Foundations of Multiscale Modelling: Kinetics. Homework 3. Time-correlation and pair-distribution functions in polar liquid. Practice in LAMMPS and VMD software. Due 23:59 24 Feb.

February 15, 2022

1 Building a molecular dynamics model of water (2 points)

Download stable release of LAMMPS compatible with your PC (Sandia National Labs, USA, `https://lammps.sandia.gov/download.html`). Make (Linux) or install (MacOS, MS Windows) a serial version for desktop machines (*see Seminar/Lab 3 presentation*). Download and install VISUAL MOLECULAR DYNAMICS (VMD) software (`https://www.ks.uiuc.edu/`, version 1.9.2 is recommended[1]). The programming language PERL should be installed, to convert input data using open script `charmm2lammps.pl`. The former can be found in `/LAMMPS/tools/` or via link

   `https://github.com/lammps/lammps/blob/master/tools/ch2lmp/`.

   Open terminal (in MS Windows, launch console via Win+R and command `cmd`), change working directory if it's necessary

   `cd d:/path-to-dir-with-your-project/`

now your are able to run LAMMPS using the command

   `lmp_serial -in _file_ -e both`

or

   `lmp_serial < _file_ -e both`

or

   `lammps -in _file_ -e both`, (depending on OS and way of installing)

where `_file_` is your input script (*see Seminar/Lab 3 presentation for details*).

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[1]VMD of version 1.9.2 is recommended, since parameters of water model is included into common prm-files.

Hint. In Linux you can run LAMMPS directly from the directory, where it is installed `/path-to-lammps/src/lmp_serial -in...`.

Build cubic computational domain $20 \times 20 \times 20$ Å, filled with water (model TIP3P). To do this use VMD program:

`VMD Main` $\rightarrow$ `Extensions` $\rightarrow$ `Modeling` $\rightarrow$ `Add Solvation Box` Make sure that in input checkbox "`Waterbox Only`" is selected. You should get a model (pdb and psf files) containing about 700 atoms (230-240 water molecules), which is a suitable size of a model to simulate it in desktop PC (if you don't change output name, VMD generates files with name `solvate` by default).

Next step is to convert model into the lammps-data format using pdb, psf, topology (top-file) and parameters (par or prm) files as input and the Perl script `charmm2lammps.pl`.

The force field parameters file, for example `par_all36_lipid.prm`, can be copied from VMD subdirectory

`/VMD/plugins/noarch/tcl/readcharmmpar#/`

(where `#` is the number of version) to our work directory. Then rename it as `par_wat.prm`. Short topology file (`wat.top`) with only TIP3P water included can be found in VMD directory:

`/VMD/plugins/noarch/tcl/solvate#/`, copy it to our work directory and rename `top_wat.rtf`. Thus, to prepare lammps-compatible MD model we need to have at least 5 files gathered in our work directory:

(1) `solvate.pdb`,
(2) `solvate.psf`,
(3) `top_wat.rtf`,
(4) `par_wat.prm` and
(5) `charmm2lammps.pl`.

Run the converter in terminal using the following command (make sure that current directory is your working one)

`perl charmm2lammps.pl -charmm -l=20 wat solvate`

The result should be `solvate.data` file, which describes modeled system in lammps-format. Make sure that all necessary blocks (atoms, bonds, angles) are written in the generated data-file.

2 Modeling of the orientational motion of water molecules (6 points)

Using LAMMPS and TIP3P model of water from Task 1, calculate the orientational autocorrelation functions of water $K_u(t) = \langle \vec{u}(0) \cdot \vec{u}(t) \rangle$ and $\Psi_{\theta,l}(t)$ for $l = 2, 3$ (*see the Lecture Notes, Lecture 5, page 9*). Take the vector $\vec{u}$ as a unit vector directed from the oxygen atom to the point between two hydrogen atoms of same molecule (*see Seminar/Lab 3 presentation*).

