Many Particle Systems - Molecular Dynamics Simulation

1. Forces

1a. We are going to simulate a monatomic liquid. We use the Lennard Potential, that means that the interaction potential V_{ij} of particle i at position x_i and particle j at position x_j is

$$V_{ij} = 4\,\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right) \tag{5}$$

where $r_{ij} = |\vec{x}_i - \vec{x}_j|$. In the simulation we will need F_{ix} etc. As preparation determine explicitly $F_{ix} = \sum_{\substack{j=1 \\ j \neq i}}^{N} -\frac{\mathrm{d}}{\mathrm{d}x_i} V_{ij}(r_{ij})$.

1b. Make a flow chart for the determination of the acceleration of all particles $\{\vec{a}_i\}$.

1c. Use the sample program
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj1_sample.cc`
and add the determination of $\{\vec{a}_i\}$ in the function `accfunc`.

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1. Forces

1c. In last class you determined that the force in x-direction on particle i is

$$F_{ix} = -48\,\epsilon \sum_{\substack{j=1 \\ j\neq i}}^{N} \left(\frac{\sigma^{12}}{r_{ij}^{14}} - 0.5\frac{\sigma^{6}}{r_{ij}^{8}} \right) (x_i - x_j) \tag{6}$$

where r_{ij} is the distance between particles i and j $r_{ij} = |\vec{x}_i - \vec{x}_j|$. Similarly you obtain F_{iy} and F_{iz}. We also use a cutoff and shifted potential, so for $r_{ij} > 2.5$ we set $\vec{F}_{ij} = 0$. Use the sample program
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj1_sample.cc`
and add the determination of $\{\vec{a}_i\}$ $(= \vec{F}_i)$ in Lennard-Jones units) for all particles i in the function `accfunc`. Compare your result in the file `accout` with the file `~kvollmay/classes.dir/capstone_s2005.dir/md.dir/accout_comp`. (The unix command `diff file1 file2` helps you to check if `file1` and `file2` are identical.)

2. Molecular Dynamics Step

2a. Next you will add the molecular dynamics (MD) step to your program. We will use the velocity Verlet algorithm

$$\begin{aligned} \vec{x}_i(t+\Delta t) &= \vec{x}_i(t) + \vec{v}_i(t)\,\Delta t + 0.5\,\vec{a}_i(t)\,(\Delta t)^2 \\ \vec{v}_i(t+\Delta t) &= \vec{v}_i(t) + 0.5\,[\vec{a}_i(t) + \vec{a}_i(t+\Delta t)]\,\Delta t \end{aligned} \tag{7}$$

Draw a flow chart for the MD program using equations (7). Include in your flow chart the periodic boundary conditions

$$\begin{aligned} -L/2 &\leq x_i < L/2 \\ -L/2 &\leq y_i < L/2 \\ -L/2 &\leq z_i < L/2 \end{aligned} \tag{8}$$

Print every `TPRINT` step $t, x_0(t), y_0(t), z_0(t), x_1(t), y_1(t), z_1(t)$.

2b Use $\Delta t = 0.001$, `TPRINT=5`, and run your program for `TOTSTEP=500` MDsteps (as already in sample program for 1.). Compare your results with
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/xoft_class2.data`
You also find the final configuration $(x_i, y_i, z_i, v_{x,i}, v_{y,i}, v_{z,i})$ in
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/confout_class2.data`

3. Potential Energy

Add to your MD program a function which determines the potential energy

$$U_{\text{pot}} = \sum_i \sum_{j>i} V_{\text{cutshift}} \tag{9}$$

where for $r_{ij} < 2.5$ $V_{\text{cutshift}} = V_{ij} + V_{\text{shift}}$, $V_{ij} = 4\,\epsilon \left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right)$, $r_{ij} = |\vec{x}_i - \vec{x}_j|$, and $V_{\text{shift}} = V_{ij}(2.5)$. For $r_{ij} \geq 2.5$ $V_{\text{cutshift}} = 0$. Include the minimum image convention similar to your determination of the acceleration. Print also U_{pot} every `TPRINT` steps.

