NUMERICAL METHOD 2

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Abstract

Molecular dynamics is the technique that uses the Newtonian mechanics to simulate the movement of atoms and molecules. In this semi-project, we simulate 20 water molecules inside a cubic unit cell with a side length 25Å. Specifically, we examine how radial distribution function, dipole fluctuation and diffusion constant of this system behave under difference temperate at 100 K, 150 K, 200 K and 300 K. Additionally, a comment on how the structural and dielectric properties can be probed experimentally will be given.

1 Introduction

In here, we use NVT ensemble for our simulation.
The following defined molecular units that I use in this note:

- The unit of energy is kJ $\times$ mol^{-1}
- The unit of time is 1×10^{-12} seconds
- The unit of length is 1×10^{-10} meters
- The unit of pressure is 163.882576 atmospheres
- The unit of dipole moment is Debye (3.33564×10^{-30} C.m)

2 Finding equilibrium region for molecular dynamics simulation for water molecule

We use the Verlet's method to examine the total energy with various interval of time. I will consider specifically with the temperature 300 K, and the pressure 0.163 atm. For other data, I will put is in the Appendix A. At first, the system fluctuated in Fig. 1 and Fig. 2, and become equilibrium from the interval from 4 ps to 20 ps. We use this region to calculate the energy drift of the system, and found out the $\Delta t = 0.0005$ ps provides the value, because of this reason, we use it for our following simulation in radial distribution function, and dipole moment fluctuation. Additionally, we find that this conclusion holds for other temperatures.

Δt **(ps)**	**Drift Energy**
0.0005	0.019419999999996662
0.0008	0.07115000000000293
0.001	0.2835800000000006
0.002	1.996780000000001

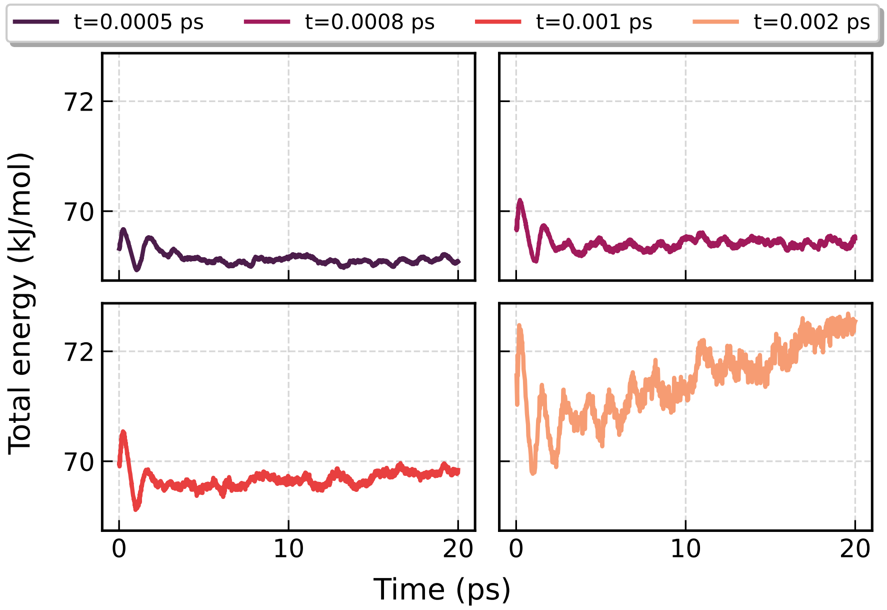
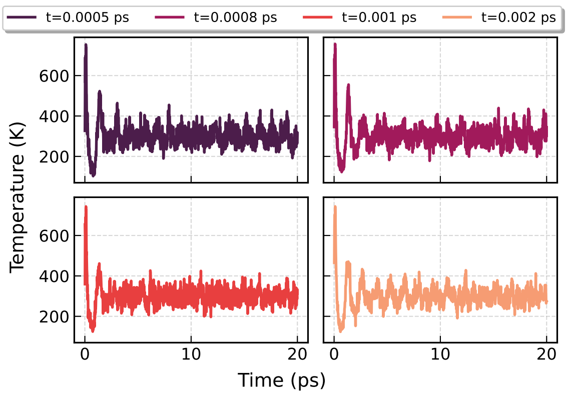
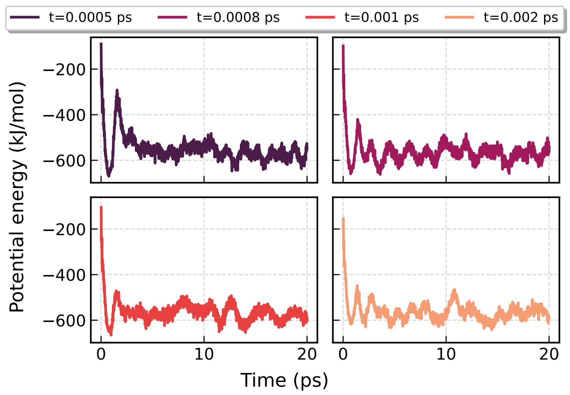


