Molecular dynamics of a classical fluid: Part 1

Claudia Filippi

March 27, 2021

We work with a conservative system of N classical particles obeying Newton's equations of motion:

$$m_i \ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)) = -\nabla_i V(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t)). \tag{1}$$

To integrate Newton's equation of motion, we will use the so-called velocity Verlet algorithm:

$$
\begin{aligned}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2 + \mathcal{O}(\Delta t^3) \\
\mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \frac{1}{2}[\mathbf{a}(t + \Delta t) + \mathbf{a}(t)]\Delta t + \mathcal{O}(\Delta t^3).
\end{aligned}
\tag{2}
$$

where $\mathbf{a} = \mathbf{F}/m$ and $\mathbf{v}$ is the velocity. The algorithm can be implemented as the following steps:

$$
\begin{aligned}
\mathbf{v}(t + \Delta t/2) &= \mathbf{v}(t) + \frac{1}{2}\mathbf{a}(t)\Delta t \\
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t + \Delta t/2)\Delta t \\
\mathbf{a}(t + \Delta t) &= \frac{1}{m}\mathbf{F}(t + \Delta t) \\
\mathbf{v}(t + \Delta t) &= \mathbf{v}(t + \Delta t/2) + \frac{1}{2}\mathbf{a}(t + \Delta t)\Delta t,
\end{aligned}
\tag{3}
$$

so you only need to store $3N_{\text{dim}}N$ quantities (positions, velocities, and forces) at each time step.

In our molecular dynamics simulations, we assign initial positions and velocities and evolve the system in time by solving Newton's equations. Since the system is closed and the forces conservative, the initial positions and velocities determine the total energy, E_0, which is conserved in time. We are therefore working in the micro-canonical ensemble (NVE) with a given total energy. We will see under what conditions a molecular dynamics simulation in NVE allows us to explore the thermodynamic behavior of the particles as in a canonical ensemble.

To estimate the properties of the system in a molecular dynamics simulation, we perform averages of the quantities of interest over the trajectory of the particles. A given property A will have an instantaneous value at time t:

$$A(t) = A(\mathbf{r}_1(t), \ldots, \mathbf{r}_N(t), \dot{\mathbf{r}}_1(t), \ldots, \dot{\mathbf{r}}_N(t)), \tag{4}$$

and an average obtained as

$$\langle A \rangle = \frac{1}{N_{\text{steps}}} \sum_{t=1}^{N_{\text{steps}}} A(t), \tag{5}$$

where the sum is over the number of steps of the simulation.

1. We will first warm up and play with molecular dynamics and some statistical mechanics concepts using harmonic oscillators in 1 dimension.

   a) Consider one particle ($N = 1$) in 1 dimension ($N_{\text{dim}} = 1$) in the external potential

   $$V(x) = \frac{1}{2}kx^2. \tag{6}$$

   Take $m = k = 1$.

   i) Before performing any calculation, determine the typical time of the problem and what you expect to be a reasonable time step.

   ii) Implement the solution of Newton's equation using the velocity Verlet algorithm. Choose some initial conditions for the position and the velocity (x_0, v_0) and solve for a few periods of oscillation.

   Verify conservation of energy. Monitor $(E(t) - E_0)/E_0$. With which time step do you get variations less that 5×10^{-3}?

   Plot $x(t)$ together with the analytical solution for your initial conditions.

   Compute the kinetic and potential energies, $K(t)$ and $V(t)$. Plot them together with the total energy $E(t)$.

   Hint: For re-use in the rest of the problem, structure your code so that you have a separate function computing the forces and the potential energy.

   b) Consider now N independent harmonic oscillators in 1 dimension.

   i) Extend your code to treat N harmonic oscillators with $m_i = k_i = 1$.

   Hint: In the code, you may have "for loops" in the computation of energies and forces but, in the Verlet step, perform operations on the N-dimensional arrays **x** and **v**, so you can use this part of the code also in the next exercise.

   ii) Set $N = 100$ and draw your initial conditions from a uniform distribution. Verify conservation of energy. Monitor $(E(t) - E_0)/E_0$. Can you use the same time step as in part (a) of the problem?

   iii) If your initial random conditions are uniformly distributed as $x_0 \in [-X_0, X_0]$ and $v_0 \in [-V_0, V_0]$. Compute $K(t)$ and $V(t)$ (and plot them together with the total energy) for the three different initial cases (corresponding to different choices of X_0 and V_0):

      1) Start your particles close to the bottom of the well and give them velocities.

      2) Give your particles small velocities but spread them in x.

