# Final Project: Simulating Water and Ethanol

**2MMN40: Introduction to Molecular Modeling and Simulation**
Last update: October 26, 2020

## Contents



## 1 Introduction

This document describes the course project. By the end of the course you have written a fairly powerful Molecular Dynamics (MD) simulator in Python. In this project you will make use of your simulator to study a water and ethanol mixture. As you work on this project, keep in mind the theory that you have learned during the lectures, and try to make connections to it in your analysis and results.

### 1.1 Groups

For this project you will be working in groups of two. You can assign yourself to a group in canvas.

## 2 Report Structure

The report should have the structure of a scientific paper, it should have an introduction explaining the problem. This should also include a short literature review which would include a summary of what has been done in a *scientific* context, experimentally or otherwise, to study ethanol in water. Outline some interesting phenomena — will you be able to study these phenomena with your code? Describe the structure of the molecules that you will study. What problems do you foresee in studying these things? Do you think that your code and force-field are enough to capture all of the Physics in this system? Why or why not?

You may use the headings in this document as a guideline of what sections to have in your report. You also have the freedom to write your report however you like, however, the questions posed in this document should be answered at a minimum. You may of course explore these topics further, or consider other topics you find interesting.

Treat this report like a scientific paper. That means that one should cite any resources used and include a properly formatted bibliography. Important scientific/mathematical statements made in your report should be either supported by a citation or by a result that you produce yourself. There is no such requirement as a *minimum* number of citations, but there should be a few that you are bound to collect during your work.

There is a hard upper limit of 15 pages for this report, not including the code and any appendices. There is no minimum page count.

# 3 Theory

Summarize the methods that you are using to study this system. Make connections to the theoretical concepts that you have learnt in the lectures.

Describe the physics of this system with some detail. Talk about some of the physical and chemical properties of the water/ethanol system and discuss what you think can and cannot be captured by classical MD. Why is this system interesting to study? Name some interesting physical or chemical phenomena that this system has. Out of the things you think can be studied with MD, do you think your code can simulate it?

## 3.1 Integrator

You have spent some time studying some different integrators, provide an analysis of the different integrators that you have used. Use $H_2$ as an example molecule. We encourage you to try an integrator that was not covered in the course. Discuss why velocity verlet is a good integrator to use for the simulation.

# 4 Simulation

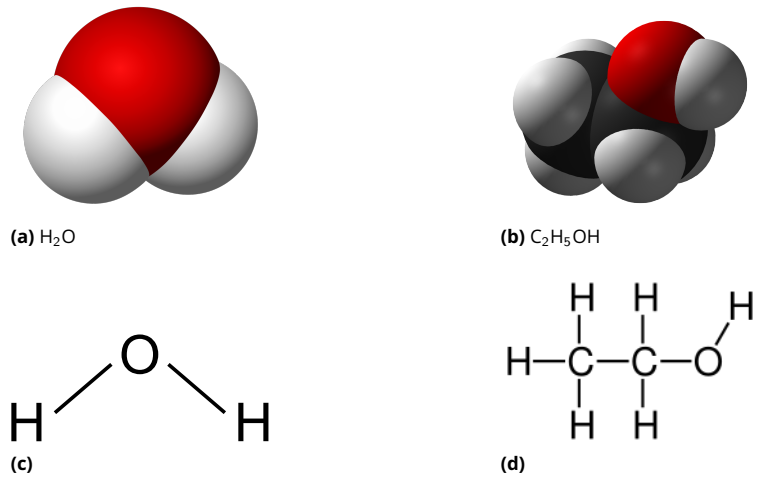



**Figure 1.** The molecules in this system.

Figure 1 shows the molecules that you will be simulating for this project. You will be simulating solutions of ethanol in water.

All force-field parameters are given in section 4.3.

## 4.1 Systems to Simulate

Simulate the following three cases with your NVT simulator:

- A system of pure water
- A system of pure ethanol
- A system of 13.5 %v/v ethanol in water

For each case, simulate a system in a $5\times5\times5$nm box. If this system seems to be running relatively fast for you, then you may simulate a larger system if you wish. Do the simulations at 300K. If you have time, try a range of temperatures in [250K, 350K].