Figure 1: Drift of total energy at 300K



(a)



(b)

Figure 2: (a) Temperaure fluctuation (b) Potential energy at 300K

2.1 Radial distribution function

The radial distribution function can be calculated with the formula

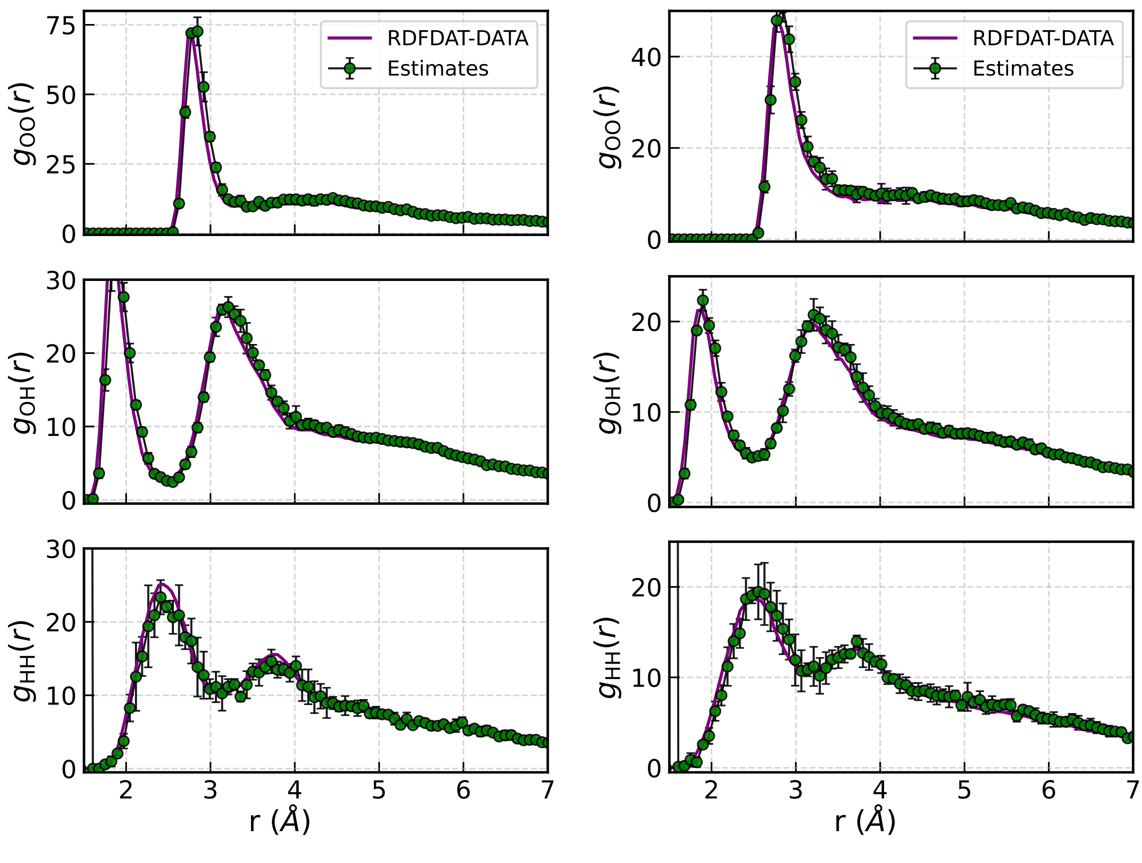
$$g(r) = \frac{dN_r}{4\pi r^2 dr \rho}, \tag{1}$$

with N_r is the number of atoms inside the spherical shell, r is distance from the origin, and ρ is the density of particles. With in this analysis, we collect the raw trajectory of Hydrogen and Oxygen atoms from HISTORY file and truncate for only 4 ps to 20 ps region, we only consider the distance between roughly 2 to 7 Å. Additionally, we can check my accuracy by the following small calculation with 1. We have $N = \int dr\, 4\pi r^2 \rho\, g(r) = \int dr\, 4\pi r^2 \frac{N}{V}\, g(r)$.

