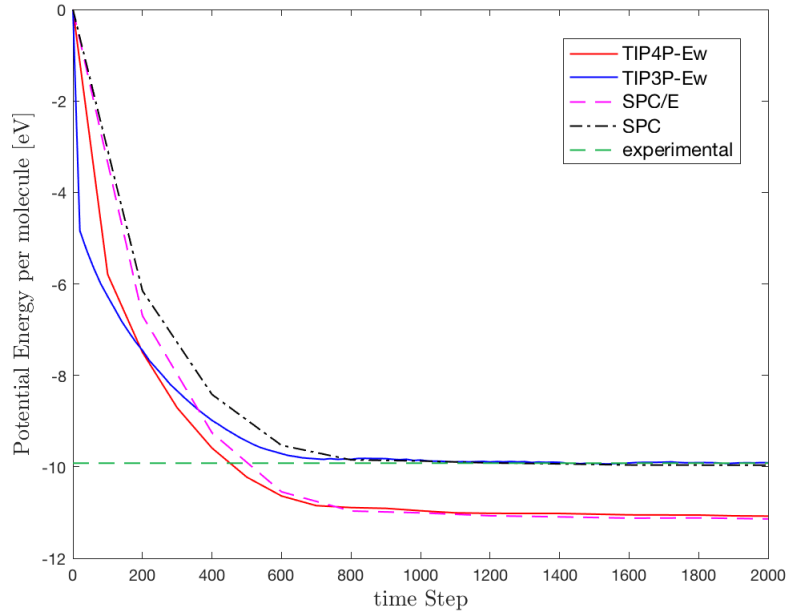


Figure 6: Potential energy per molecule compared among different models and experimental result

3. Enlarge the simulation box in z direction to create vacancy

Tests have been run with both small system size for 1,000 molecules as a $10 \times 10 \times 10$ replicate for box size of 3.1\AA , as well as $20 \times 20 \times 20$ molecules with the same box size. As a comparison of different system size, the resultant surface tension force is $36 \text{ mN} \cdot \text{m}^{-1}$ for small system versus $69 \text{ mN} \cdot \text{m}^{-1}$ for large system at 4,000 time steps, however, as addressed in section 2, the results are not converged, large fluctuation still exists. Fig. 7 shows the simulation box of $10 \times 10 \times 10$ molecules, while Fig. 7b shows the evolution of $20 \times 20 \times 20$ molecules.



Figure 7: $10 \times 10 \times 10$ molecules with step size 1.0fs

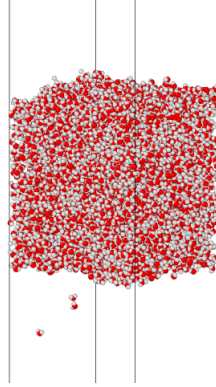
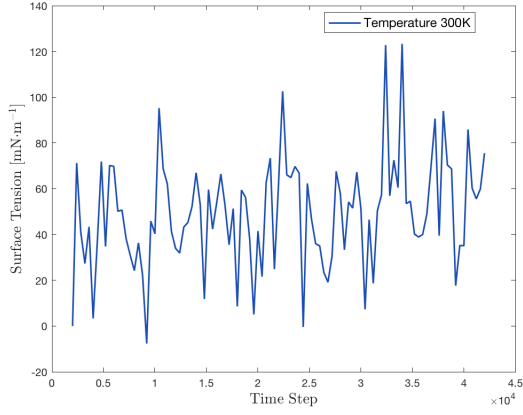


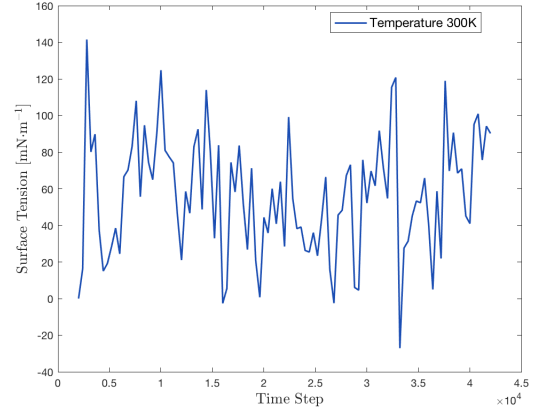
Figure 8: System size of $20 \times 20 \times 20$ molecules after running 2,000 time steps with step size 2.0fs

