Computations of radial distributions functions, PMFs and diffusion constants

After studying this chapter, you will be able to perform the

1) Calculations of radial distribution functions between two argon atoms in liquid argon.
2) Calculations of Potentials of mean force between two argon atoms in liquid argon.
3) Calculation of diffusion constant of argon atom in liquid argon.

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

Introduction

You have seen in an earlier chapter some details about molecular dynamics as well as a detailedfortran program for molecular dynamics simulation of liquid argon

Molecular dynamics simulation of liquid argon gives, among other quantities, the radial distribution function between two argon atoms. With the help of the radial distribution function you can calculate the potentials of mean force between two argon atoms. The advantage of a general purpose program like gromacs is that the program is sufficiently flexible to do simulations on a variety of systems with a wide range of potential energy parameters. For performing MD of liquid argon using the gromacs software you need following files.

.mdpfile**, .top** file**, .ndx**file**, .gro** file

Here, .mdp is extension of a file.

Generation of initial configuration

The initial configuration can be generated from packmole. From packmole, you will get initial configuration file in pdb format and then, by giving following command you will get an initial configuration file in gro format.

editconf –f initalconf.pdb –o initialconf.gro

Then you have to go to the last line of your initialconf.gro file and change the box length according to the required density of the liquid.

Note: Please note that the line which starts with a semicolon (;) is a comment line which will not be executed and is included just to help the user to understand the details of the contents.

Formation of itp file

It is a file which contains force field parameters for one argon atom, like mass, charge etc. The itp file for argon atom is given below

; .itp file for rigid argon atom

[moleculetype]
; Name nrexcl
Ar3

[atoms]
; nr type resnrresiduatom cgnrcharge mass
1 Ar1 ArAr1 0.0000 39.948

Formation of topol.top file for liquid argon

```
; Argon is taken from OPLS / UNITED ATOM.
; The following line with [ defaults ] has to be provided because
; it gives information about the parameters in the line that follow it

[ defaults ]
;  nbfunc     comb-rule      gen-pairs     fudgeLJfudgeQQ
     1           3              yes           0.5        0.8333

[ atomtypes ]
; name mass     charge     ptypesigma(nm)  epsilon(kJ/mole)
Ar39.9480.000000     A    3.41000e-012.74580e-02
;
;

#include "argon.itp"

[ system ]
Liquid argon

[ molecules ]
;mol_name number
Ar256
```

; herenonbonded function (nbfunc) 1 is for 12-6-1 potential and 2 is exp-6-1 potential.

; comb rule 3 is $\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha} * \varepsilon_{\beta\beta})^{1/2}$ and $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} * \sigma_{\beta\beta})^{1/2}$

; comb rule 2 is $\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha} * \varepsilon_{\beta\beta})^{1/2}$ and $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})^{1/2}$

; gen-pairs, fudgeLJ and fugeQQ are not used for argon atom they are used for triatomic and

; polyatomic molecules.

Formation of index.ndx file

You can generate index.ndx file by giving the following command.

make_ndx –f initialconf.gro –o index.ndx

<enter>

q

<enter>

After that *index.ndx* file is generated.

Note: If you want to know what are input the files and output files of gromacs command,you have to type

Command –h

<enter>

Details of the command will come on the screen.

For example

grompp –h

<enter>

Option Filename Type Description

-f grompp.mdp Inputgrompp input file with MD parameters

-pomdout.mdp Outputgrompp input file with MD parameters

-c conf.gro Input Structure file: gro g96 pdbtpr etc.

-r conf.gro Input, Opt. Structure file: gro g96 pdbtpr etc.

-rbconf.gro Input, Opt. Structure file: gro g96 pdbtpr etc.

-n index.ndx Input, Opt. Index file

-p topol.top Input Topology file

-pp processed.top Output, Opt. Topology file

-o topol.tpr Output Run input file: tprtpbtpa

-t traj.trr Input, Opt. Full precision trajectory: trrtrjcpt

-e ener.edr Input, Opt. Energy file

Option Type Value Description

-[no]h bool yes Print help info and quit

-[no]version bool no Print version info and quit

-nice int 0 Set the nicelevel

-[no]v bool no Be loud and noisy

-time real -1 Take frame at or first after this time.