So that,

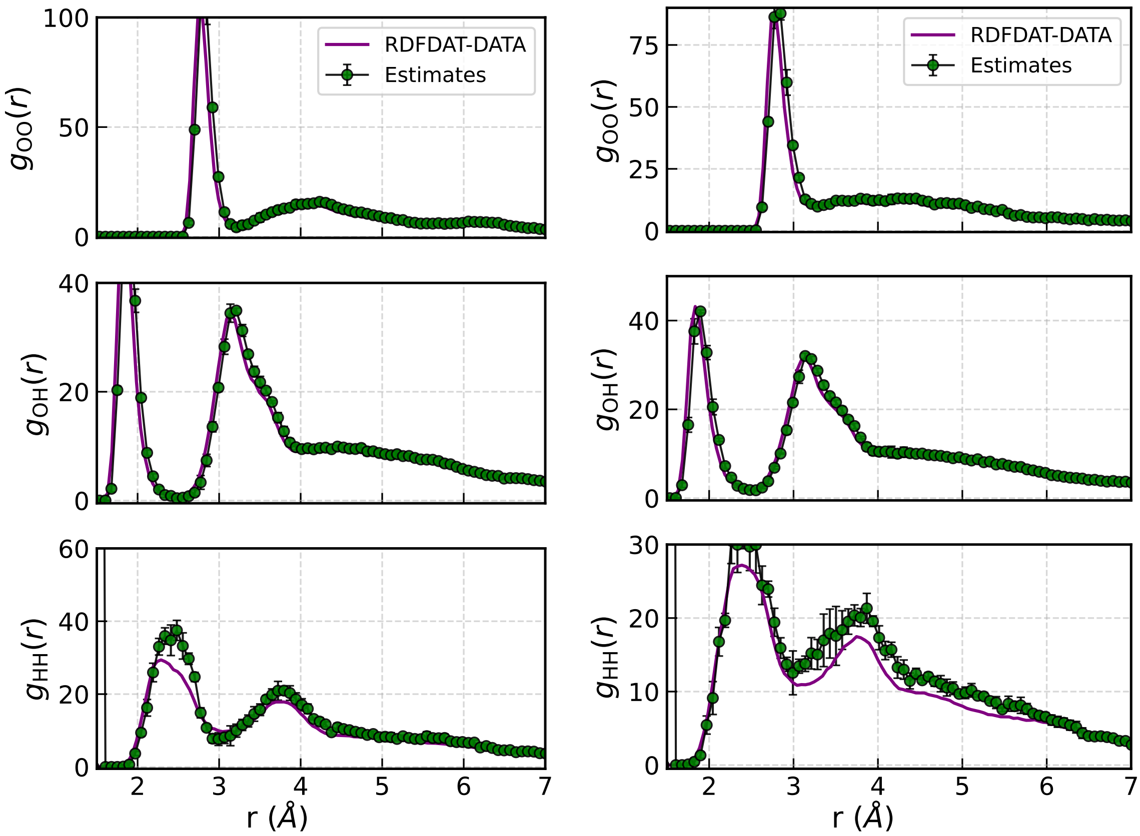
$$\frac{1}{V}\int dr\, 4\pi r^2 g(r) = 1. \tag{2}$$

By applying this formula in my code, you can observe that increasing the number of bins causes the result to approach 1 more closely in an asymptotic manner.



