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**Chem 8021
Spring 2005
Project II**

Calculation of Self-Diffusion Coefficient of Water Using Molecular Dynamics

Project Description. In a molecular dynamics simulation the diffusion coefficient, D , of a given species can be expressed as a function of its mean square displacement (MSD) and time.¹

$$6Dt = \left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle$$

The purpose of this project was to carry out an MD simulation in the NpT ensemble to calculate the diffusion coefficient of TIP3P water by the above relation.

Computational Details. The simulation was carried out with a cubic periodic box of 216 TIP3P² water molecules using the CHARMM³ suite of programs. During the simulation, the temperature was held fixed at 298 K using the Nose-Hoover thermostat⁴ and the pressure was kept at 1 atm. Bond lengths were also held fixed by use of the SHAKE⁵ algorithm. A cutoff of 9.0 Å was used since this would be less than half the box length of the system at TIP3P density. The starting configuration of simulation box was generated by placing the center of mass of each molecule on a fcc lattice point then giving it a random rotational orientation. The structure of the box was then allowed to equilibrate for 10 ps following which a production run of 50 ps was carried out to collect the MSD data. Both the production and equilibration cycles had timesteps of 1 fs. The input script for the run is given at the end of this report.

Results and Discussion. The starting and equilibrated configurations of the simulation box are shown in Figure 1. It was established that equilibrium had been reached after 10 ps when the energy had stabilized and only fluctuated about a mean of about -1860 kcal. The average RMS fluctuation in the energy was 0.0025 kcal over the last picosecond of the equilibration.

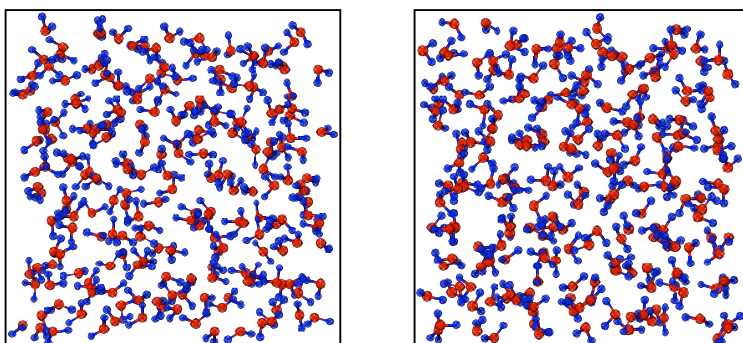


Figure 1. Snapshots of the simulation box before, left, and after, right, equilibration. Note that upon close inspection one can see the randomness of the water orientation in the initial structure while the equilibrated structure appears to have more hydrogen bonding.

Figure 2 shows the plot of MSD vs. time for both production cycle of the simulation. From this plot it is evident that the MSD for the first few picoseconds was not linear in time. Therefore, this portion of the plot was not used to calculate the diffusion coefficient. A linear regression of the plot gave a diffusion coefficient of $3.58 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This does not agree well with a previous MD calculation of the diffusion coefficient for TIP3P⁶ (Table 1). The difference between the previous value and the one reported here may be attributed to many things. First, the *NVT* rather than the *NpT* was used in that study. In the thermodynamic limit, the two ensembles should give the same answers, however for a finite system size one does expect differences. Second, the other study used 901 water molecules, a longer cutoff and longer simulation times. These three reasons suggest that the other study has a better value for the TIP3P model, despite the fact the value found here is closer to the experimental value. Which is not alarming as TIP3P is known to give diffusion coefficients which are too high compared to experiment.⁶

Table 1. Comparison of the diffusion coefficient to other studies

Study	Diffusion Coefficient ($\text{m}^2 \text{ s}^{-1} \times 10^{-9}$)
This work	3.58
Previous study ⁶	5.65
Experimental ⁷	2.30

