



The Abdus Salam
**International Centre
for Theoretical Physics**

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 focus on simulating 20 water molecules inside a cubic unit cell with a side length 25\AA . 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 $\text{kJ} \times \text{mol}^{-1}$
- 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	0.0194199999999996662
0.0008	0.071150000000000293
0.001	0.283580000000000006
0.002	1.996780000000000001

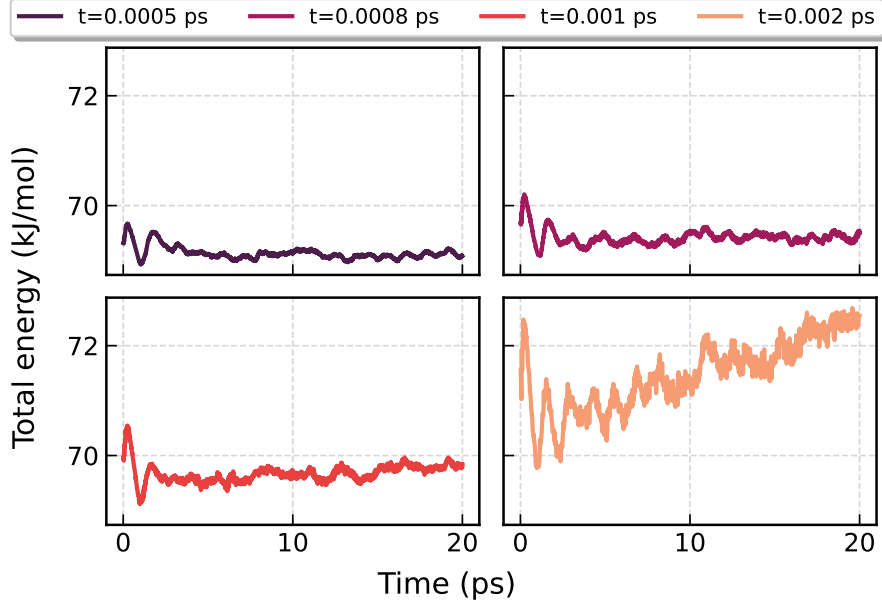


Figure 1: Drift of total energy at 300K

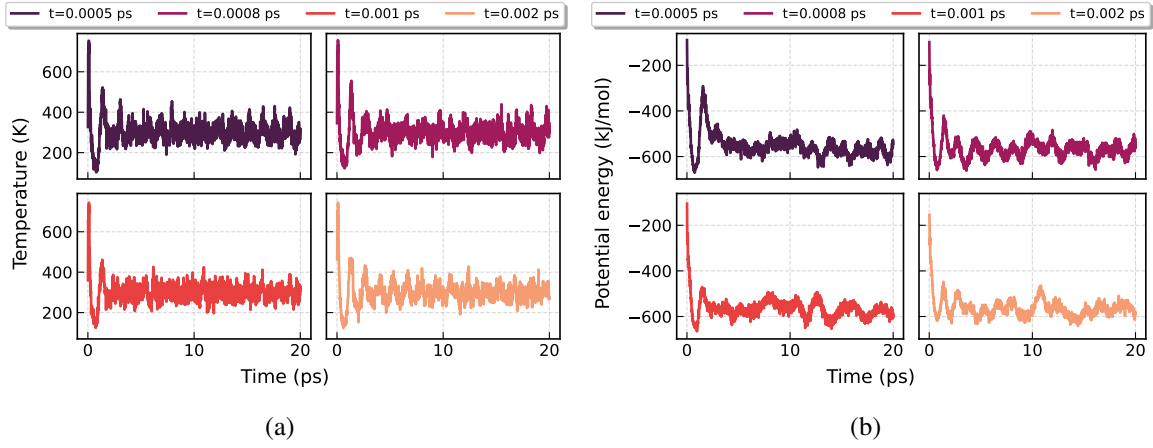


Figure 2: (a) Temperature fluctuation (b) Potential energy at 300K

2.1 Radial distribution function

The radial distribution function can be calculated with the formula

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

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,

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

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.