(a) (b)

Figure 3: Radial distribution functions of water molecules at (a) 200 K and (b) 300 K



(a)

(b)

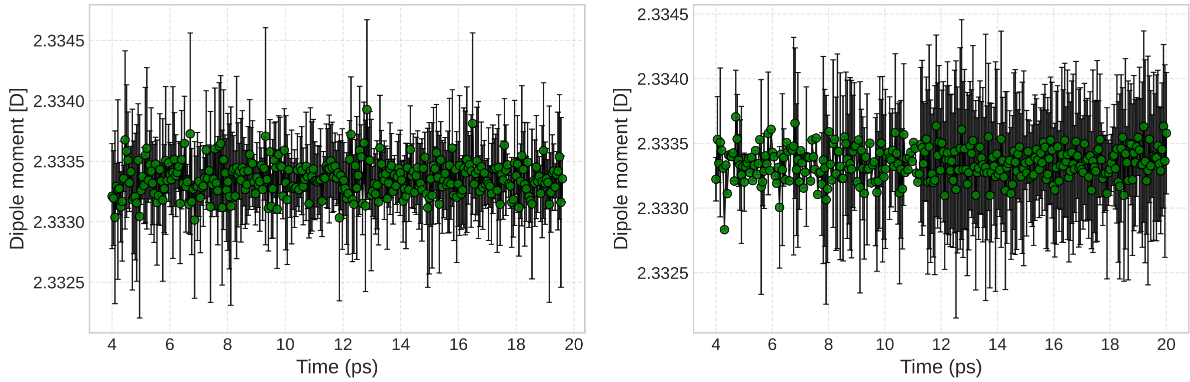
Figure 4: Radial distribution functions of water molecules at (a) 100 K and (b) 150 K

3 Dipole moment

In this analysis, we only examine the two-nearest neighbor hydrogen atoms of the oxygen atom in the radius of 1.2 Å. We need to transform from our unit to Debye unit with a factor [1]

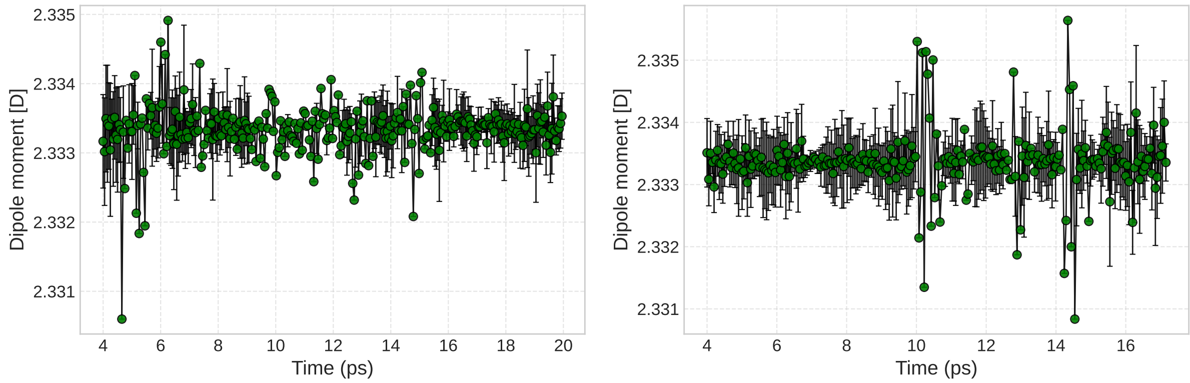
$$\epsilon = \frac{\text{O-H partial charge} \cdot e \cdot \text{Å}}{3.33564 \times 10^{-30}\,\text{C.m}} = \frac{0.42 \times 1.602 \times 10^{-19} \times 10^{-10}\,\text{C.m}}{3.33564 \times 10^{-30}\,\text{C.m}} = 2.01734655502. \tag{3}$$

And again, we only consider the time interval 4 ps to 20 ps.



(a) (b)

Figure 5: Radial distribution functions of water molecules at (a) 100 K and (b) 150 K



(a) (b)

Figure 6: Radial distribution functions of water molecules at (a) 200 K and (b) 300 K

4 Comment and discuss on how the structural and dielectric properties can be probed experimentally

Under construction.