      3) Which choice of X_0 and V_0 will somewhat mimic equipartition of energy for a system of oscillators in thermal equilibrium (with equal average potential

and kinetic energies)?

Note that, with your last choice of X_0 and V_0, you are <u>not</u> equipartitioning your energy among the degrees of freedom but are just exploiting phase cancellation in the particle oscillations. Recall that you are solving Newton's equation for a set of independent particles and each particle will evolve independently, conserving its own energy.

c) Consider a 1-dimensional chain of N particles interacting with nearest-neighbor harmonic interactions and impose periodic boundary conditions. Therefore, your system is a ring of particles connected by springs. The energy of the system is given by

$$E = \frac{m}{2} \sum_{i=1}^{N} v_i^2 + \frac{k}{2} \sum_{i=1}^{N} (x_{i+1} - x_i)^2 \,, \tag{7}$$

where $\{x_i\}$ denote the displacements from equilibrium and we have $x_{N+1} = x_1$. Keep working with $N = 100$.

i) Modify your code (force and potential energy functions) to treat this system. Verify energy conservation to establish that your choice of time step is adequate.

ii) Perform three runs with the three different choices of initial conditions of point (b.iii) and plot the total kinetic and potential energies, $K(t)$ and $V(t)$ (together with the total energy $E(t)$). In which case, do you obtain equipartition of energy?

Note: At the start of the run, after having initialized the velocities, remove the translation mode of the whole system by subtracting the velocity of the center of mass from the velocity of each particle.

iii) For a set of initial conditions, plot the instantaneous temperature $T(t)$ defined as[1]

$$T(t) = \frac{2}{N} K(t) \,. \tag{8}$$

Discard an appropriate equilibration time and, using the equipartition theorem, compute the temperature T of your system as the average $\langle T \rangle$.

iv) Compute the distribution of the velocities and compare your findings with the analytical expression of the 1-dimensional Boltzmann distribution $P(v)$ you obtain with the computed average temperature, $T = \langle T \rangle$.

Hint: To compute $P(v)$, you will need to histogram your velocity.

You might remember that a system of particles coupled through a harmonic potential can be mapped to a non-interacting system of normal modes. Therefore, even though the collective modes are oscillating independently and behave like the independent 1-dimensional oscillators of problem b), particles (our subsystems) thermalize, their energies are not constant, and their kinetic and potential energies behave Boltzmann-like if one chooses a "typical" set of initial conditions (which do for instance not populate only a single mode).[2]

---

[1]Note that you have N and not $3N$ in the denominator because the chain is 1-dimensional.

[2]For a recent discussion on the thermal behavior of a system of coupled oscillators, see F. Jin *et al.*, "Equilibration and thermalization of classical systems", New Journal of Physics, **15**, 033009 (2013). http://iopscience.iop.org/article/10.1088/1367-2630/15/3/033009/pdf

2. We now move to 3 dimensions ($N_{\text{dim}} = 3$) and consider a system of N classical particles with mass m interacting via the 6-12 Lennard-Jones pair potential:

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{9}$$

This (anharmonic) potential is adequate to model systems which interact weakly through van der Waals dispersion forces as closed-shell atoms such as Argon or Krypton.

This potential has infinite range and, to simplify the problem (and the program), we shift the potential so that it vanishes beyond a cutoff radius R_c:

$$u(r) = \begin{cases} u_{\text{LJ}}(r) - u_{\text{LJ}}(R_c) & r \le R_c \\ 0 & r > R_c \end{cases} \tag{10}$$

where a common choice is $R_c = 2.5\sigma$.

The total interatomic potential of the system is

$$V(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} \sum_{j<i} u(r_{ij}), \tag{11}$$

and the force on atom i is

$$\mathbf{F}_i = -\nabla_i V(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{j \ne i}^{N} \mathbf{f}_{ij}. \tag{12}$$

We place the N particles in a cubic box of side L and work with periodic boundary conditions to minimize surface effects. Fortunately, we do not need to worry about a particle interacting with a very large number of particles in the repeated boxes since we have made the potential short range: if two particles are at a distance $r > R_c$, they do not interact.

Furthermore, if we require that $L > 2R_c$, we can use the so-called minimum image criterion: For a given particle i, only the closest of all the images of j can interact with i, so you can discard all other images as illustrated in Figure 1.

a) Let us derive the forces and recast the problem in dimensionless variables.

   i) Derive the expression of the contribution of the force on i due to atom j, namely, $\mathbf{f}_{ij} = -\nabla_i u(r_{ij})$.