You should follow the guidelines in this section in your simulations. However, please make some arguments with regards to why the numbers here are, or aren't reasonable. These arguments may be physical or computational (performance reasons).

## 4.2 Simulation Parameters

Run the simulations for 0.1ns with a time step of 2fs. You may run longer simulations if you are able. 1ns would be ideal. For Lennard-Jones, use a cut-off length of 0.8 nm. Do not calculate any Lennard-Jones between atoms within the same molecule (is this the right thing to do?).

### 4.2.1 Mixing Rules

The Lennard-Jones (LJ) potential assumes that we are considering interactions between identical atom types. They have to be tweaked slightly when considering the interaction between two different atom types. This amounts to a slight rescaling of the LJ constants. If $\sigma_i$ and $\sigma_j$ are the constants for two different atoms $i$ and $j$ (say Oxygen and Carbon), then the value corresponding to their interaction will be

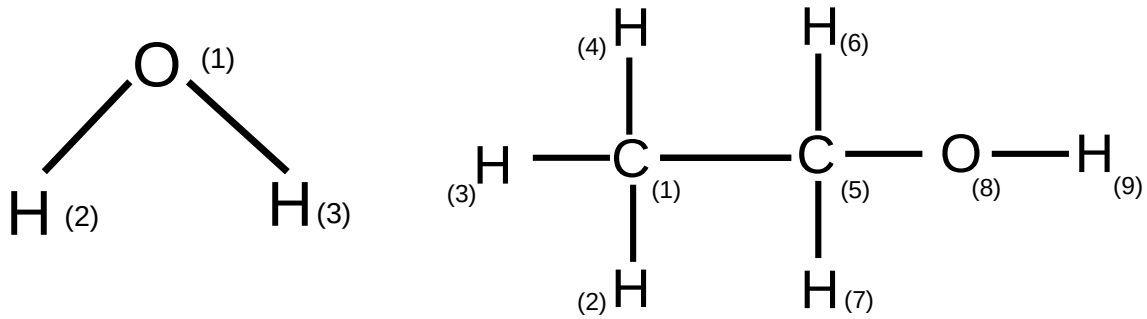
$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j). \tag{1}$$

And for the $\epsilon$'s,

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}. \tag{2}$$

Give some details with regards to why these mixing rules are needed. Can you think of a better way to consider the mixing?

## 4.3 Force-Field Parameters




**(a)** **(b)**

**Figure 2.** Labelled structure for Water and Ethanol. You may, naturally, change the indexing to whatever you like. The bonds, angles, and dihedrals below are defined with these indices in mind.

### 4.3.1 Water

The bonds and angles defined below use the indices in figure 2. The parameters below were taken from the TIP3P water model.

| Species | Mass (amu) |
|---|---|
| H | 1.0080 |
| O | 15.9994 |

**Table 1.** $H_2O$ masses

| Species | $\sigma$ (nm) | $\epsilon$ (kJ/mol) |
|---|---|---|
| O | 0.315061 | 0.66386 |
| H | 0 | 0 |

**Table 2.** $H_2O$ Lennard-Jones parameters.

| $ij$ | $R_o$ (nm) | $k_b$ (kJ mol$^{-1}$ nm$^{-2}$) |
|---|---|---|
| 12, 13 | 0.09572 | 502416 |

**Table 3.** $H_2O$ bonds.

| $ijk$ | $\theta_o$ (°) | $k_\theta$ (kJ mol$^{-1}$ rad$^{-2}$) |
|---|---|---|
| 213 | 104.52 | 628.02 |

**Table 4.** $H_2O$ Angles.

### 4.3.2 Ethanol

Refer to figure 2. These parameters were taken from the OPLS/AA force-field.