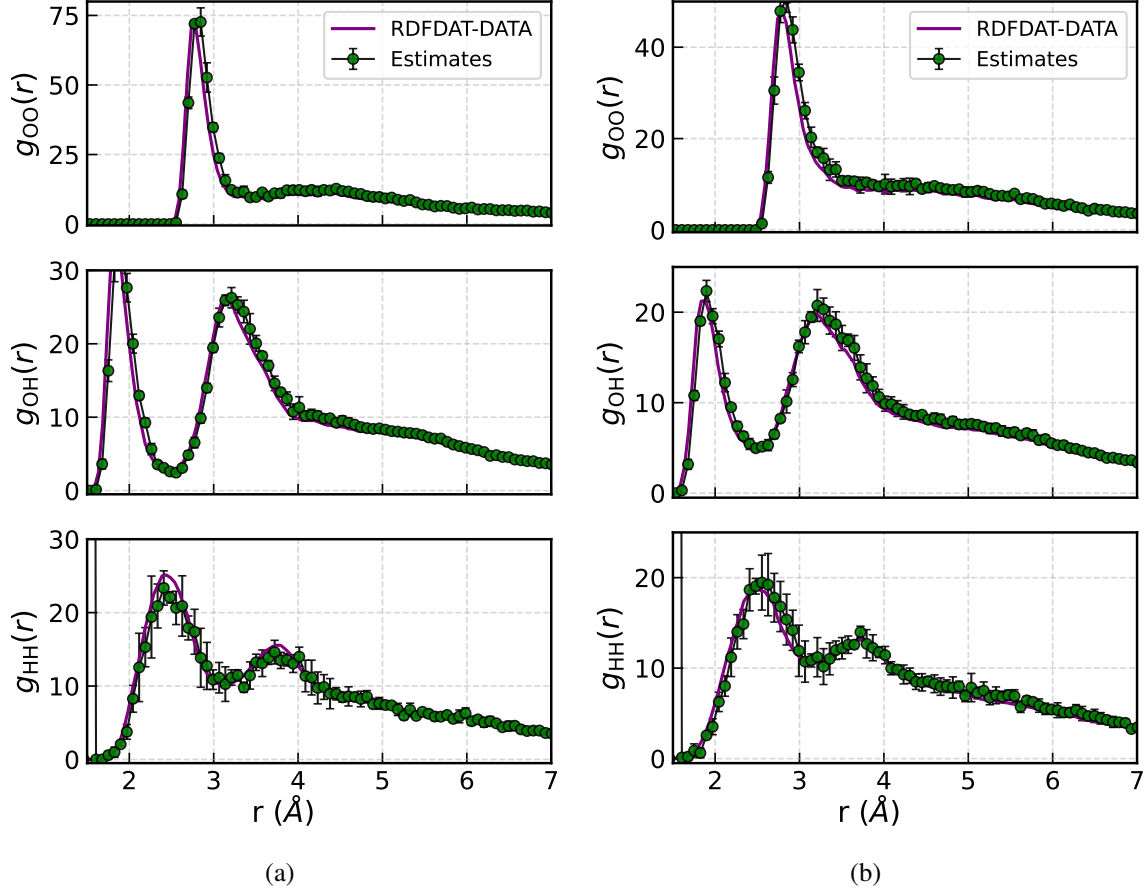


Figure 3: Radial distribution functions of water molecules at (a) 200 K and (b) 300 K