     What is the expression of $\mathbf{f}_{ji}$, namely, the contribution of the force on j due to atom i?

   ii) When using Lennard-Jones potentials in simulations, it is customary to work in units of σ, m, ϵ for length, mass, and energy, respectively. Therefore, we replace

$$\begin{aligned} r &\rightarrow \tilde{r} = r/\sigma \\ E &\rightarrow \tilde{E} = E/\epsilon \\ t &\rightarrow \tilde{t} = t/\tau \quad \text{with} \quad \tau = \sigma\sqrt{m/\epsilon}. \end{aligned}$$

     Derive Newton's equations of motion and the expression of the kinetic and potential energies in terms of the reduced (dimensionless) variables.
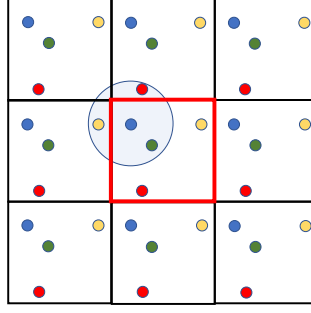
Figure 1: Periodic boundary conditions and the minimal image criterion. The simulation box (red) of size L is periodically repeated. If $2R_c < L$, the blue particle in the box only interacts with the closest image of the other particles in the simulation box (within the circle of radius R_c centered on the particle).

Physical quantity	Conversion unit	Value for Argon
Length	σ	3.41×10^{-10} m
Energy	ϵ	1.65×10^{-21} J
Mass	m	6.69×10^{-26} kg
Time	$\sigma\sqrt{m/\epsilon}$	2.17×10^{-12} s
Temperature	ϵ/k_B	? K
Pressure	ϵ/σ^3	? N/m^2

    iii) We summarize the units and their values for Argon in the Table below. Compute the conversion units for temperature and pressure for Argon.

b) Before doing any coding, think and explain how you impose periodic boundary conditions and make use of the minimum image criterion in computing the energy and the forces.

c) Start from the code of the harmonic oscillators, generalize it to 3 dimensions, and implement energy and forces for the shifted Lennard-Jones potential.

Here are some points of attention:

- At the start, always check that $L > 2R_c$.
- Since the expressions of the energy and the forces make use of the same quantities, compute them within the same function in Matlab.
- At the start, since the potential is highly repulsive, it is better not to place the particles randomly in the box to avoid that some particles might gain very high kinetic energy by being too close to each other. Write an initialization function which places the atoms on a cubic grid contained within the simulation box.
- Initialize the velocities from a uniform distribution and subtract the center-of-mass velocity. Rescale your velocities so that your system has a given (input) temperature T_0. How do you achieve this? Explain your procedure.

d) Set $N = 125$ and the density $\rho = 0.75$. Rescale the velocities so that $T_0 = 3$.

    i) Monitor $(E(t) - E_0)/E_0$ and find a time step so that the simulation is stable and you get variations less that 10^{-2} in a run of a few picoseconds.[3]

---

[3]A more meaningful criterion is to compare differences of energy with other differences of energy and

ii) Plot $E(t)/N$, $K(t)/N$, and $V(t)/N$. Plot also $T(t)$.

iii) After discarding an appropriate number of equilibration steps, compute the temperature of the system, $T = \langle T \rangle$. Verify that the velocities v are distributed according to the Boltzmann distribution with this average temperature (do so for one component of the velocity, e.g. v_x).

Visualizing the dynamics: It may help you to visualize your particles as a function of time in order to understand what is happening in your simulation. I describe below a possible way of doing this in Matlab by creating a handle to plot3.

```
figure(1)
xlim([0,L]);

dynam=plot3(x(:,1),x(:,2),x(:,3),'o');
dynam.MarkerSize=5;
axis equal
drawnow;

box_vertx = [0 0 0; 0 1 0; 1 1 0; 1 0 0; 0 0 1; 0 1 1; 1 1 1; 1 0 1]*L;
box_faces = [1 2 3 4; 2 6 7 3; 4 3 7 8; 1 5 8 4; 1 2 6 5; 5 6 7 8];
patch('Vertices', box_vertx, 'Faces', box_faces,...
      'FaceColor', 'r','FaceAlpha', 0.1);

for step = 1:Nsteps

    % Compute your new positions

    dynam.XData=x(:,1);
    dynam.YData=x(:,2);
    dynam.ZData=x(:,3);
    drawnow;

    % etc. etc.

end
```

---

choose the time step so that the variation in the energy are smaller (at least two order of magnitude) than the fluctuations of the potential (or kinetic) energy.