4. Averaged Surface Tension of different water models

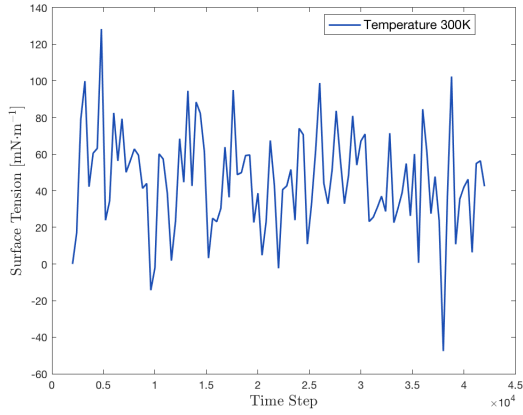
Fig.9 shows the surface tension term of different water models. Large fluctuation exists even after the system is equilibrated for 2,000 time steps with 274K, then increase the temperature towards 300K. An average measurement of surface tension is consequently calculated and shown in Table.2. The surface tension results of this project are in general smaller than the values from literature.



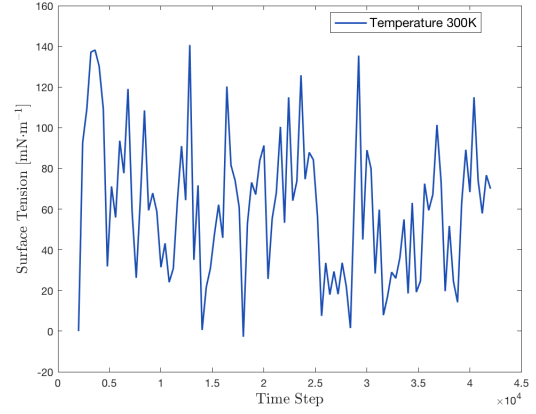
(a) SPC model



(b) SPC/E model



(c) TIP3PEW model



(d) TIP4PEW model

Figure 9: Water surface tension at 300K, large fluctuation exists even after equilibration at 274K for 2,000 time steps

Water Models	This project	Reference [5]
SPC	47.4	48.1
SPC/E	52.7	55.2
TIP3P-Ew	42.9	45.2
TIP4P-Ew	55.1	58.1
Experimental [6]	71.7	71.7

Table 2: Average surface tension at 300K without tail correction

4 Create a bulk of methanol molecules

Methanol is one of the simplest nonaqueous solvents, also the simplest alcohol, consisting of a hydrogen-bonding hydroxyl (OH) group linked to a hydrophobic methyl (CH₃) group. As a polar liquid, the structure of hydrogen bonds in liquid methanol and relevant physical properties have been thoroughly studied both in theory and in experiments [7].

1. OPLS-AA force field

OPLS-AA force field is used in the simulation of Methanol molecules. The original OPLS model refers to OPLS-UA (optimized potentials for liquid simulations with a partially united-atoms). In OPLS-UA model, nonbonded parameters are emphasized, which means sites for nonbonded interactions are only placed on all non-hydrogen atoms and on hydrogens attached to heteroatoms or carbons in aromatic rings [8]. As in Methanol case, only the carbon (C) and oxygen (O) nuclei and hydroxyl proton (H_O) are considered as the centers of interaction. The interaction energy between molecules a and b can be represented in Eq. (4) [9].

$$E_{ab} = \sum_i^{\text{ona}} \sum_j^{\text{onb}} \frac{k_C q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) \quad (4)$$

Although OPLS-UA is preferable for the efficiency of computation, it lacks in flexibility for charge distributions and torsional energetics, whereas torsions play an important role in the internal degrees of freedom for organic systems. Therefore, more sites need to be incorporated in the force field to allow for better fit to reproduce properties of organic liquids, for instance, Methanol, as the interest of this project. Parameters from OPLS-AA model will be used herein.

2. Determine lattice constant

Lattice constant selection is to be aligned with the density at ambient temperature (298K) from the experimental result (0.786 g·cm⁻³). As a comparison with [10], they used a box size of 12.9Å for 32 methanol molecules and a box size of 16.3Å for 64 methanol molecules, which yields an average unit cell size of 4.06Å. In this project, the simulation box size is set to be 24.36Å as a replicate of 6 × 6 × 6 methanol molecules. A different lattice constant may apply for a larger system size.

3. Generate data file for LAMMPS input

Different from the previous setup for water molecules, which was relatively simple and the input data file required by `read.data` command in LAMMPS could be written manually, methanol models contain more atoms, thus more angles, bonds and dihedrals that will take much more effort to build manually. A handful tool `moltemplate` [11] as a general molecule builder and force-field database system for LAMMPS is used to translate the force field into recognizable input files for LAMMPS. Additionally, a useful tutorial from M.A. Gonzalez and E.Pellegrini at Institut Laue-Langevin [12]

provides a python script to generate input files for `moltemplate`. In their tutorials, a process of ethanol simulation helps a lot as the starting point of methanol simulation of this project.