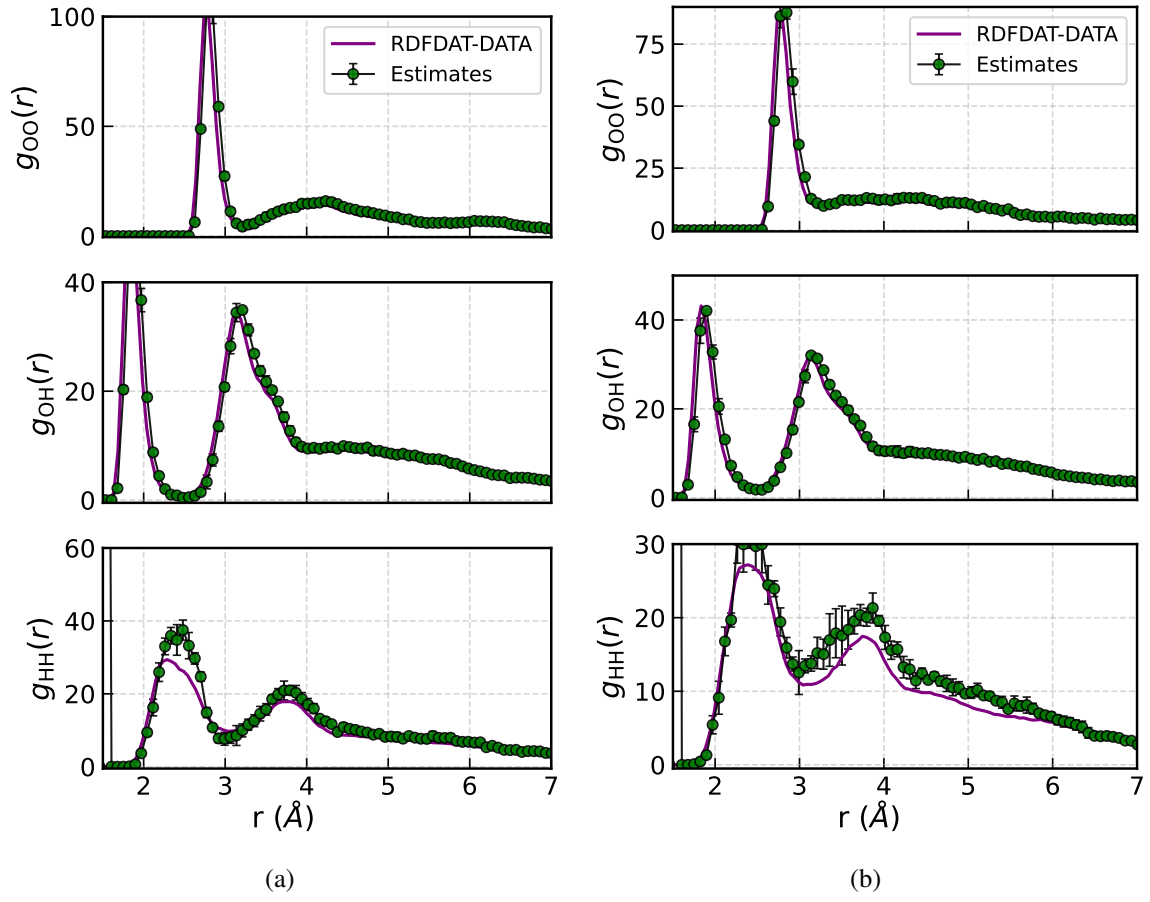


Figure 4: Radial distribution functions of water molecules at (a) 100 K and (b) 150 K

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]

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

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

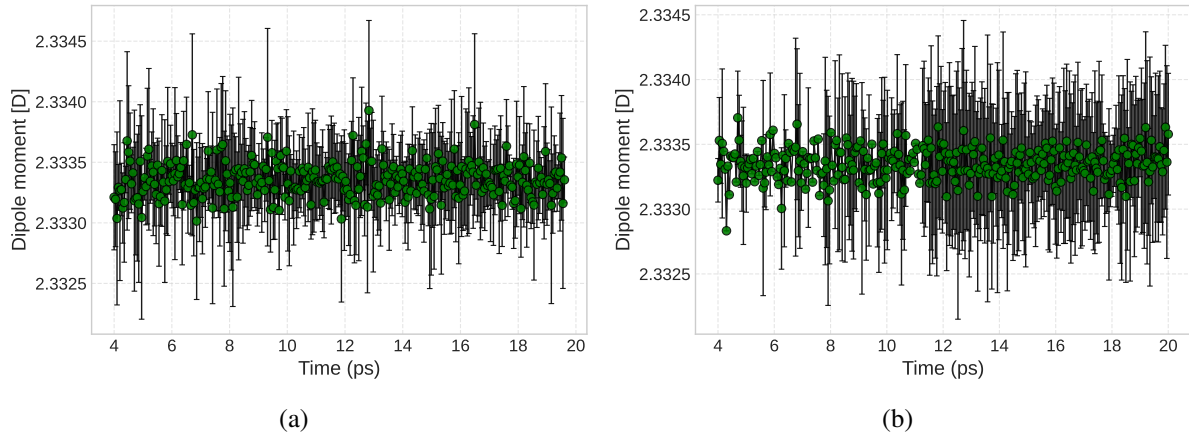


Figure 5: Radial distribution functions of water molecules at (a) 100 K and (b) 150 K

