

## Weeks 1 & 2: Introduction to molecular dynamics (MD) simulations

### Introductory reading material:

MD is used for studying many-particle systems by solving Newton's equations of motion for each individual particle. Many of the concepts in this module are explained in a nice video on YouTube: [Basics of Molecular Dynamics Simulations](#).

Some of the problems are based on the material in Chapter 6 of "[Molecular Modeling](#)" by Andrew R. Leach. Make sure to read it!

This module will require some simple input-file editing in the open-source software LAMMPS. Please consult the program manual available online: [LAMMPS manual](#)

Of course, you can always consult Wikipedia for more details about MD: [Wiki page](#)

### Goals of this Section:

Get familiar with fundamental principles in MD and an MD simulator (LAMMPS). Simulate simple model systems and processes in LAMMPS. Use [VMD](#) to visualize the simulation and analyze important properties of systems at equilibrium.

### Problem 1.1 - Basics

a. Calculate the de-Broglie wavelength of Argon at 300K. Is Newtonian classical mechanics a good approximation of the motion of atoms and ions?

Tip: The de-Broglie wavelength is given by  $\lambda = \frac{h}{p}$ . Assume that the particle has the Maxwell-Boltzmann root-mean-square velocity.

Find the typical size of an Argon atom online. What is your conclusion? Is Ar at 300K a classical or quantum particle? Explain your answer.

b. We will simulate a single Argon atom in LAMMPS- a classical molecular dynamics code focusing on materials modeling. To download and install LAMMPS, refer to the software [website](#).

**Please make sure that the packages MOLECULE, RIGID and KSPACE are installed**

LAMMPS requires an input file to define the simulation environment, initial parameters, variables, and other conditions. Open a text editor and set up the input file for a simulation.

Add the following lines:

```
units real
atom_style atomic
dimension 3
boundary p p p
```

Using these LAMMPS commands, we define the simulation units, type of particles (here as atoms), 3D simulation (x, y, z), and periodic boundaries in x, y, z. All the information is available at [LAMMPS documentation](#). Refer to the documentation often and whenever you are unsure of the meaning of a command.

c. Define a simulation box, in which the simulation will run. create a single Ar atom (with appropriate mass) and set its initial coordinates. Add the following lines:

```
region box block 0 10 0 10 0 10
create_box 1 box
create_atoms 1 single 0 0 0
mass 1 39.948
```

Make sure you understand all the commands above. Refer to the documentation for clarification.

d. Next, we specify how positions and velocities are updated as the simulation progresses; this can be done using fix commands. Add the following line:

```
fix 1 all nve
```

The group specifier “all” indicates that this fix is applied to all atoms in the system.

The style nve indicates that particle positions and velocities will be updated following the microcanonical ensemble (NVE ensemble).

e. LAMMPS provides a dump command to output information to a file. We will use the dump command to output the x, y, z coordinates of the Ar atom. We will use the VMD software for visualization. Add the following line to the script.

```
dump positions all custom 1 positions.lammpstrj id x y z
```

Make sure you understand all the commands above. Refer to the documentation for clarification.

Once the simulation is done, the created dump file named position.lammpstrj can be opened with VMD. Open VMD, click File->New Molecule and open the file. Click Graphics->Representations to change the drawing method to VDW style (sphere representation).

f. Add the following line to indicate how long the simulation will run. This is done with the run command.

```
run 100
```

Save the input file and run the simulation. Check the documentation on how to run LAMMPS in cmd (Windows) or terminal (Linux).

### **Problem 1.2 - Conservation of Energy**

Show that for a conservative force  $F(x) = -\frac{dV(x)}{dx}$ , Newton's 2<sup>nd</sup> law leads to the conservation of total energy.

To answer some of the sections from here onwards, you will need to edit the input file yourselves, based on the example in Problem 1.1.

### Problem 1.3 - Propagation in time

The [Verlet algorithm](#) is commonly used in MD simulation to propagate the equations of motion.