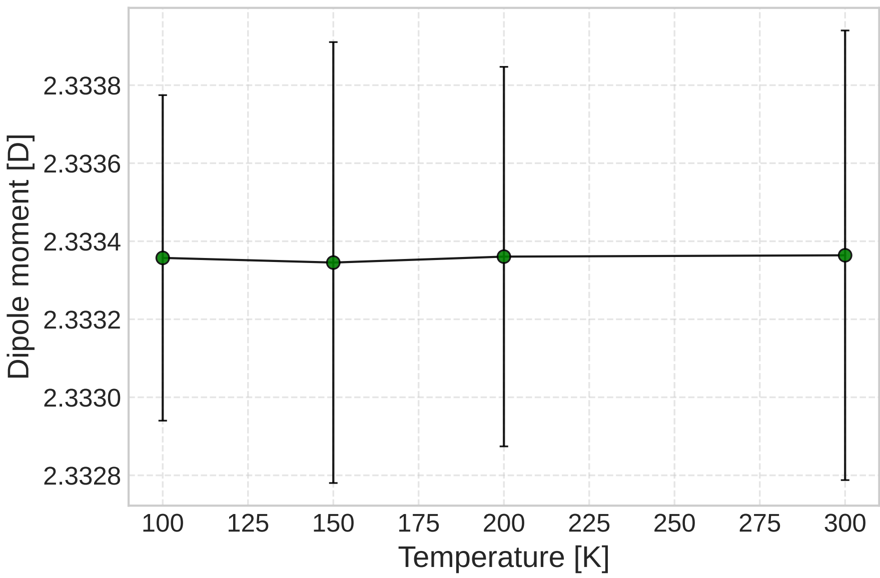


Figure 7: Dipole fluctuation with various temperature

5 Diffusion constant

Under construction.

References

[1] D. Kang, J. Dai, and J. Yuan, “Changes of structure and dipole moment of water with temperature and pressure: A first principles study,” *The Journal of Chemical Physics*, vol. 135, no. 2, p. 024505, 07 2011. [Online]. Available: https://doi.org/10.1063/1.3608412

Appendix

A Finding equilibrium

The full data of the fluctuation of the temperature, potential energy and total energy of the system. We can see the fluctuation of the temperature between the indicate temperature, below the total energy plot, we provide the small table describing the drift of the energy in the region from 4 ps to 20 ps.

A.1 T = 100 K

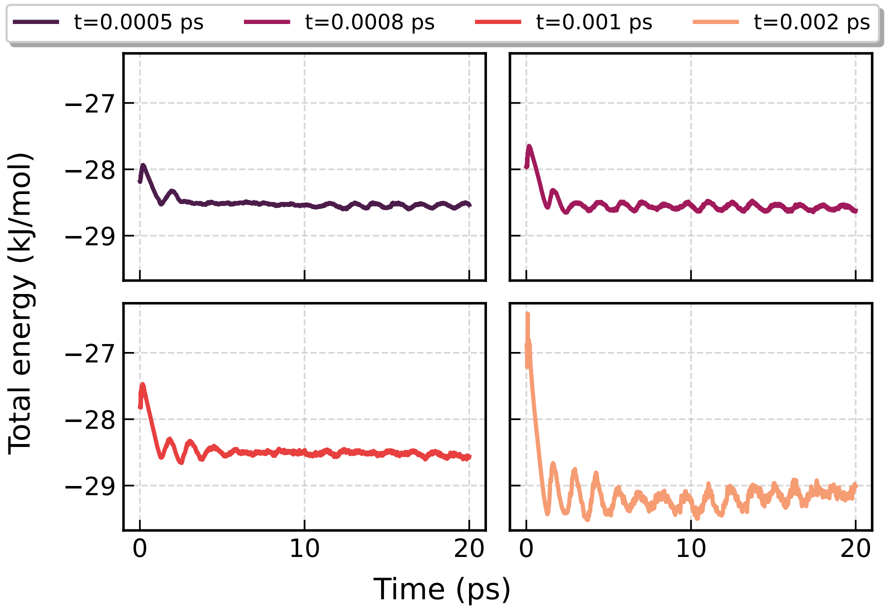
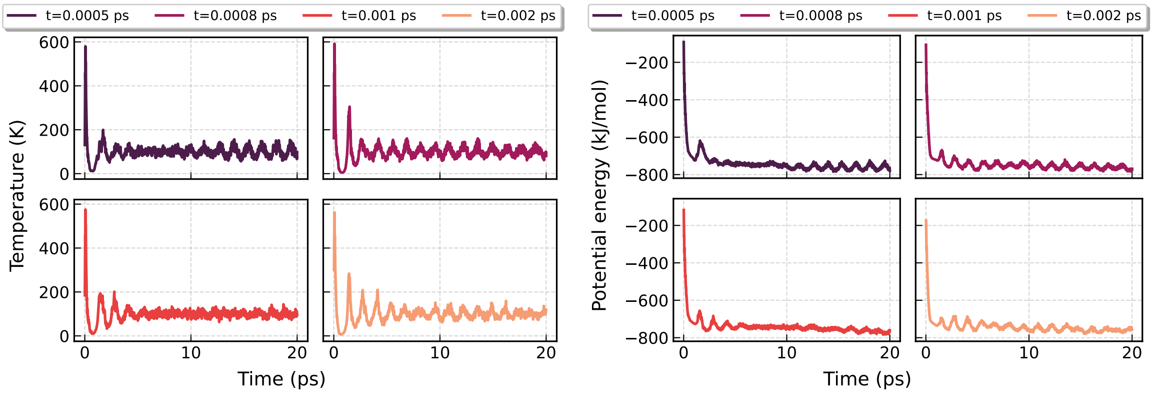