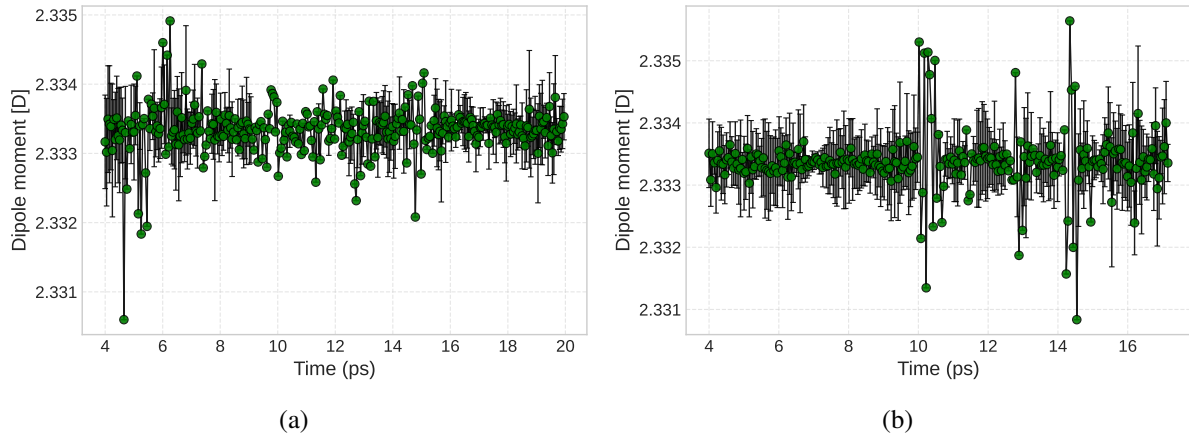


Figure 6: Radial distribution functions of water molecules at (a) 200 K and (b) 300 K

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

4.1 Structure properties

For experimentalist, they can examine the structure of the water molecule by utilizing the neutron diffraction or X-ray diffraction to calculate the structure factor of a molecular liquid. From

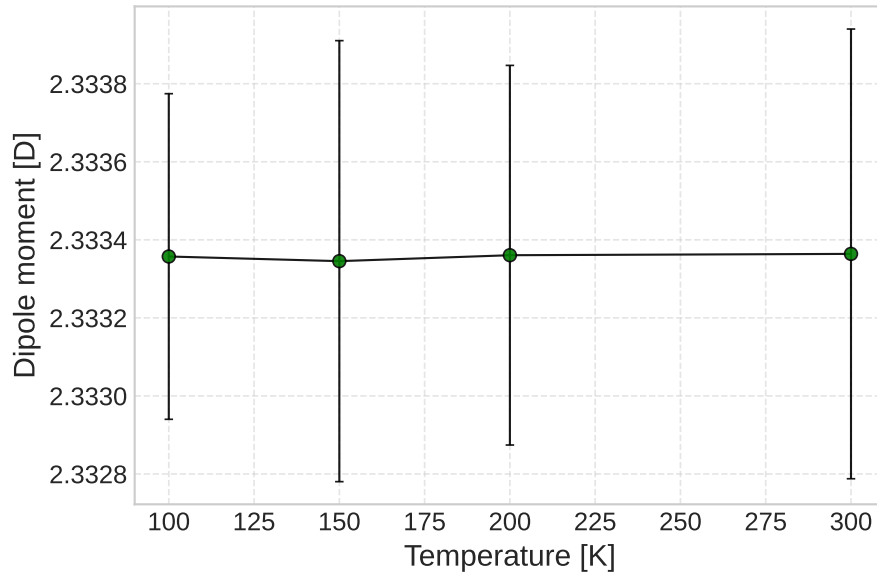


Figure 7: Dipole fluctuation with various temperature

these result, they can construct the radial distribution function by Fourier transform, however, the error is often hard to track [2], followed by unphysical oscillations and erroneous peaks in radial distribution function $g(r)$.

From my point of view, this is the reason why we need numerical result to compare and keep track when we have weird and untrustful result

4.2 Dielectric properties

We can use electrometer [3] to measure the dielectric constant of the liquids, I will read it, when I have more time. The most relevant [source](#) for me provides a formula to calculate the dielectric constant based on the amount of energy stored in the medium when an external electric field is applied, minus the amount of energy lost in the material under the influence of that field.