4. Kinetic Energy

Add to your MD program a function which determines the kinetic energy $E_{\text{kin}} = 0.5 \sum_i \vec{v}_i^2$. Print E_{kin} also every `TPRINT` steps.

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2. Particle Trajectories

Use your MD program from last class (if it was working) or use the sample MD program
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj2_sample.cc`
Run your simulation for 2500 MD steps of stepsize $\Delta t = 0.001$. Print every 5 MD steps. Look at $x_0(t), y_0(t), z_0(t), x_1(t), y_1(t)$, and $z_1(t)$. Interpret the graphs.

3. Potential Energy

Add to the MD program a function which determines the potential energy per particle

$$U_{\rm pot}/N = \sum_{i=1}^{N} \sum_{j>i} V_{\rm cutshift} \tag{10}$$

where for $r_{ij} < 2.5$ $V_{\rm cutshift} = V_{ij} + V_{\rm shift}$, $V_{ij} = 4\,\epsilon \left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right)$, $r_{ij} = |\vec{x}_i - \vec{x}_j|$, and $V_{\rm shift} = V_{ij}(2.5)$. For $r_{ij} \geq 2.5$ $V_{\rm cutshift} = 0$. Include the minimum image convention similar to your determination of the acceleration. Run the simulation for 500 MD steps. Print also $U_{\rm pot}$ every `TPRINT=5` steps. Let us together have a look at your result.

4. Kinetic Energy

Add to your MD program a function which determines the kinetic energy per particle $E_{\rm kin}/N = 0.5 \sum_{i=1}^{N} \vec{v}_i^2$. Print $E_{\rm kin}/N$ also every `TPRINT` steps.

5. Temperature

Temperature T is related to the kinetic energy. How? (If time permits try to find the relation otherwise get me.) Determine and plot $T(t)$.

6. Velocity Distribution

6a. Next let us check if the velocity distribution is normal distributed. To get an equilibrated configuration run your original MD program (or sample program `lj2_sample.cc`) for 5000 MD steps. It should print out at the end the file `confout`. Before you continue get me for some explanations at the white board. Use the sample program
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/pofvx_sample.cc`
Add to the program the determination of the velocity distribution $P(v_x)$ (in program `Pofvx[bin]`). Test your program with
`gawk '{print $4,$5,$6}' confout | executable`
`xgraph -m Pofvx.data` where executable is the name of your pofvx program.

6b. Now we compare this distribution $P(v_x)$ with the expected normal distribution $G(v_x) = \frac{1.0}{\sqrt{2\pi}\sigma} \exp\left(-v_x^2/(2\sigma^2)\right)$ where $\sigma = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{kT}{m}}$. Write into the file `Gofvx.data` the expected distribution using the same v_x values as you had used them for $P(v_x)$. Look at the comparison with `xgraph -m Gofvx.data Pofvx.data`.

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6. Velocity Distribution

6a. Next let us check if the velocity distribution is normal distributed. To get an equilibrated configuration run your original MD program (or sample program `lj2_sample.cc`) for 5000 MD steps. It should print out at the end the file `confout`. To determine the velocity distribution use the sample program
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj6_sample.cc`
The program determines the velocity distribution $P(v_x)$ (in program `Pofvx[bin]`). Look at the result with
`gawk '{print $4,$5,$6}' confout | executable`
`xgraph -m Pofvx.data` where executable is the name of the executable of this program.

6b. Now we compare this distribution $P(v_x)$ with the expected normal distribution $G(v_x) = \frac{1.0}{\sqrt{2\pi}\sigma} \exp\left(-v_x^2/(2\sigma^2)\right)$ where $\sigma = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{kT}{m}}$. Write into the file `Gofvx.data` the expected distribution using the same v_x values as you had used them for $P(v_x)$. Look at the comparison with `xgraph -m Gofvx.data Pofvx.data`.

6c. So far you have checked the velocity distribtuion using the file `confout`. Repeat the comparison of $P(v_x)$ and $G(v_x)$ using the initial configuartion file `vvinit_N200_2`. Interpret your result.

