Molecular Dynamics simulation of a single ion pair in pure water

After studying this chapter, you will be able to

1) Calculate the radial distribution functions between an ion pair and oxygen or hydrogen of water molecules.
2) Calculate potentials of mean force between an ion pair using the pull method.
3) Calculate of diffusion constants of the anion or the cation.

Keywords: Potential of mean force, diffusion constant, radial distribution function

Introduction

Many important chemical transformations occur in ionic and polar media and therefore, it is essential to have an understanding of the nature of ion pairs in polar solvents. Here, we are going to perform constrained Molecular Dynamics simulation of sodium chloride ion pair in pure water and we will study potentials of mean force of the ion pair and the solvation structure of the ion pair in water.

Initial Configuration of NaCl in water:

The input files needed to generate the initial configuration of NaCl in water are Na.pdb, Cl.pdb and water.pdb

The pdb file of sodium is given below.

```
**************************************************

HEADER

HETATM    1  NaNa    1       -1.00  0.000  0.000

 *************************************************
```

The pdb file of chlorine atom is given below.

```
************************************************

HEADER

HETATM    1  ClCl    2      1.000   0.000  0.000

***************************************************
```

The pdb file of water molecule is given below.

```
*********************************************************************
HEADER    water
COMPND
SOURCE
HETATM    1  OW  SOL    1      0.000   0.000   0.000
HETATM    2  HW1 SOL    1     -0.560  -0.410  -0.750
HETATM    3  HW2 SOL    1     -0.541   0.733   0.462
CONECT    1    3
CONECT    2    3
CONECT    3    1    2
END
******************************************************************
******************************************************************
```

In linuxoprating system, you have already installed packmole. Then go to the directory packmole:

```
cd home/username/packmole
```

After that, make a file NaClpwt.inp. The format of this is given below

```
************************************************************************
#
# A mixture of nacl in pure water spce
#
tolerance 2.0
filetypepdb
output NaClpwt.pdb
structure na.pdb
```

```
number 1

fixed  20.0 20.0 20.0 0.0 0.0 0.0

end structure

structure cl.pdb

number 1

fixed  20.0 20.0 20.0 0.0 0.0 0.0

end structure

structure  pwtt.pdb

number 2048

inside cube 0. 0. 0. 40.0

end structure
```

****

Then give the command

```
./packmole<NaClpwt.inp
<enter>
```

When the job will be completed, the NaClpwt.pdb file is generated.

In this file, initial configuration of NaCl in water is given.

Conversion of pdb to gro:

First of all, make a directory by giving the command

```
mkdirnaclpwt
```

Then copy NaClpwt.pdb file into this directory. Then convert this file into gro format by,

```
editconf –f  NaClpwt.pdb –o NaClpwt.gro
<enter>
```

Generation of index file:

```
Make_ndx –f NaClpwt.gro –o index.ndx
```

<enter>

q

<enter>

The index file has been generated.

The itp file of Sodium ion

****

```
; .itp file for Sodium ion

[moleculetype]
; Name   nrexcl
 Na        3

[ atoms ]
;   nr    type   resnrresidu    atom     cgnr     charge    mass
     1     Na+       1    Na       Na        1       1.00    22.9898
**************************************************************************
```

The itp file of Cloride ion

****

```
; .itp file for Chloride ion

[moleculetype]
; Name   nrexcl
Cl3

[ atoms ]
;   nr    type    resnrresidu    atom     cgnr      charge    mass
     1    Cl-        1    ClCl        1       -1.00    35.4527
```

****

The itp file of water molecule

****

; .itp file for SPC rigid water

```
[moleculetype]
; Name   nrexcl
  SOL      3


[ atoms ]
;   nr    type   resnrresidu    atom    cgnr   charge      mass
     1     OW       1     SOL       OW       1    -0.8476    15.99940
     2     HW       1     SOL       HW1     1      0.4238     1.00800
     3     HW       1     SOL       HW2     1      0.4238     1.00800


[ settles ]
; OW    functdohdhh
  1       1       0.1    0.16330


[ exclusions ]
1       2       3
2       1       3
3       1       2
********************************************************************************
```