In additional, we can measure the dielectric constant [4] by the dipole moment fluctuation which is possible to calculate from our simulation.

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>
- [2] K. Amann-Winkel, M.-C. Bellissent-Funel, L. E. Bove, T. Loerting, A. Nilsson, A. Paciaroni, D. Schlesinger, and L. Skinner, “X-ray and neutron scattering of water,” *Chemical Reviews*, vol. 116, no. 13, pp. 7570–7589, 2016, pMID: 27195477. [Online]. Available: <https://doi.org/10.1021/acs.chemrev.5b00663>
- [3] A. P. Carman, “An electrometer method for measuring dielectric constants of liquids,” *Phys. Rev.*, vol. 24, pp. 396–399, Oct 1924. [Online]. Available: <https://link.aps.org/doi/10.1103/PhysRev.24.396>
- [4] H. R. Sánchez, “Uncertainties in the static dielectric constants computed from molecular dynamics simulations,” *Journal of Molecular Liquids*, vol. 288, p. 111021, 2019. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0167732219321427>

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

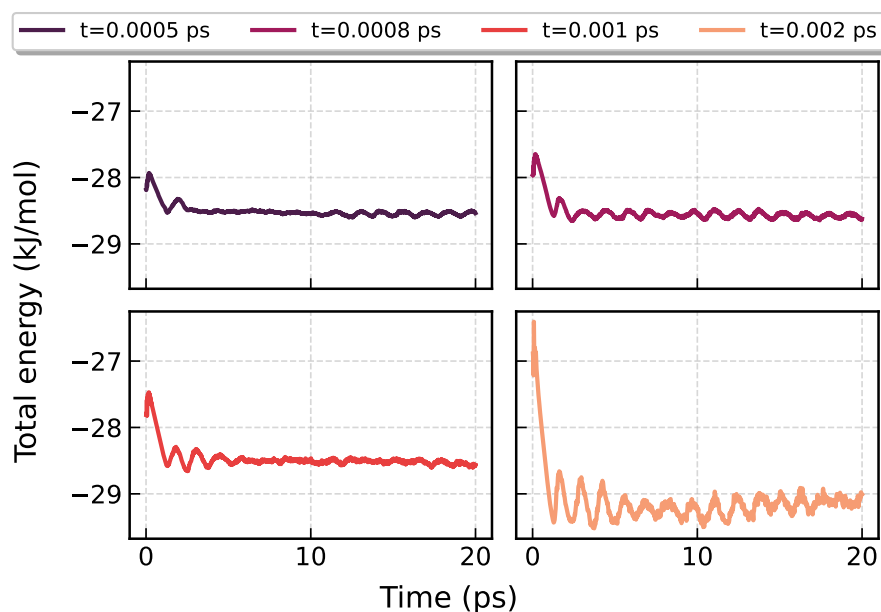


Figure 8: Drift of total energy at 100K

Δt (ps)	Drift Energy
0.0005	0.0247300000000001695
0.0008	0.0278899999999999304
0.001	0.0425100000000000005
0.002	0.38232999999999996