4. **Running simulation with PBC in all dimensions**

To begin with the simulation, a bulk of methanol molecules with PBC is run with OPLS-AA force field parameters and pre-determined lattice constant. After equilibration for 40,000 time steps with step size 2.0fs, radial distribution function of different pairs is shown in Fig.10, as compared to [13].

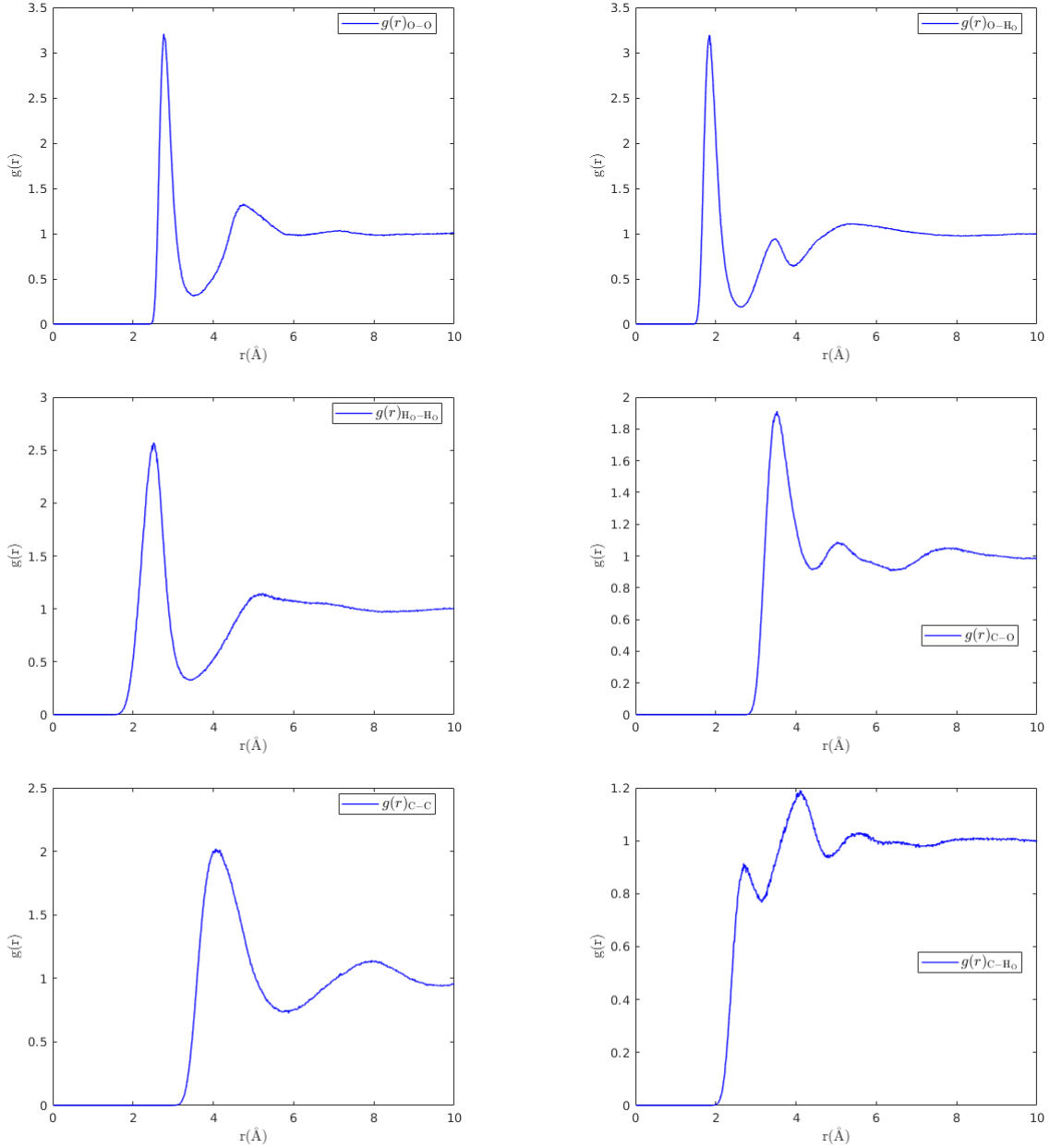


Figure 10: Water surface tension at 300K, large fluctuation exists even after equilibration at 274K for 2,000 time steps

5 Create vacancy in the simulation box for methanol

1. A proper constraint method

It's been found in the literature that different constraint methods exist to treat the bond-stretching interactions in different perspectives. For instance, popular algorithms like SHAKE [14] and RATTLE [15] have been intensively used to simulate rigid methanol molecules [16], normally with a residual of 10^{-4} .