The topology file of NaCl in water is given below.

```
***************************************************
;  force field is OPLS / UNITED ATOM.


[ defaults ]
```

```
;  nbfunc     comb-rule      gen-pairs     fudgeLJfudgeQQ
    1          2             yes          0.5       0.8333

[ atomtypes ]
; name     mass       charge    ptype       sigma          epsilon


  OW    15.99940     -0.8476     A      3.166e-01         0.65060
  HW    1.008000      0.4238     A      0.00000           0.00000


;
;
  Na+   22.9898       1.000       A       0.333045         0.1158696
Cl-   35.4527      -1.000       A       0.441724         0.4923622

#include "water.itp"
#include "Na.itp"
#include "Cl.itp"

[ system ]
NaCl in pure water

[ molecules ]
;mol_name number
 SOL     2048
 Na       1
```

```
Cl      1
```

****

Now we have water.itp, Na.itp, Cl.itp, index.ndx, topol.top, NaClpwt.gro files. In the NaClpwt.gro, the distance between Na and Cl is 2.0 Å.

Determination of potentials of mean force between ion pair by using pull constraint method

We are going to discuss how to calculate force between Na and Cl at each ion-ion separation ranging from 2.0 Å to 12.0 Å.

First of all, you have to make distance directories in **home/user/naclpwt**directory.

Then make distance directories in **naclpwt**directory. For that, give the following commands.

```
mkdir 2.1

mkdir 2.2

mkdir 2.3

…………………….

……………………..

……………………..

mkdir 12.0
```

Now give the following command to go to the **2.1**directory.

```
cd home/user/naclpwt/2.1
```

Now copy water.itp, Na.itp, Cl.itp, index.ndx, topol.top, NaClpwt.gro files into this directory.

Here, you want to generate a configuration in which distance between Na and Cl is 2.1 Å. First of all move NaClpwt.gro file into NaClpwt.2.1.gro. Now with the help of pull method, you can increase the distance between Na and Cl from 2.0 to 2.1 Å.

Formation of shortMD.mdp file

****

```
integrator = md
```

```
dt = 0.002 ; ps
nsteps = 500000 ; = 20 ns tot
nstcomm = 1
nstxout = 0
nstvout = 0
nstfout = 0
nstlog = 50000
nstenergy = 50000
nstxtcout= 0

nstlist = 10
ns_type = grid
coulombtype = PME
rcoulomb = 1.0
vdwtype = cutoff
rvdw = 1.5
pme_order = 4
optimize_fft = yes

;Couplig Temp
tcoupl = v-rescale
tau_t = 0.1
tc-grps = System
ref_t = 298
```

```
;Costrain Bond
constraints = all-bonds
constraint_algorithm = LINCS

;Coupling P
Pcoupl = berendsen
Pcoupltype = isotropic
tau_p = 1
compressibility = 4.5e-5
ref_p=1

;Generate velocity
gen_vel = yes
gen_temp = 298.0
gen_seed = 173529

pull=constraint
pull_group1=Na
pull_group0=Cl
pull_init1= 0.210
pull_constr_tol=1E-6
***************************************************************************
```

; pull = constraint; method is using to calculate the force between Na and Cl at constrained
;distance, in **pull_group1** and **pull_group0** you have to define the two groups between which
;you want to calculate constrained force. In **pull_init1** you have to define constrained distance
;between ion pair**.** **pull_constr_tol** is the tolerance in the constrained distance between ion pair.

Now we will give the following command to generate the configuration in which distance between Na and Cl is 2.1 Å.

```
grompp –f shortMD.mdp –c NaClpwt.2.1.gro –n index.ndx –p topol.top–o shortMD.tpr–maxwarn 2
```

The shortMD.tpr is generated. It is used to perform MD simulation by giving following command

```
mdrun –v –s shortMD.tpr –o shortconf.2.1.gro
```

In the shortconf.2.1.gro file, the distance between Na and Cl is 2.1 Å.

Now we are going to perform long MD.