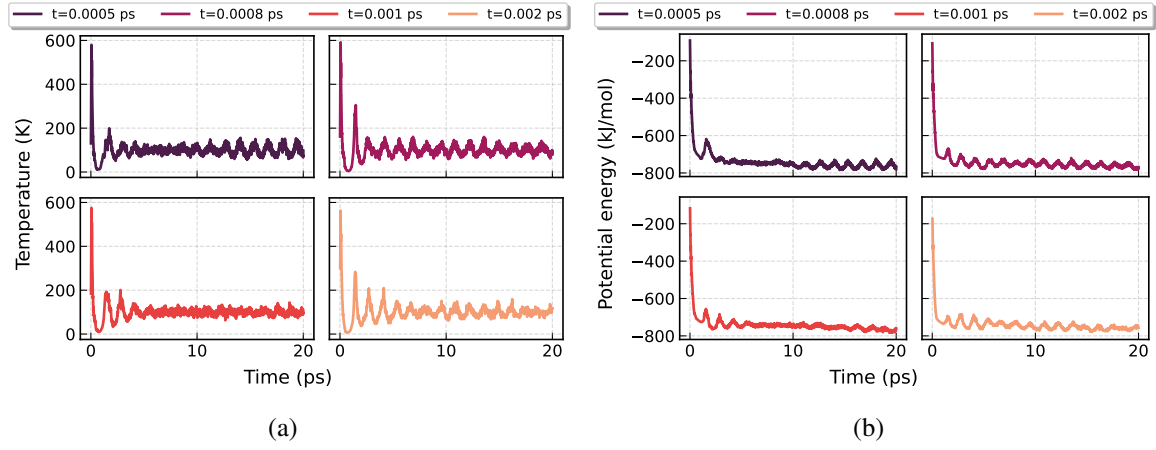


Figure 9: (a) Temperature fluctuation (b) Potential energy at 100K

A.2 T = 150 K

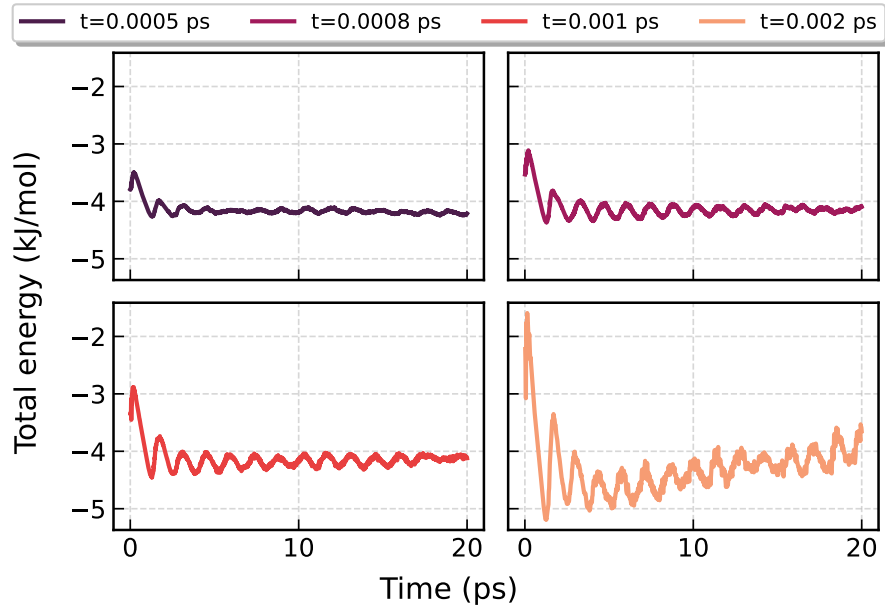


Figure 10: Drift of total energy at 150K

Δt (ps)	Drift Energy
0.0005	0.0171689999999999
0.0008	0.073071000000000055
0.001	0.126182000000000002
0.002	1.197121