-[no]rmvsbdsbool yes Remove constant bonded interactions with virtual sites

-maxwarnint 0 Number of allowed warnings during input

processing. Not for normal use and may generate

unstable systems

-[no]zero bool no Set parameters for bonded interactions without

defaults to zero instead of generating an error

-[no]renumbool yes Renumber atomtypes and minimize number of

Atomtype

****

With the help of the above table you will know what are the input files required to run this command.

Energy Minimization of liquid argon

For energy minimization of liquid argon,em.mdp file is needed. The detailed description of em.mdp file is given below

****

; em.mdp - used as input into grompp to generate topol.tpr

; Parameters describing what to do, when to stop and what to save

integrator = steep ; Algorithm (steep = steepest descent minimization)

emtol = 1000.0 ; Stop minimization when the maximum force < 1000.0 kJ/mol/nm

emstep = 0.01 ; Energy step size

nsteps = 5000 ; Maximum number of (minimization) steps to perform

; Parameters describing how to find the neighbors of each atom and how to calculate the interactions

nstlist = 1 ; Frequency to update the neighbor list and long range forces

ns_type = grid ; Method to determine neighbor list (simple, grid)

rlist = 1.0 ; Cut-off for making neighbor list (short range forces)

coulombtype = PME ; Treatment of long range electrostatic interactions

rcoulomb = 1.0 ; Short-range electrostatic cut-off

rvdw = 1.5 ; Short-range Van der Waals cut-off

pbc = xyz ; Periodic Boundary Conditions

****

Performance of energy minimization

Step 1- give the following command to generate topol.tpr file. It is the input for mdrun.

grompp –f em.mdp –c initialconf.gro –n index.ndx –p topol.top –o topol.tpr

<enter>

Then you will see that topol.tpr file is generated.

Step 2- Now give the following command to generate minimum energy configuration.

mdrun –v –o em.gro

After energy minimization, it will show following set of lines

****

writing lowest energy coordinates.

Steepest Descents converged to Fmax< 1000 in 11 steps

Potential Energy = 2.6899719e+05

Maximum force = 9.4305457e+02 on atom 3373

Norm of force = 6.2714920e+01

gcq#337: "Act like Prometheus would" (Gogol Bordello)

****

Now you have the lowest energy configuration (in the form of em.gro) of liquid argon.

Molecular Dynamics simulation of liquid argon:

The em.gro is energy minimized configuration file for liquid argon. It is the input file for molecular dynamics.

The .mdp file for full MD run is fullMD.mdp. The details of this file are given below.

****

integrator = md

dt = 0.002 ; ps

nsteps = 20000 ; = 40 ps tot

nstcomm = 10

nstxout = 0

nstvout = 0

```
nstfout = 0
nstlog = 90000
nstenergy = 90000
nstxtcout= 500
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 = 298.0
;Costrain Bond
constraints = none
constraint_algorithm = LINCS
;Coupling P
Pcoupl = no
Pcoupltype = isotropic
tau_p = 4
compressibility = 4.5e-5
```

ref_p=1

;Generate velocity

gen_vel = yes

gen_temp = 298.0

gen_seed = 173529

;