Figure 8: Drift of total energy at 100K

Δt (ps)	Drift Energy
0.0005	0.024730000000001695
0.0008	0.027889999999999304
0.001	0.04251000000000005
0.002	0.3823299999999996



(a) (b)

Figure 9: (a) Temperature fluctuation (b) Potential energy at 100K

A.2 T = 150 K

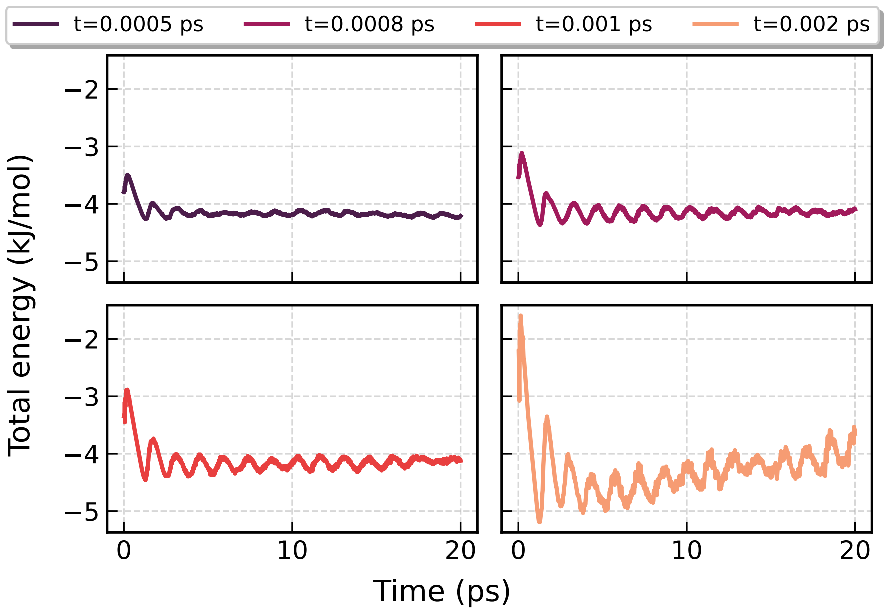
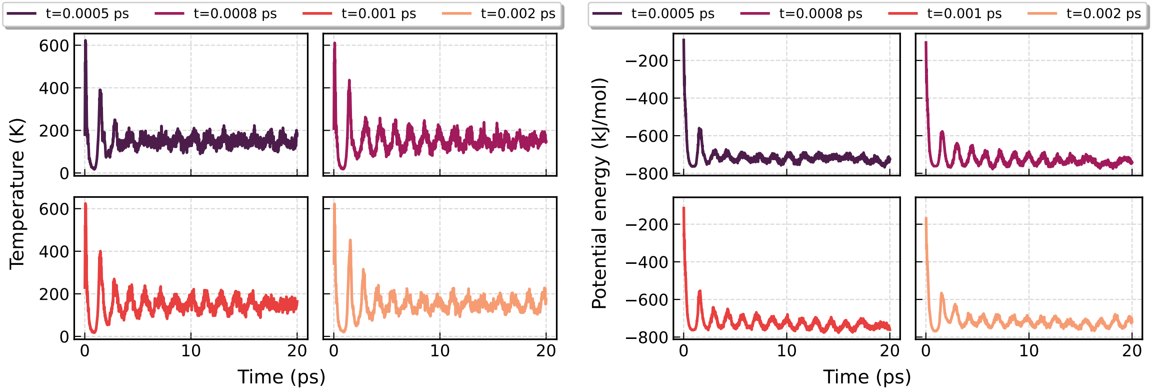