- a. Show analytically that the global error of Verlet integrator is on the order of  $\Delta t^2$ . Tip: write the position in time  $t + \Delta t$  and  $t - \Delta t$ .
- b. Simulate a single particle with initial velocity in the x-direction. (use the provided script file - in.1p). What kind of motion do you observe? Explain briefly.
- c. Edit the input file to simulate the motion of a particle in 1D (x-direction) under the influence of a harmonic external potential with  $k= 0.02$  in LJ units (tip: use fix-addforce). Plot the potential, kinetic and total energy as a function of time step and show that the total energy is conserved (tip: use compute/ke, compute/pe and define a variable which sums both ke and pe, to keep track of the kinetic and potential energies. Use the thermo command and thermo\_style custom to output the desired values).

#### Tips:

- a. Use “variable equal” to define k.
  - b. Use “variable atom” to define  $F_x$  (the force applied on the particle in the x-direction) and the potential energy.
  - c. Use “fix\_modify energy” to update the energy.
- d. What is the classical probability of a single particle in a 1D harmonic trap to be between  $x$  and  $x+dx$ . Plot the probability density histogram (tip: use fix ave/histo) you get out of the LAMMPS simulation. Do they agree?
- e. What is the probability for a quantum particle in the ground state of the same 1D harmonic trap? In what way a quantum oscillator differs from the classic oscillator? What happens at higher quantum states?

f. Change the value of the velocity from 0.1 to 0.2, 0.3, 0.5, 1, plot the position of the turning points as a function of the velocity. What behavior do you observe? Explain. Write down the expression for dependence of the position of the turning points as a function of the velocity.

### Problem 1.4 - Interaction potential

Lennard-Jones (LJ) fluid is a model system for noble gasses, such as Argon. The LJ potential is:

$$V_{LJ} = 4\epsilon \cdot \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

- Plot the potential as a function of  $r$ . What is the meaning of the parameters  $\sigma$  and  $\epsilon$ ?
- Evaluate the value of  $r$  for which the potential has a minimum.
- Calculate the van der Waals radius for the Xenon atom, given that  $\epsilon(\text{Xe}) = 1.77$  kJ/mol,  $\sigma(\text{Xe}) = 4.10$  Å. Next, calculate the intermolecular potential between two Xenon atoms separated by 6.0 Å.
- When we have many particles, the interactions potential sums over all distinct pairs.

$$V_{LJ} = 4\epsilon \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

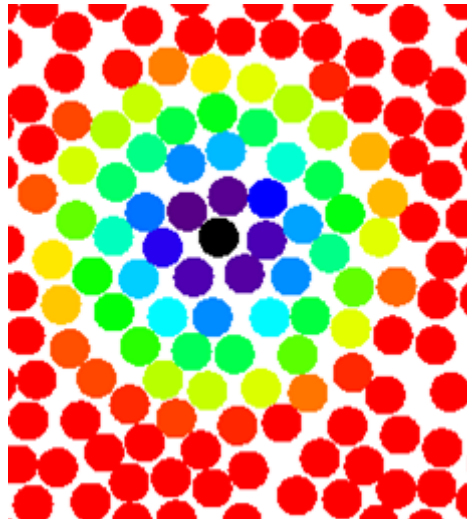
where  $r_{ij} = |r_i - r_j|$ .

Derive the expression for the force acting of atom  $k$  using the potential above.

### Problem 1.5 - Radial distribution function

The radial distribution function (RDF) describes how the density of the surroundings of a reference particle varies as a function of distance from this particle. Read about RDF in Frenkel, Daan; Smit, Berend (2002). [Understanding molecular simulation from algorithms to applications](#) (2nd ed.), page 85, or "[Molecular Modeling](#)" by Andrew R. Leach., page 269

Plot the RDF as a function of the radius with respect to the black atom. Assume all particles are of equal sizes. Draw circles of increasing radius and count the particles within each shell to build a histogram. Normalize the histogram by the area of each shell. In your solution file, provide the image with the circles and the input of the histogram.