| Species | Mass (amu) |
|---|---|
| C | 12.0110 |
| Rest | Table 5 |

**Table 5.** Ethanol masses

| Species | $\sigma$ (nm) | $\epsilon$ (kJ/mol) |
|---|---|---|
| H (bonded to C) | 0.25 | 0.125520 |
| H (bonded to O) | 0.00 | 0.00 |
| C | 0.35 | 0.276144 |
| O | 0.312 | 0.711280 |

**Table 6.** Ethanol Lennard-Jones parameters.

| $ij$ | $R_o$ (nm) | $k_b$ (kJ mol$^{-1}$ nm$^{-2}$) |
|---|---|---|
| 15 | 0.1529 | 224262.4 |
| 31,41,21,65,75 | 0.1090 | 284512.0 |
| 58 | 0.1410 | 267776.0 |
| 98 | 0.0945 | 462750.0 |

**Table 7.** Ethanol bonds.

| $ijk$ | $\theta_o$ (°) | $k_\theta$ (kJ mol$^{-1}$ rad$^{-2}$) |
|---|---|---|
| 215, 315, 415 | 108.5 | 292.880 |
| 413, 412, 312, 657 | 107.8 | 276.144 |
| 157,156 | 110.7 | 313.800 |
| 158 | 109.5 | 414.400 |
| 589 | 108.5 | 460.240 |
| 658, 758 | 109.5 | 292.880 |

**Table 8.** Ethanol Angles.

### 4.3.3 Dihedrals

You will need to include dihedrals for the ethanol molecule. We will use a slightly more complicated potential named the Ryckaert-Bellman potentials. These are not that complicated actually because they're periodic, so taking their gradients is straight-forward.

$$V(\psi) = \frac{1}{2}\left(C_1(1+\cos(\psi)) + C_2(1-\cos(2\psi)) + C_3(1+\cos(3\psi)) + C_4(1-\cos(4\psi))\right)$$

where $\psi = \theta_{ijkl} - 180°$.

| $ijkl$ | $C_1$ (kJ mol$^{-1}$) | $C_2$ (kJ mol$^{-1}$) | $C_3$ (kJ mol$^{-1}$ | $C_4$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| 2156, 3156, 4156 2157, 3157, 4157 | 0.62760 | 1.88280 | 0.00000 | -3.91622 |
| 2158, 3158, 4158 | 0.97905 | 2.93716 | 0.00000 | -3.91622 |
| 1589 | -0.44310 | 3.83255 | 0.72801 | -4.11705 |
| 6589, 7589 | 0.94140 | 2.82420 | 0.00000 | -3.76560 |

**Table 9.** Ethanol Dihedrals.

### 4.4 Thermostat

Use the simple velocity rescaling thermostat to set the temperature of your system. This is done by simply rescaling the momenta up and down towards the desired temperature by a factor $\lambda$

$$\vec{p}_s = \lambda \vec{p}$$

where $\lambda = \sqrt{(T/T_i)}$. $T$ being the desired temperature, and $T_i$ being the current temperature.

Discuss the efficacy of this thermostat. Do you think that it is suitable for your simulation? If you have time, you may implement one of the other thermostats covered in the lectures and compare.

## 5 Code

Attach your code to this report in a single file[1]. The code should be well commented and you should provide enough documentation such that it can be understood and run by us. It should also run flawlessly with a standard Anaconda3 installation. You may use libraries that are not included[2] in Anaconda3, but then these libraries should be clearly listed. Obviously, you may not use any libraries that do the MD computations for you...

In your report, make a flowchart showing how your code works. Make an assessment of the performance, and flexibility of your code. Outline the things you have learnt while writing it. What do you think is particularly impressive regarding your code? What is not so impressive? Would you change anything? Make some proposals that you think will improve your code[3].

## 6 Results

For each of your simulations measure:

1. Total Energy
2. Potential Energy
3. Kinetic Energy
4. Temperature
5. Some Radial Distribution Functions (Pair Correlation Functions)
   (a) O-O (water-water, ethanol-ethanol, and ethanol-water)
   (b) O-H (water-water, ethanol-ethanol, and ethanol-water)

Compare your results to other known results or results from other simulations in the literature. For example, see Guo *et al.* Phys.Rev.Lett. 91, 157401 (2003).