Figure 10: Drift of total energy at 150K

Δt **(ps)**	**Drift Energy**
0.0005	0.017168999999999999
0.0008	0.073071000000000055
0.001	0.126182000000000002
0.002	1.197121



(a) (b)

Figure 11: (a) Temperature fluctuation (b) Potential energy at 150K

A.3 T = 200K

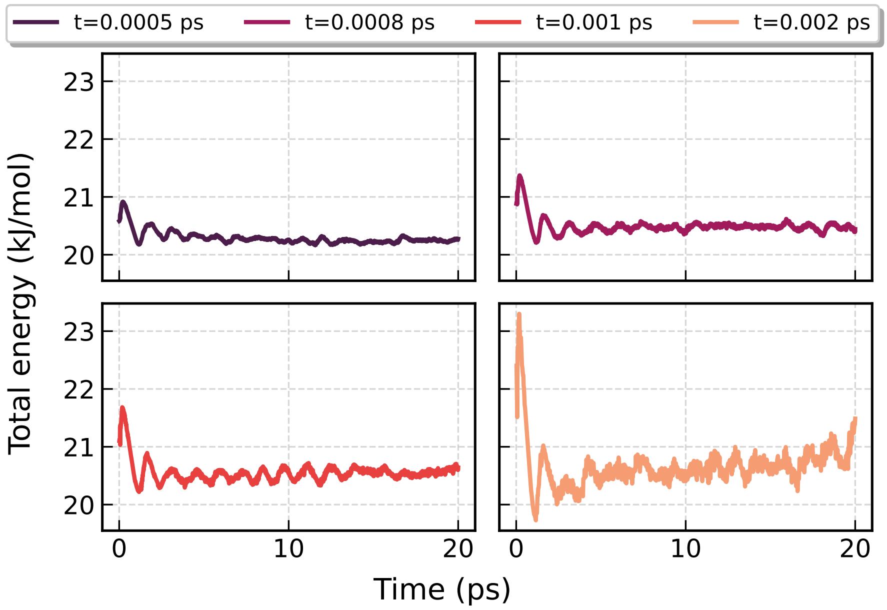
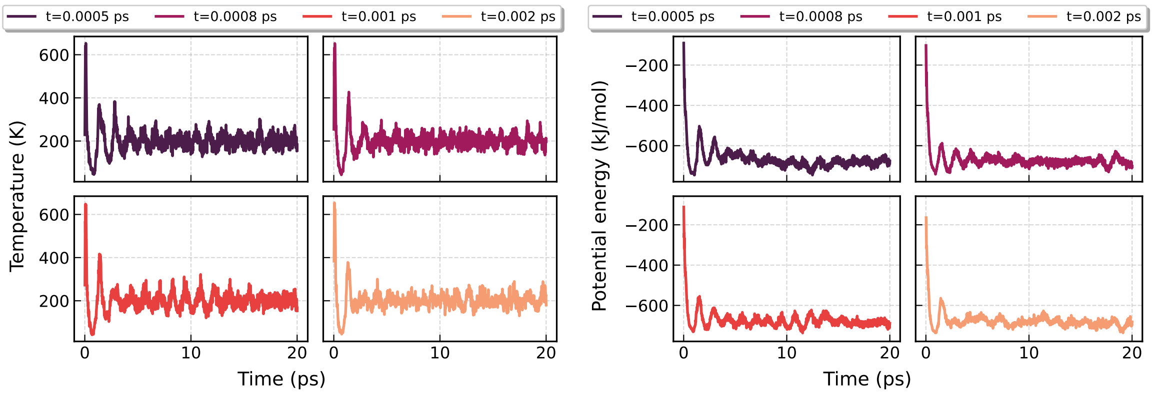


Figure 12: Drift of total energy at 200K

Δt (ps)	Drift Energy
0.0005	0.012660000000000338
0.0008	0.028990000000000293
0.001	0.1914200000000008
0.002	1.0669799999999974



(a) (b)

Figure 13: (a) Temperature fluctuation (b) Potential energy at 200K

B How to collect data

HOME/MDTutorial/Exercises/Exc1

- final_exam-100
- final_exam-150
- final_exam-200
- final_exam-300
  - compile_different_deltaT.sh
    RUN DIFFERENT TIME STEP Δt
  - read_HW_data.sh
    READ HYDROGEN DATA TRAJECTORY
  - read_OW_data.sh
    READ OXYGEN DATA TRAJECTORY