In all simulations use NpT ensemble[2] with p = 1 atm and T = 300 K, a recommended timestep δt is 1 fs. Save unwrapped[3] coordinates of all atoms every 10-100 fs, where the whole simulation time should be at least 10000 fs (excluding equilibration). Then analyze the coordinates using Python (Jupyter Notebook). Include to your input LAMMPS script command `dump 2 ... dcd ...` to save trajectories. Don't forget to unwrap coordinates to prevent scission of bonds:

`dump_modify 2 unwrap yes`

(a) Plot the dependencies $K_u(t)$, $\Psi_{\theta,2}(t)$ and $\Psi_{\theta,3}(t)$. In order to control the system during the simulation as well as to be sure that the system is equilibrated, store T, p and L (the length of simulation box)[4], energy (kinetic, potential, total) and density ρ of water to the file (you may use `fix ... print ... file` command) and then plot them versus time.

(b) Compute and compare the correlation times: τ_u, $\tau_{\theta,2}$ and $\tau_{\theta,3}$ (see L5 for the definitions).

(c) Apply the strong external electric field ($E_z = 0.05$ V/Å) to the system using the command `fix ... efield` and get an estimate of the orientation autocorrelation function in strong field $K_u^E(t)$. Plot the result and compare with field-free function $K_u(t)$. What is the difference? Is it correct to apply FDT in this case?

Open the initial psf-file (`solvate.psf`) in VMD and then load into it generated by LAMMPS dcd-file with computed trajectories:

`VMD Main → File → Load Data Into Molecule...`

Wrap coordinates using Tk Console of VMD (`VMD Main → Extensions → Tk Console`) and command

`pbc wrap -all -compound resid -center origin`

Are water molecules oriented along the electric field? Choose a representation style you like and make a screenshot of the studied system.

Hint 1. Don't forget first to equilibrate the system as NVT-ensemble and then at NpT conditions at least for $10^3 - 10^4$ fs. Don't reset the velocities after equilibration!

Hint 2. For saving the system thermodynamic parameters via

`fix ... print ... file` command it is necessary to add them in `thermo` output before. You can do this, for example, by:

`thermo_style custom step temp press lx ke pe etotal density`
`thermo 1000`

Hint 3. It is convenient to save atomic coordinates at every 10 steps for the further analysis using `dump` command as follows:

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[2]LAMMPS allows to model different thermodynamic ensembles, which are characterized by the control variables. For NpT ensemble N, p and T are fixed, for NVT ensemble N, V and T are fixed (canonical ensemble) etc.

[3]see Seminar/Lab 3 presentation

[4]Since p is supposed to be fixed (in average), the volume, that is L^3, may fluctuate, since it is not the control variable.

```
dump 1 all custom 10 dump.*.txt mol type xu yu zu
```
Stored files can be easily read in Python via, for example, `scipy.genfromtxt()` function of `SciPy` module.

For convenience, it is possible so sort output lines for atoms by atom index. To do this the following command may be added:
```
dump_modify ... sort id
```

3 Mean square displacement and pair distribution function (2 points)

Using the water model built in Task 1 and LAMMPS get an estimate of the diffusion coefficient D of water at T = 300 K and p = 1 atm and find the most probable distances between oxygen-oxygen d_{O-O} and oxygen-hydrogen d_{O-H} atoms of different molecules. To do this:

(a) Calculate the mean square displacement (MSD) averaged over oxygen atoms using command `compute ...msd` (don't take hydrogen atoms into account, make proper selection via `group` command). Save result into file with `fix ...print ...file` and then analyse in Python. The diffusion coefficient D can be estimated using the Einstein relation

$$6Dt = \lim_{t \to \infty} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \implies$$

$$D \approx \frac{1}{6\tau} \frac{1}{N} \sum_{i=1}^{N} |\vec{r_i}(\tau) - \vec{r_i}(0)|^2 = \frac{1}{6\tau} \text{MSD}(\tau)$$

where time τ must be at least $10^4 - 10^5$ fs. Plot $\text{MSD}(\tau)$. Do you know any other method to find D? Which?

Hint. It is recommended to extract possible motions of the system center of mass (CoM), using the option `compute ...msd com yes`.