****

Detailed Description

- Integrator is **md** in which leap frog algorithm is used to integrate the equation of motion.
- **dt** is time step of MD simulation, in gromacs you can use time step upto 10 fs and nsteps is the total number of steps. The product of dt and nsteps give total simulation time.
- The output results are controlled with the help of following:
- **nstxout = 100**, it means the coordinates of each particle of system will be written for every (100*dt) time.
- **nstvout = 100**, it means the velocities of each particle of system will be written for every (100*dt) time.
- **nstfout = 100**, it means the forces of each particle of system will be written for every (100*dt) time.
- **nstlog = 90000**, it means the energy of system will be written in log file after every (9000*dt) time.
- **nstxtcout= 500**, it means that the the trajectories of whole system will be written in traj.xtc file after every (9000*dt) time.
- **nstlist = 10**, it is used to update the neighbor list for long-range forces after 10*dt time.
- **ns_type = grid**, it will make a grid in the box and only check atoms in neighboring grid cells when constructing a new neighbor list every nslist steps.
- **coulombtype = PME**, particle mess Ewald (PME) is used to calculate long range interaction. You can also use Ewald sum and reaction field.
- **rcoulomb = 1.0**, it is cutoff distance for coulomb interaction.
- **pme_order = 4**, it means that electrostatic forces have an accuracy of $2\text{-}3*10^{-4}$.
- **vdwtype = cutoff**,
- **rvdw = 1.5**, it is cutoff for wander wall interactions.
- **tcoupl = v-rescale**, it is used to fix the temperature of the system.
- **tc-grps = System**
- **ref_t = 298.0**, it is the reference temperature of the system.

- **constraints = no**, it means molecules of system are flexible and force constant are used to make the bond flexible.
- **constraints = all-bonds**, it means molecules of system are rigid .
- **constraint_algorithm = LINCS**, lincs is used to maintain the geometry of molecules during simulations. You can also use shake, settle etc.
- **Pcoupl = berendson**, this algorithm is used to fix the pressure of the system.
- **Pcoupltype = isotropic**
- **tau_p = 4**
- **compressibility = 4.5e-5**
- **ref_p=1**
- **gen_vel = yes**, It will generate initial velocities to particles of system.

Step 1- give following command to generate topol.tpr file. It is input file for mdrun.

grompp –f fullMD.mdp –c em.gro –n index.ndx –p topol.top –o topol.tpr

<enter>

Then you will see that topol.tpr file is generated.

Step 2- Now give the fallowing command to generate minimum trajectories of system.

mdrun –v –s topol.tpr–cfullMD.gro

After completing the job, it will generate followingoutput files

fullMD.gro, traj.xtc, traj.trr, topo.tpr etc

Now you can analyze the trajectories of your system.

Calculation of radial distribution functions between two argon atom:

With the help of following command, you can determine radial distribution function between two argon atoms

g_dist –f traj.xtc –s topol.tpr –n index.ndx –o rdfAr-Ar.xvg

<enter>

It will ask select first group

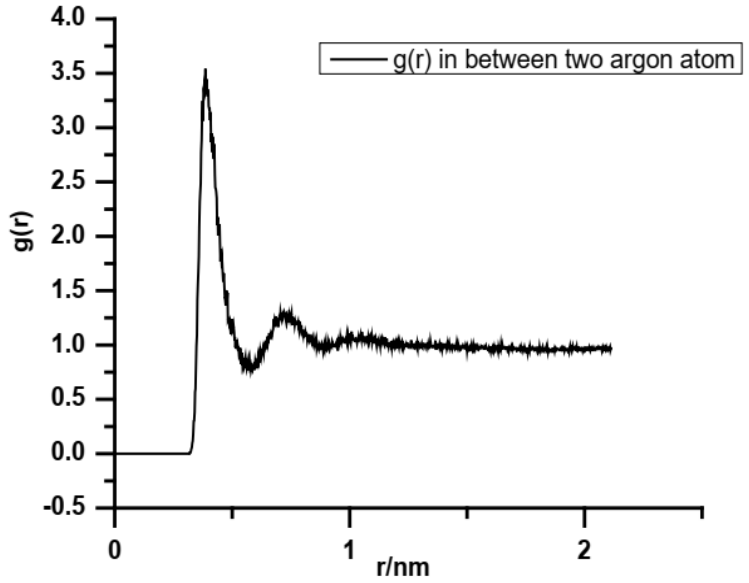
Type Ar

<enter>

Again type Ar

<enter>

When it will complete the task, you will see rdfAr-Ar.xvg output file.