The files required to perform long MD simulations are given below **water.itp, Na.itp, Cl.itp, index.ndx, topol.top, shortconf.2.1.gro and longMD.mdp**

The longMD.mdp file is given below

****

```
integrator = md

dt = 0.002 ; ps

nsteps = 4000000 ; = 8 ns tot

nstcomm = 1

nstxout = 0

nstvout = 0

nstfout = 0

nstlog = 400000

nstenergy = 400000
```

```
nstxtcout= 0

nstlist = 10
ns_type = grid
coulombtype = PME
rcoulomb = 1.0
vdwtype = cutoff
rvdw = 1.5
pme_order = 4
optimize_fft = yes

;Couplig Temp
tcoupl = v-rescale
tau_t = 0.1
tc-grps = System
ref_t = 298

;Costrain Bond
constraints = all-bonds
constraint_algorithm = LINCS

;Coupling P
Pcoupl = berendsen
Pcoupltype = isotropic
tau_p = 1
```

```
compressibility = 4.5e-5

ref_p=1


;Generate velocity

gen_vel = yes

gen_temp = 298.0

gen_seed = 173529


pull=constraint

pull_group1=Na

pull_group0=Cl

pull_init1= 0.210

pull_constr_tol=1E-6
```

****

Now we are going to perform long MD simulation in **2.1**directory.

We will generate longMD.tpr file by giving the following command.

```
grompp –f longMD.mdp –c shortconf.2.1.gro –n index.ndx –p topol.top–o longMD.tpr–maxwarn 2
```

The longMD.tpr is generated. It is used to perform MD simulation by giving the following command

```
mdrun –v –s longMD.tpr –clongconf.2.1.gro  -pfpullf1t8ns.xvg
```

In the pullf1t8ns.xvg file, on x-axis time is given and on y-axis, mean force between ion pair is given.

Now copy **water.itp, Na.itp, Cl.itp, index.ndx, topol.top, shortconf.2.1.gro and shortMD.mdp** files into **2.2** distance directory. After that, give the following command:

```
mvshortconf.2.1.gro shortconf.2.2.gro
```

Now repeat the same process as in the **2.2** distance directory. Thus, by repeating the same process in other distances directories, we will get mean force at each distance between the ion pair. Now we can calculate the mean potential between ion pair at each distance ranging from 2.0 to 12.0 Å by direct integration of the mean forces. You will need the value of the potential of mean force at a reference point, which can be taken at large separation as the direct potential divided by the solution dielectric constant. The formula is arrived at by the following arguments.

The constrained molecular dynamics method requires that not only the intra-solvent site–site separations be held constant, but the ion–ion separation also be kept fixed. The equations of motion were solved numerically using the Verlet algorithm with a time step of 0.1fs.For the system consisting of two ions (A, B) and N solvent molecules, the force due to solute–solvent interactions, acting along the inter-ionic axis is evaluated as,

$$\Delta F\,(r,t) = \mu\,[\{F_{AS}(r,t) / m_A\} - \{F_{BS}\,(r,t) / m_B\}]\,.\,(\mathbf{r}/|\mathbf{r}|) \qquad (1)$$

where $F_{AS}(r,t)$ and $F_{BS}(r,t)$ are total forces on solute particles A and B respectively due to solvent molecules; m_A and m_B are individual masses of the ions, μ is the reduced mass of the ion pair and $(\mathbf{r}/|\mathbf{r}|)$is the unit vector along the AB direction. The $\Delta F(r,t)$ values are calculated at each time step and then averaged over the whole simulation. The total mean force is the sum of direct (bare) ion–ion force, $F_d(r)$ and the solvent contribution, $\Delta F(r)$.That is

$$F(r) = F_d(r) + \Delta F\,(r)(2)$$

where, $\Delta F(r) = \langle\Delta F(r,t)\rangle$, the angular brackets denoting an ensemble average. The potential of mean force, $W(r)$, of the ion pair in the presence of solvent can then be calculated as

$$W(r) = W\,(r_0) - \int_{r_0}^{r} F(r)dr\,(3)$$

The choice of $W(r_0)$ is to be taken in such a way that the calculated mean force potential matches the macroscopic Coulombic potential in a mediumof dielectric constant ε at long distances.

$$W(r) = \frac{q_i q_j}{r_0 \varepsilon}\,(4)$$

Summary

In this chapter, you have been introduced to the algorithms to

1) Calculate the radial distribution functions between an ion pair and oxygen or hydrogen of water molecules.
2) Calculate potentials of mean force between an ion pair using the pull method.
3) Calculate of diffusion constants of anion or cation.

Exercise:

Using the Gromacs software, generate the potentials of mean force between sodium and chloride ion pair. Extend the approach to the potassium chloride ion pair.