## Weeks 2 & 3: Simulations of real systems

### Introductory reading material:

This part of the module is based on the following concepts: Lennard-Jones fluid (model fluid), polymer physics, and diffusion. Make Sure you understand the fundamentals of these concepts.

Some of the problems are based on the material in:

Rubinstein and Colby, Polymer Physics, [Chapter 3.2](#).

Andrew R. Leach. Molecular modeling, [Chapter 6](#).

### Goals of this Section:

Simulating real systems and phenomena. Calculating characteristic thermodynamic properties using LAMMPS and comparing them to the literature/experimental values.

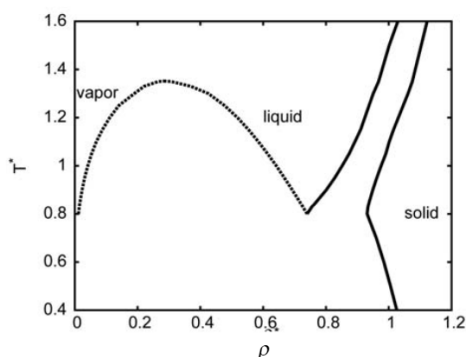


### Problem 2.1 - Use LAMMPS to simulate a LJ fluid.

In classical molecular dynamics, simulations are naturally done in the NVE (microcanonical) ensemble (constant number of particles, volume, and energy). In experiments, often, the temperature is controlled (NVT - canonical ensemble). Several methods have been introduced to keep the temperature constant while using the microcanonical ensemble, such as the Andersen thermostat, the Nosé–Hoover thermostat, Langevin dynamics, and the Berendsen thermostat. We will use such a thermostat in the following problem. For further reading “[Molecular Modeling](#)” by Andrew R. Leach, page 265.

**Here, and in the following exercises, remember to always add a relaxation stage at the final temp/pressure before collecting statistics!**

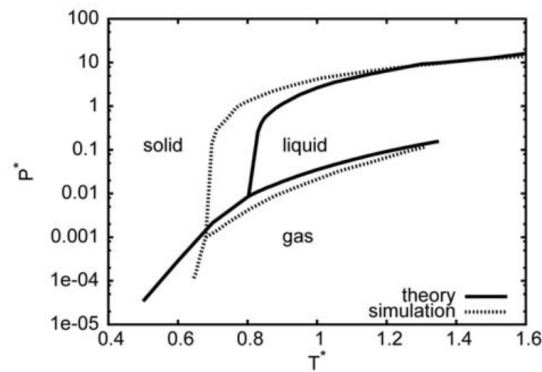
- Simulate Lennard-Jones fluid with a density of 0.8 and temperature 1.0, let the atoms equilibrate for a period of 50000 steps. Use the provided script (in.lj).
- Change the density of the fluid to obtain gas, liquid and solid phases. See the phase diagram below. Save snapshots of the final configuration in VMD. Plot the RDF vs.  $R/\sigma$ . Explain the difference between the three phases obtained.



*Figure -phase diagram of LJ fluid: reduced temperature as function of reduced density (image from Acta Chim. Slov. 2009, 56, 166–171)*

- Decrease the temperature of the gas system to 0.3 under constant volume (NVT ensemble). Use a damping factor of 0.5 and 100000 time steps. Visualize the simulation in VMD and plot the RDF vs.  $R/\sigma$ . Tip: After cooling, run the simulation for 500000 more time steps to reach equilibrium.
- Simulate different cooling rates by changing the number of time steps to 50000 and 500000. Visualize the simulations in VMD and plot the RDF vs.  $R/\sigma$ .

- e. For the fastest cooling rate above, increase the pressure of the system to obtain a compact solid. Remember to add a relaxation stage at the end. (tip: use fix/npt and monitor the obtained density, or use the phase diagram below). Compare the obtained RDF to LJ solid phases and discuss obtained results.



*Figure -phase diagram of LJ fluid: reduced pressure as function of reduced temperature (image from Acta Chim. Slov. 2009, 56, 166–171)*

## Problem 2.2 - Simulation of a polymer chain.

A polymer can be modeled as a chain of short, stiff rods that are free to rotate with respect to each other (freely jointed chain).