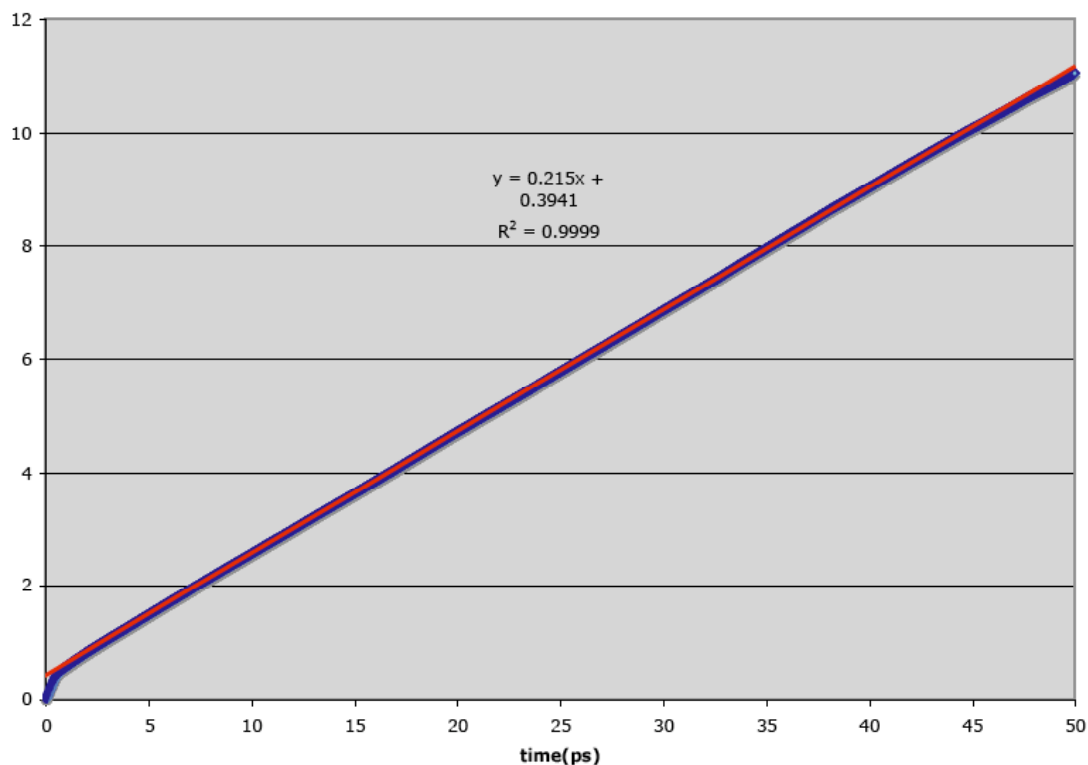


Figure 2. MSD as a function of time for the production cycle. The left plot is for the whole run while the right is the linear portion from which the diffusion coefficient was calculated.

References

- 1) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Oxford Science: Oxford, 1987.
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- 3) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S. and Karplus, M. *J. Comp. Chem.* **1983**, 4, 187.
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- 5) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. *J. Comput. Phys.* **1977**, 23, 327.
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Appendix – CHARMM input script

```
* NPT MD simulation of 216 water, CHEM8021, spring 2005

open read formatted unit 11 name prot.top
open read formatted unit 12 name prot.par

read rtf card unit 11
read parameter card unit 12

close unit 11
close unit 12

READ SEQU TIP3 216
GENE WATER first none last none SETU NOANGLE NODIhedral

OPEN READ UNIT 10 CARD NAME wat216.crd
READ COOR UNIT 10 CARD
CLOSE UNIT 10

SET Z 19.7129

CRYSTAL DEFINE CUBIC @Z @Z @Z 90.0 90.0 90.0
CRYSTAL BUILD CUTOFF 14.0 NOOPERATIONS 0

IMAGE BYRES XCEN 0.0 YCEN 0.0 ZCEN 0.0 SELE ALL END

SHAKE BONH PARAM SELE ALL END

mini sd nstep 1

open write unit 31 card name water216eq.rst
open write unform unit 35 name watereq.trj

dynamics cpt leap start time 0.001 nstep 10000 iseed 314159 -
  firstt 298.0 finalt 298.0 tstruc 298.0 -
  iunrea -1 iunwri 31 -
  ihbfrq 0 iprfrq 20 nprint 10 -
  iasors 1 iasvel 1 ieqfrq 0 iuncrd 35 nsavc 5 -
  inbfrq 10 imgfrq 10 cutnb 9.0 cutim 9.0 -
  pconstant pmass 100.0 pref 1.0 pgamma 10.0 -
  hoover rept 298.0 tmass 250.0 tbath 298.0

open write unit 33 card name water216eq.pdb
write coor pdb unit 33

open write unit 32 card name water216prod.rst
open read unit 31 card name water216eq.rst
open write unit 36 unformatted name waterprod.trj

dynamics cpt leap restart time 0.001 nstep 50000 iseed 314159 -
  firstt 298.0 finalt 298.0 tstruc 298.0 -
  iunrea 31 iunwri 32 -
  ihbfrq 0 iprfrq 20 nprint 10 -
  iasors 1 iasvel 1 ieqfrq 0 iuncrd 36 nsavc 5 -
  inbfrq 10 imgfrq 10 cutnb 9.0 cutim 9.0 -
  pconstant pmass 100.0 pref 1.0 pgamma 10.0 -
  hoover rept 298.0 tmass 250.0 tbath 298.0
```

close unit 36

open write formatted unit 25 name wat216prod.pdb
write coor pdb unit 25

open read unit 38 unformatted name waterprod.trj

coor anal sele type OH2 end firstu 38 nunit 1 skip 5 -
imsd 37 -
rspin 0.0 rspout 999.9 -
ncors 20 -
xbox @Z ybox @Z zbox @Z

STOP