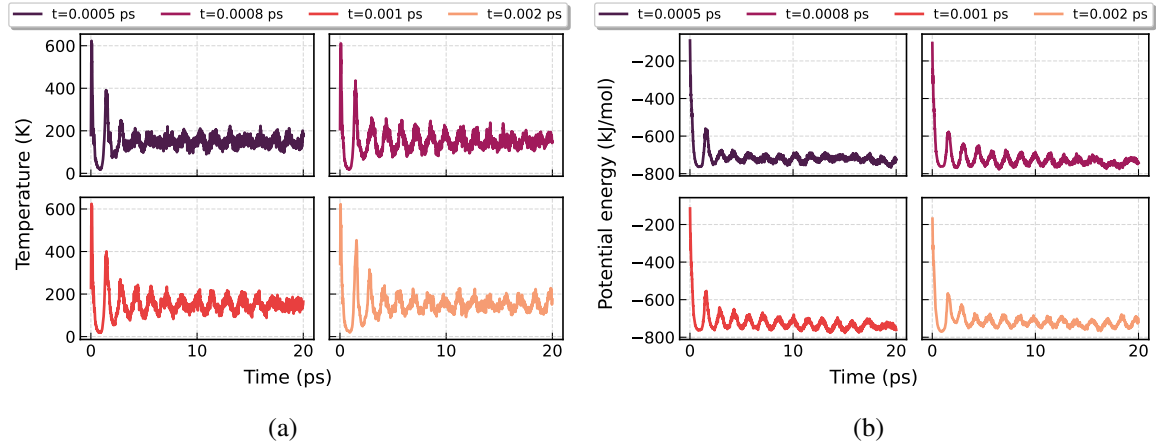


Figure 11: (a) Temperature fluctuation (b) Potential energy at 150K

A.3 T = 200K

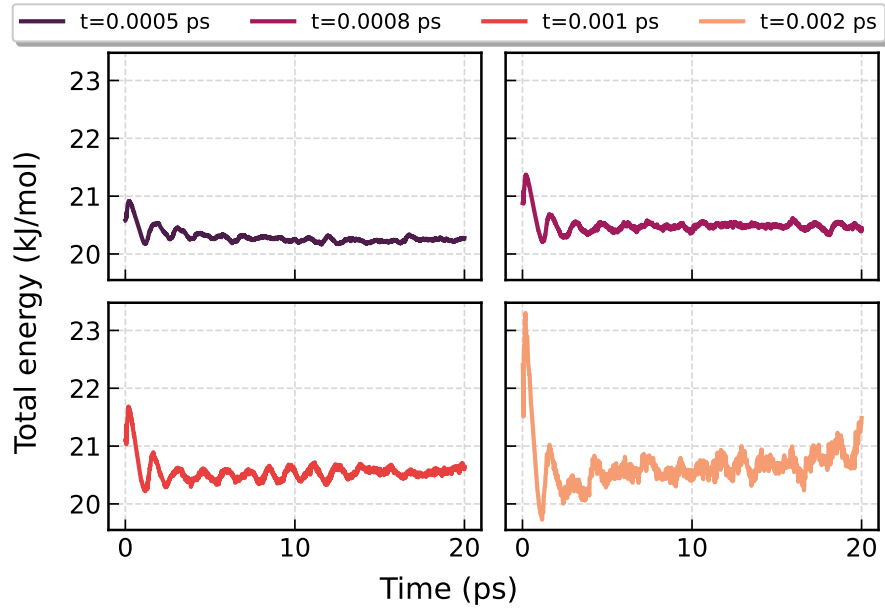


Figure 12: Drift of total energy at 200K

Δt (ps)	Drift Energy
0.0005	0.012660000000000338
0.0008	0.028990000000000293
0.001	0.19142000000000008
0.002	1.06697999999999974

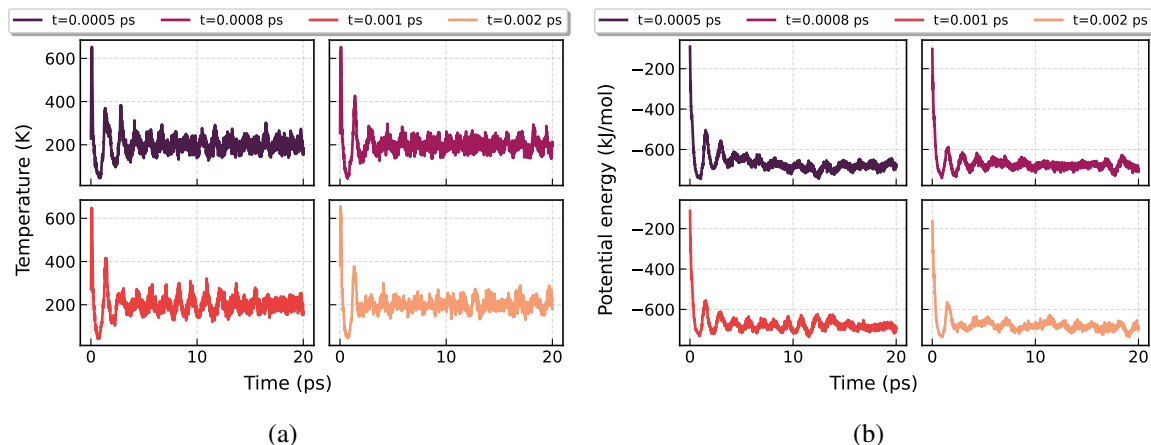


Figure 13: (a) Temperature fluctuation (b) Potential energy at 200K

B How to collect data

```
HOME/MDTutorial/Exercises/Excl
├── final_exam-100
├── final_exam-150
├── final_exam-200
├── final_exam-300
│   ├── compile_different_deltaT.sh
│   │   └── RUN DIFFERENT TIME STEP  $\Delta t$ 
│   ├── 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.

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

Source Code 1: Compile_data.sh

We use this bash file simultaneously run different time step.