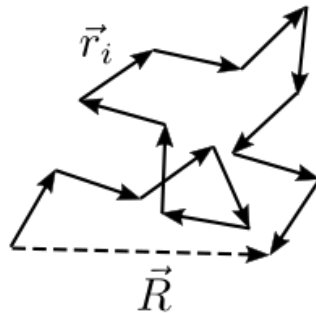


Figure- A sketch of freely jointed chain model (image from Wiki page)

The radius of gyration ( $R_g$ ), characterizes the size of the chain (read Rubinstein and Colby, Polymer Physics, page 63). The freely jointed chain is a simplistic model that provides an analytical solution for the 'ideal' chain. However, a more realistic chain can be modeled by MD simulations where the bonds between the atoms are represented by dynamic bonds instead of stiff rods.

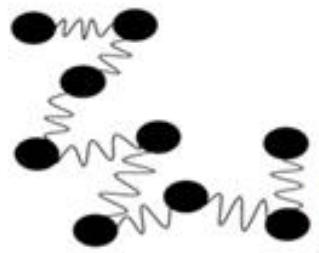


Figure – A sketch of an alternative model of harmonic strings (image from American Journal of Physics and Applications, 2016, 4.2: 20-26)

We will use the finite extensible nonlinear elastic (FENE) bond model to describe the bonds between the atoms (see [Physical Review E 96.5 \(2017\): 052502](#), and [read about the model in LAMMPS](#)).

The FENE model used in LAMMPS is composed of two parts: harmonic and non-harmonic

- Plot both terms and the total potential as a function of  $r/\sigma$ . Write down the equilibrium distance.
- Calculate the analytical value of  $R_g$  for a freely-jointed chain model.

Monomer-solvent, monomer-monomer, and solvent-solvent interactions are of primary importance in determining the configuration of the polymer chain and affect its dynamics in solution. A theta solvent results with a close to ideal configuration, while poor and good solvents result with collapsed or open structure, respectively (read Rubinstein and Colby, Polymer Physics, page 101).

We will use an effective, implicit representation for the solvent effect by defining a LJ potential between non-bonded atoms.

c. In LAMMPS, If the system is large, it is recommended to create a separated data file and load it to the simulation. Run the provided script and initial data file (in.chain and data.chain), view the simulation in VMD, calculate the average  $R_g$  of the polymer, and the associated error (use block averaging using 10 blocks, see section 2.2 in [Annual reports in computational chemistry 5 \(2009\): 23-48.](#)). Tip- use fix ave/time

d. Change the  $\epsilon$  in the non-bonded interaction to receive a good, theta, and poor solvent-polymer system. View the simulation in VMD. Plot the  $R_g$  (and the associated error as in c) as a function of  $\epsilon$ , and compare it to the analytical value of a freely-jointed chain model.

### Problem 2.3 - Diffusion of water molecules

As we already saw, MD simulations can be used to study the equilibrium properties of various systems. However, MD can also provide insight into dynamical properties, such as diffusion, chemical reaction rates, spectroscopy, and more.

Water is an essential molecule to life. In this module, we will simulate and find several characteristic properties of liquid water. Please note that the simulation consists of 1500 water molecules; thus, the simulation's run time can be long.

The diffusion constant of water is reported in the literature ([Physical Chemistry Chemical Physics, Vol. 2, 4740–4742 \(2000\)](#)). Using MD simulation, we will calculate the diffusion constant of water at 298K and compare the obtained value to the reported one. The constant can be extracted in two different ways.

a. The first method is to measure the mean-squared displacement (MSD). The MSD needs to be calculated using the center of mass of the molecule. You can assume that the center of mass of the molecule is approximately given by the position of the oxygen atom. Use the provided script and calculate the diffusion constant using the MSD value.

b. The second approach is to measure the velocity auto-correlation function (VACF) of the system. The time-integral of the VACF gives the diffusion coefficient. Calculate the diffusion coefficient based on VACF.

c. Compare the obtained results in a and b to the reported value in the literature (experimental/theoretical).