(b) Calculate the radial distribution functions (RDF) for O-O and O-H pairs using, for example, the command
```
compute 3 all rdf 100 2 2 1 2
```
where 2 and 1 are oxygen and hydrogen atom types, respectively. The result must be averaged and saved into a file via, for example, command
`fix...ave/time... c_3[*] ave running file RDF.txt mode vector`[5]

Using Python, plot diagrams $\text{RDF}_{O-O}(r)$ and $\text{RDF}_{O-H}(r)$, find positions of the first local maximum d_{O-O} and d_{O-H} and compare the results with the typical donor-acceptor distance of hydrogen bond (H-bonds) in water, which is about 3 Å. Open dcd-file with the results in VMD, wrap coordinates, and add to representation the visualization of H-bonds: VMD Main $\to$

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[5]Detailed description of the command can be found at `https://lammps.sandia.gov/doc/fix_ave_time.html`

`Graphics → Representations → Drawing Method` choose `HBonds`. Make a screenshot of the studied system.

4 Solid, liquid and gaseous argon: VACF(t)* (2 points)

Calculate the velocity autocorrelation function VACF(t) for argon at different aggregate states. System must contain $10^3 - 10^4$ atoms. Use LAMMPS `units real`, styles:

```
atom_style atomic
pair_style lj/cut 8.5
```

Lennard-Jones parameters and mass of argon can be specified by commands:

```
pair_coeff * * 0.238 3.405
mass * 39.948
```

(a) To obtain the VACF of solid argon it is recommended to a start simulation with face-centered cubic (FCC) crystal (see the explanations below, *Hint 3*) with a lattice constant of 5.26 Å. Try the temperature about 40 K and pressure about 100 MPa. Recommended duration of simulation is 2000-3000 fs. Plot VACF(t), does this function oscillate?

Hint 1. It is recommended to use `fix...box/relax iso...vmax 0.1` in energy minimization before the equilibration.

Hint 2. Note, the option `drag` may be useful for equilibrating your system with `fix...npt...`.

Hint 3. You can generate the simulation system of 4000 Ar atoms with FCC crystal structure by:

```
lattice fcc 5.26
region box block 0 1 0 1 0 1 units lattice
create_box 1 box
create_atoms 1 box
replicate 10 10 10
```

(b) Liquid argon can be obtained by melting of FCC crystal (what parameters are to be changed to melt a crystal?). Recommended simulation time is 1500-2000 fs. Plot VACF(t).

Hint 4. Try, for example, T = 80 K and p = 0.1 MPa.

(c) Calculate VACF(t) and MSD(t) for gaseous Ar (how can you go from liquid to gas?). The simulation time should be at least $2 \cdot 10^6$ fs. Plot VACF(t) and compare with (a) and (b). Find an estimate for the diffusion coefficient D_{Ar} using the FDT relation

$$D = \frac{1}{3} \int_0^\infty \langle \vec{v}(0)\vec{v}(\tau)\rangle d\tau.$$

Compute the diffusion coefficient from the MSD (see the Problem 3). Compare two values.

5   Stochastic equation with multiplicative and colored noise (2 points)

a) Solve numerically the stochastic differential equation with the multiplicative noise

$$\dot{y} = -\gamma y + C(y)\xi(t),$$

where $\gamma = 1$, $C(y) = y^2$ and $\xi(t)$ is the Gaussian white noise with zero mean and unit dispersion. Plot the normalized time correlation function $\langle y(0)y(t)\rangle / \langle y(0)^2\rangle$

   Hint. Use the Lecture Notes, Lecture 7.

b) Compare the diffusion, that is, plot the MSD(t) for the white noise (i) and colored noise (ii), solving numerically the according stochastic differential equations,

   (i)

$$x = \xi(t),$$

   (ii)

$$\begin{cases} \dot{x} = y, \\ \dot{y} = -\frac{y}{\tau} + \frac{\sqrt{2B}}{\tau}\xi. \end{cases}$$

Here $\xi(t)$ is the Gaussian white noise with zero mean and unit dispersion.

   Hint. Use the Lecture Notes, Lecture 7.