We use this bash file to collect data of temperature, total energy and also the potential energy of our system.

```
# Transpile data
./../../../pickstatis 1 <STATIS> output.dat
./../../../pickstatis 2 <STATIS> engtemp.dat
./../../../pickstatis 3 <STATIS> engcfg.dat
```

Source Code 1: Compile_data.sh

We use this bash file simultaneously run different time step.

```
timesteps=(0.001 0.002 0.0005 0.0008)
time=20

for ts in "${timesteps[@]}"; do
  step=$(echo "scale=0; $time / $ts" | bc) # scale is the decimal point

```

```bash
  mkdir "time$ts"

  # Changing different time step inside the CONTROL file
  sed -i "s/^\(timestep[[:space:]]*\).*/\1$ts/" CONTROL
  sed -i "s/^\(steps[[:space:]]*\).*/\1i $step/" CONTROL

  # Copy from the mail folder to other folder the necessity file for simulation
  cp CONTROL time$ts/CONTROL
  cp CONFIG time$ts/CONFIG
  cp FIELD time$ts/FIELD
  cp read_HW_data.sh time$ts/read_HW_data.sh
  cp read_OW_data.sh time$ts/read_OW_data.sh
  cp compile_data.sh time$ts/compile_data.sh
  cd time$ts

  # Run DLPOLY.X module
  ./../../../../execute/DLPOLY.X

  # Compile to txt file
  ./compile_data.sh
  cd ..
done
```

Source Code 2: compile_different_deltaT.sh

We use this bash file collect the trajectory data of the hydrogen

```bash
#!/bin/bash

# Input file (replace with your file name)
input_file="HISTORY"

# Output file
output_file="timestep_data.txt"

> $output_file
# Time step multiplier
#multiplier=100

# Time step increment (from the last number)
multiplier=0.001000

# Initialize time variable
time=0

#if ! test -d "/path/to/directory"; then
mkdir ./HW-HW
#fi

for i in {1..58..3}
do
  > "HW-HW/H$((i+1)).txt"
  > "HW-HW/H$((i+2)).txt"
done

for i in {1..58..3}
```

```
do
  #awk -v var="$i" '/^OW[[:space:]]+'${i}' .*/ {getline; print}' $input_file >> "oxygen_data/O$i.txt"
  awk -v var="$i" '/^HW[[:space:]]+'$((i+1))' .*/ {getline; print}' $input_file >>  "./HW-HW/H$((i+1)).txt"
  awk -v var="$i" '/^HW[[:space:]]+'$((i+2))' .*/ {getline; print}' $input_file >>  "./HW-HW/H$((i+2)).txt"
done

> displacement-HW.txt

paste -d " " ./HW-HW/*.txt >> displacement-HW.txt

#paste -d " " O1.txt O4.txt O7.txt O10.txt O13.txt O16.txt >> combineO1O16.txt

#awk '/^OW[[:space:]]+4 .*/ {getline; print}' $input_file >> "O2.txt"
echo "Time step data has been written to $output_file"
```

Source Code 3: read_HW_data.sh

We use this bash file collect the trajectory data of the oxygen

```
#!/bin/bash

# Input file (replace with your file name)
input_file="HISTORY"

# Output file
output_file="timestep_data.txt"

> $output_file
# Time step multiplier
#multiplier=100

# Time step increment (from the last number)
multiplier=0.001000

# Initialize time variable
time=0

#if ! test -d "/path/to/directory"; then
mkdir OW-OW
#fi

for i in {1..58..3}
do
  > "OW-OW/O$i.txt"
done

for i in {1..58..3}
do
  awk -v var="$i" '/^OW[[:space:]]+'${i}' .*/ {getline; print}' $input_file >> "OW-OW/O$i.txt"
done

> displacement-OW.txt
```

```
paste -d " " ./OW-OW/*.txt >> displacement-OW.txt

#paste -d " " O1.txt O4.txt O7.txt O10.txt O13.txt O16.txt >>
    combineO1O16.txt

#awk '/^OW[[:space:]]+4 .*/ {getline; print}' $input_file >> "O2.txt"
echo "Time step data has been written to $output_file"
```

Source Code 4: read_OW_data.sh