7. Maxwell Boltzmann Distributed Velocities

To be able to redraw all velocities Maxwell Boltzmann distributed we use the program `lj7_sample.cc`. This will allow us to apply a temperature bath at the desired temperature. Copy
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj7_sample.cc`
into your working directory. Have a quick look at it. Run the program and check if the resulting velocities in file `vout` are normal distributed. To do so use your program from 6c.

Project IV: Lennard-Jones MD Simulations

Get together in groups of two or three. You will work today more with molecular dynamics simulations of the Lennard-Jones system and their analysis. Pick one of the projects described below. Each group will present in class for about 7 min what they have worked on and what their results are.
Work with your group until about 10:20am on your analysis. From 10:20 – 10:35 work as a group on your presentation. You may use the transparencies and pens provided in class. From 10:35 until the end of the class each group will give their presentation.

Project IV.1

8. Equilibrate

With the method of last class we can now apply a temperature bath to our Lennard-Jones system. We start with a high temperature to equilibrate our system well. Copy
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj8_sample.cc`
Have a look at the program and run it for 5000 MDsteps at $T = 2.0$. Look at the resulting $U_{\rm pot}(t), U_{\rm kin}(t)$, and $T(t)$. Move the final configuration (in file `confout`) to file `confout_T2_5000MD`.

9. Cooling Process

9a. From now on start with the initial configuration of file `confout_T2_5000MD`. Next you will cool your system. Change the program from 8. so that the temperature `temp` is changed every `TCOOLSTEP=50` MDsteps from T to $T - \Delta T$, where $\Delta T = 0.1$. Run your program for 2000 MDsteps. Look at the resulting $U_{\rm pot}(t), U_{\rm kin}(t), T(t)$, and $U_{\rm pot}(T)$. Save your file `energies` by moving it to `energies_COOL50`

9b. Now cool with a different cooling rate. For example cool every `TCOOLSTEP=20` MDsteps and run your simulation for 800 MDsteps. To compare your results of the two cooling rates easily copy the shellscript
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/columnchoice.sh`
into your working directory. To compare for example $U_{\rm pot}(t)$ for the two cooling processes use the command
`columnchoice.sh 1 2 energies* | xgraph -m -nl`
Compare $U_{\rm pot}(T)$.

9c. Redo 9b. for different cooling rates (including `TCOOLSTEP=100`). Remember to adjust TOTSTEP accordingly.

Project IV.2

10. Equilibrate

Copy
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj10_sample.cc`
into your working directory. Have a look at the program what it does and let it run for 5000 MD steps. Look at the resulting $U_{\rm pot}(t), U_{\rm kin}(t)$, and $T(t)$. Save the final configuration by moving file `confout` to file `confout_T2_5000MD`.

11. Radial Pairdistribution Function

11a. The goal of your group is to study the structure of the Lennard-Jones system. Read the hand-out about the radial pair distribution function $g(r)$. (One of your group might focus on this task).

11b. Copy
`~kvollmay/classes.dir/capstone_s2005.dir/md.dir/lj11_sample.cc`
into your working directory. This program measures $g(r)$ (lines 112-124). Run the program and look at the resulting $g(r)$ which is in file `gofr.data`.

11c. Your graph in 11b. indicates that we need better statistics. To do so, add to your program that your histogram of $g(r)$ is taken several times during a simulation run at the desired temperature. For testing your program run it for 200 MD steps and measure the histogram every 50 MD steps. You will have to normalize your $g(r)$ appropriately. Print $g(r)$ still only once at the end of the simulation. Once your program is working run it for 5000 MD steps and measure every `GMEASSTEP=200` MD steps. Save your $g(r)$ of file `gofr.data` in file `gofr_T2.data`.

11d. Our next goal is to study how $g(r)$ depends on the temperature T. To do so rerun your program from 10. at $T = 1.0$ and safe your final configuration in file `confout_T1`. Then rerun your program from 11c. but at $T = 1.0$ and with the initial configuration from `confout_T1`. Save your $g(r)$ in file `gofr_T1.data`. Plot your results for $g(r)$ at the two temperatures in one xgraph. Redo these simulations of equilibration and measurement of $g(r)$ at different temperatures.