The way that constraint algorithm works is as the following [17]: (i) choose novel unconstrained coordinates (internal coordinates), (ii) introduce explicit constraint forces, (iii) minimize constraint forces implicitly by the technique of Lagrange multipliers or projection methods. Many literatures selected SHAKE algorithm [18] with GRO-MOS96 [19] force field to mitigate the constraint issue. While a formal definition regarding Flexible-Constrained, Hard-Constrained and Non-Constrained MD simulations has also been studied with respect to water and methanol models [20].

2. Current problems about fix shake command in LAMMPS

In `fix shake` command, I've tried to constrain the O-H bond and the C-H bonds, ideally it's more convenient to have the methyl (CH_3) be a rigid group, but it was not able to be achieved by the time I have to submit the project. It would be potentially related to the "missing atoms" error found in the simulation when enlarge the z dimension box size to create vacancy.

3. What can be done to mitigate the issue

A proper constraint would help to stabilize the system, and to consider the methyl (CH_3) group as a rigid body would prevent the hydrogen atoms exploding at the beginning of simulation. Current implementation can be seen from Fig. 11. The initial lattice configuration, and the stabilized system from PBC can be seen from Fig. 12. A confirmation of the potential energy convergence can be seen from Fig. 13.

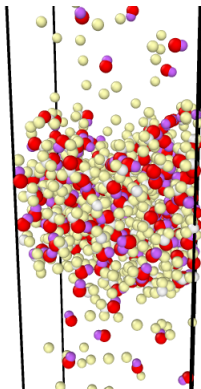
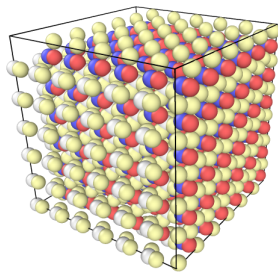
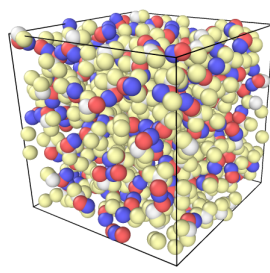


Figure 11: Hydrogen atoms fly out of the CH_3 constraint, red is Oxygen, purple is H in HO, yellow is C, grey is H in HC



(a) Initial lattice



(b) 40,000 time steps

Figure 12: $6 \times 6 \times 6$ methanol molecules with step size 1.0fs

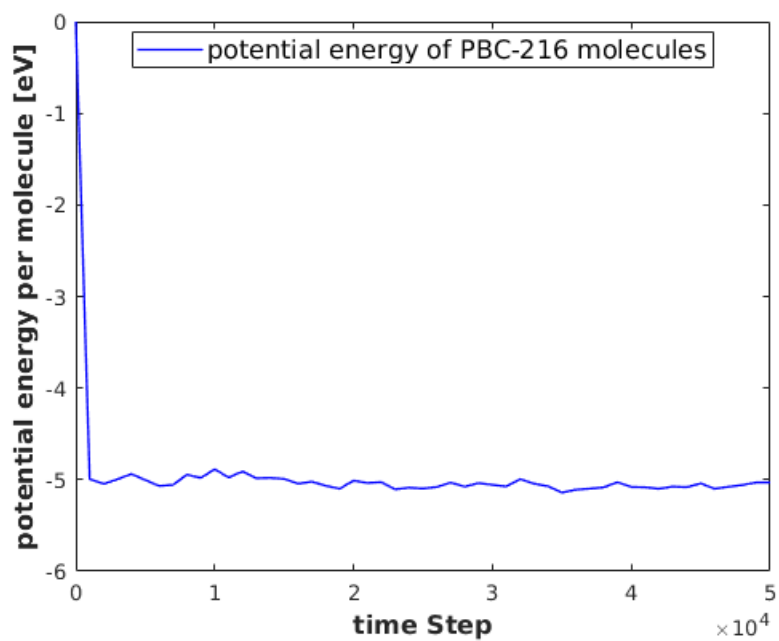


Figure 13: Convergence of potential energy for PBC case

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