```
1 timesteps=(0.001 0.002 0.0005 0.0008)
2 time=20
3
4 for ts in "${timesteps[@]}; do
5     step=$(echo "scale=0; $time / $ts" | bc) # scale is the decimal point
6
```

```

7  mkdir "time$ts"
8
9  # Changing different time step inside the CONTROL file
10 sed -i "s/^\(timestep[[:space:]]*\).*\/\1$ts/" CONTROL
11 sed -i "s/^\(steps[[:space:]]*\).*\/\1i $step/" CONTROL
12
13 # Copy from the mail folder to other folder the necessity file for
   simulation
14 cp CONTROL time$ts/CONTROL
15 cp CONFIG time$ts/CONFIG
16 cp FIELD time$ts/FIELD
17 cp read_HW_data.sh time$ts/read_HW_data.sh
18 cp read_OW_data.sh time$ts/read_OW_data.sh
19 cp compile_data.sh time$ts/compile_data.sh
20 cd time$ts
21
22 # Run DLPOLY.X module
23 ../../../../execute/DLPOLY.X
24
25 # Compile to txt file
26 ./compile_data.sh
27 cd ..
28 done

```

Source Code 2: compile_different_deltaT.sh

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

```

1  #!/bin/bash
2
3  # Input file (replace with your file name)
4  input_file="HISTORY"
5
6  # Output file
7  output_file="timestep_data.txt"
8
9  > $output_file
10 # Time step multiplier
11 #multiplier=100
12
13 # Time step increment (from the last number)
14 multiplier=0.001000
15
16 # Initialize time variable
17 time=0
18
19 #if ! test -d "/path/to/directory"; then
20 mkdir ./HW-HW
21 #fi
22
23 for i in {1..58..3}
24 do
25   > "HW-HW/H$((i+1)).txt"
26   > "HW-HW/H$((i+2)).txt"
27 done
28
29 for i in {1..58..3}

```

```

30 do
31   #awk -v var="$i" '/^OW[[:space:]]+'${i}' .*/ {getline; print}'
   $input_file >> "oxygen_data/O$i.txt"
32   awk -v var="$i" '/^HW[[:space:]]+'${(i+1)}' .*/ {getline; print}'
   $input_file >> " ./HW-HW/H${(i+1)}.txt"
33   awk -v var="$i" '/^HW[[:space:]]+'${(i+2)}' .*/ {getline; print}'
   $input_file >> " ./HW-HW/H${(i+2)}.txt"
34 done
35
36 > displacement-HW.txt
37
38 paste -d " " ./HW-HW/*.txt >> displacement-HW.txt
39
40 #paste -d " " O1.txt O4.txt O7.txt O10.txt O13.txt O16.txt >>
   combineO1O16.txt
41
42 #awk '/^OW[[:space:]]+4 .*/ {getline; print}' $input_file >> "O2.txt"
43 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

```

1 #!/bin/bash
2
3 # Input file (replace with your file name)
4 input_file="HISTORY"
5
6 # Output file
7 output_file="timestep_data.txt"
8
9 > $output_file
10 # Time step multiplier
11 #multiplier=100
12
13 # Time step increment (from the last number)
14 multiplier=0.001000
15
16 # Initialize time variable
17 time=0
18
19 #if ! test -d "/path/to/directory"; then
20 mkdir OW-OW
21 #fi
22
23 for i in {1..58..3}
24 do
25   > "OW-OW/O$i.txt"
26 done
27
28 for i in {1..58..3}
29 do
30   awk -v var="$i" '/^OW[[:space:]]+'${i}' .*/ {getline; print}'
   $input_file >> "OW-OW/O$i.txt"
31 done
32
33 > displacement-OW.txt

```



```
34
35 paste -d " " ./OW-OW/*.txt >> displacement-OW.txt
36
37 #paste -d " " 01.txt 04.txt 07.txt 010.txt 013.txt 016.txt >>
    combine01016.txt
38
39 #awk '/^OW[[:space:]]+4 .*/ {getline; print}' $input_file >> "02.txt"
40 echo "Time step data has been written to $output_file"
```

Source Code 4: read_OW_data.sh