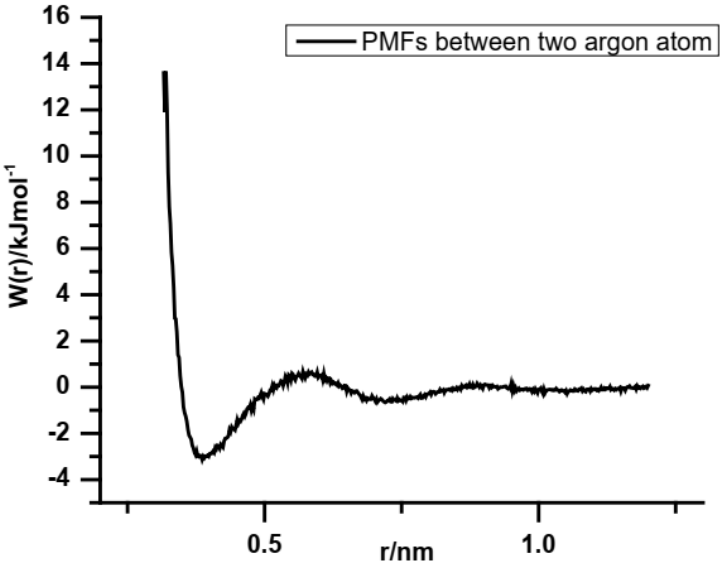


Calculation of Potentials of mean force (PMFs) between two argon atoms:

With the help of radial distribution function g(r), you can calculate PMFs. The relation between PMFs and g(r) is given below

$$W(r) = -kT \ln g(r) \qquad (1)$$

W(r) is the potential of mean force between two argon atoms, k is boltzman constant, T is temperature of system and g(r) is radial distribution function between two argon atoms.



Calculation of diffusion coefficient of argon atom:

The diffusion constant of liquid argon atom can be calculated as

Step 1

g_msd -f traj.xtc –s topol.tpr –n index.ndx –o diffusionAr.xvg

<enter>

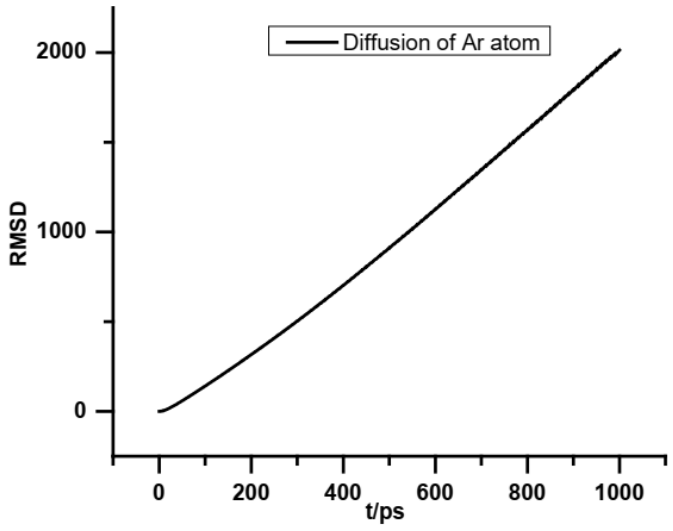
Select group

Type Ar

<enter>

When job is completed, **diffusionAr.xvg** file will be generated.

Analyze this file properly. In this file, x-axis is time in picoseconds and on y-axis, root mean square displacement (rmsd) of argon atoms is given. If you plot a graph between rmsdandtime, you will get a straight line. The slope of this straight line gives the value of the diffusion coefficient of argon atoms.



Summary

In this chapter, you have been introduced to the methods for the

1) Calculations of radial distribution functions between two argon atoms in liquid argon.
2) Calculations of Potentials of mean force between two argon atoms in liquid argon.
3) Calculation of diffusion constant of argon atom in liquid argon.

Exercise:

Execute all the steps outlined in this chapter.