## 7 Conclusion

Summarize your report and present some interesting conclusions. Propose some extensions to this project in the future.

[1] This means either one source file or a zip file if you have multiple source files

[2] We don't expect you to do this, but we allow it nevertheless.

[3] At the end of this course, we encourage you to publish your code on github and share it with the world. We think it will look particularly impressive on a CV.

## Appendix A Tips and Hints

Some hints you can follow but you do not have to do:

- Running an MD simulation requires three steps. Setting up an initial structure, running an MD simulation and analyzing the data. Writing three programs, where each does one of these tasks, will make your code more readable and give you more safety as you can save intermediate results. It requires a bit more code for writing and reading input files though.
- Besides the geometry and the topology your program will require additional input options, timestep, temperature , number of steps etc.... You can write these parameters into your code or better make an option file which is read by your code. It separates your data more from your code and makes running multiple simulations easier.

# Appendix B Assessment Rubric for the Final Project 2MMN40

| Criteria | Excellent (4) | Good (3) | Sufficient (2) | Insufficient (1) |
|---|---|---|---|---|
| Organization of written report (A: 10%) | Report is clear and logical. Reader can easily follow line of reasoning. | Report is generally clear. A few minor points may be confusing. | Reader can follow the report with effort. Organization not well thought out. | Report is very confusing and unclear. Reader cannot follow it. |
| Report style (B: 10%) | Style is appropriate and makes use of the field's terminology. Not too casual. Reader can clearly understand impact and purpose of the work. | Style is generally appropriate. May have some trouble in explaining results or purpose of the work. | Report is too informal or unprepared. Difficult to understand. Much of information lacks focus and clarity. | Report is consistently at an inappropriate level. Information is not well synthesized. Reader can't understand the point of the work. |
| Content: Depth (C: 30%) | Theory, methods, results, discussion and conclusions are clearly and coherently elucidated. Logical and persuasive agreement between data and conclusions. Impact and implications of results. | Description of project and results is generally clear. Some discussion of what results mean. | Some components of project description are minimal or missing. Little discussion of what results mean. | Description of the project and results is very difficult to follow. No discussion of meaning of results. Readers learn little. |
| Content: Accuracy (D: 20%) | Information given is consistently accurate. Facts and calculations are correct. | No significant errors are made. Readers recognize errors as result of oversight and offer advice to correct. | Enough errors made to be distracting, but some information is accurate. | Information is so inaccurate that reader cannot depend on the reported results and work. |
| Code quality (E: 10%) | Code runs and is well documented (i.e. there are sufficient but not too many comments). The code has a good structure (i.e. it can be read and understood easily without the need of an excessive number of comments) | Code runs and is well documented. The code is somewhat structured. | Code works partially. Some comments are present and the code is somewhat structured. | Code does not work. |
| Use of Figures and Tables (F: 10%) | Figures and tables are prepared in a professional manner. Font is large enough to be seen. Well organized. Main points stand out. | Figures contribute, but not all material is visually represented well. Font size is appropriate for reading. | Figures are poorly prepared or used inappropriately font is too small. Too much information is included. | No Figures are used, or they are so poorly prepared that they detract from the report. |
| Final synthesis and summary of results (G: 10%) | Main study questions are directly addressed and clarified in the discussion. | Generally responsive to main study questions. Work is put in a general framework of related work. | Report poorly addresses research questions. Very little connection to related work. | Not responsive to research questions. Little to no connection to prior work in the field, and how this work extends that. |

# Appendix C Determination of the Final Grade

## Grade for the report

To compute the grade for the report we will use the following formula

$$\text{Report Grade} = 2.5 \cdot [0.1(A + B + E + F + G) + 0.3C + 0.2D],$$

capitalized letters refer to elements of the rubric, the points can be found between the parentheses in the rubric (e.g. Excellent (4), means you get 4 points).

## Final grade

Your final grade will be determined after a small oral exam. We will ask you a few questions about the project, but it will not be a full defense. Your final grade will be the grade for the report, plus or minus a small adjustment based on your oral exam.