Computational Assignment 3: Molecular Dynamics of the Lennard-Jones Gas

Philip Cherian

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In this assignment's computational exercise we will develop a simple molecular dynamics program to simulate a two-dimensional system of particles interacting through a "realistic" potential. The potential we will consider is called the Lennard-Jones potential, which is simple but still describes the essential features of interactions between simple atoms and molecules: Interactions are pairwise, two interacting particles repel each other when they are close together, attract each other at moderate distance, and effectively do not interact as the distance increases. The form of this potential is given by

$$u_{ij}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{1}$$

where ϵ is an energy scale (the minimum of the potential energy), and σ a length-scale. If we have particles of equal mass m, we also have a mass scale in the problem. These scales further induce natural velocity and time-scales in the problem. In terms of all of these natural units, we can greatly simplify the form of the potential and the force that each particle exerts on each other. Note than in these units, this is equivalent to choosing $\sigma = 1, \epsilon = 1$, and $m = 1$:

$$u_{ij}(r_{ij}) = 4\left[\left(\frac{1}{r_{ij}}\right)^{12} - \left(\frac{1}{r_{ij}}\right)^{6}\right], \quad \iff \quad m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = \sum_{j\neq i}\frac{48}{r_{ij}^2}\left[\left(\frac{1}{r_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{1}{r_{ij}}\right)^{6}\right]\mathbf{r}_{ij}. \tag{2}$$

We can use the above equation to model the acceleration that every particle i experiences due to all the other $N-1$ particles, and compute all of their trajectories.

Additionally, we can use this to model a thermodynamic system using the fact that the principle of equipartition of energy tells us that the mean kinetic energy per particle per degree of freedom is $T/2$. As a result, we can generalise this relation to define the temperature at time t by

$$T(t) = \frac{2}{d}\frac{K(t)}{N} = \frac{1}{Nd}\sum_{i=1}^{N} m\mathbf{v}_i\cdot\mathbf{v}_i, \tag{3}$$

where K is the total kinetic energy of the system and d is the spatial dimension of the system ($d = 2$ in our case). In this exercise, we will try to see what happens to a gas of "Lennard-Jonesium" as it tends to equilibrium, and try to see the what the distribution of velocities looks like.

To model such a system, however, we need to solve Newton's laws, which we will do using the Verlet Algorithm which is known to converge fast without causing runaway errors in energy. In this three-step

algorithm, the positions and velocities of each particle are evolved through

$$\begin{aligned}
&\texttt{Evolve 'r' by half a time-step:} && \mathbf{r}_i(t+\Delta t/2) = \mathbf{r}_i(t) + \frac{\Delta t}{2} \times \mathbf{v}_i(t) \\
&\texttt{Use new 'r' in 'a' to find 'v':} && \mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) + \Delta t \times \mathbf{a}_i(t+\Delta t/2) \\
&\texttt{Use 'v' to reach 'r' at 't+dt':} && \mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t+\Delta t/2) + \frac{\Delta t}{2} \times \mathbf{v}_i(t+\Delta t)
\end{aligned} \tag{4}$$

(a) Ignore the Lennard-Jones acceleration, choose $N = 25$, and complete the Verlet algorithm to simulate the system. Show that the kinetic and potential energies are constant (within some precision). Keep in mind that at every step, you must update *all* the particles' positions before computing their accelerations.

Since we are modelling a finite system, we also need to take care of the boundary of the box in which we are placing our particles. While we could make the particles "bounce" off the walls, a simpler solution is to get rid of the walls altogether and impose periodic boundary conditions. In our problem, we will be considering the system to be in a box stretching from $x, y = 0$ to $x, y = L$. As a result, periodic boundary conditions imply

(i) if $x > L \implies x \longrightarrow x - L$,

(ii) if $x < 0 \implies x \longrightarrow x + L$.

An `animate` function is provided to help you visualise your results. [2]

(b) Next, fill in the `lj_acc`, `get_pe`, and `get_ke` functions with the Lennard-Jones functions. An important point needs to be made here: since we are imposing periodic boundary conditions, if you think about it, it should be clear that these conditions also affect the *distance* between two particles! For instance, consider two particles with coordinates $(L/10, y)$ and $(9L/10, y)$. Naively, one would compute their distance to be $8L/10$. However, since we have imposed periodic boundary conditions, the *true* distance between them is $2L/10$. It is this "corrected" distance that should be used to compute the accelerations in Equation (2). In order to do this, implement the `pbc_distance` function using the following algorithm: Suppose the distance between two particles is $\rho = x\hat{\mathbf{x}} + y\hat{\mathbf{y}}$, then

(i) if $|x| > 0.5L \implies x \longrightarrow x - L \times \text{sign}(x)$, and similarly

(ii) if $|y| > 0.5L \implies y \longrightarrow y - L \times \text{sign}(y)$,

where $\text{sign}(x) = 1$ if $x > 0$ and -1 if $x < 0$. Complete the `simulate` function and run this for a couple of systems to see how the interactions change the dynamics.

Note: If you choose `dt>0.01`, your particles will move too close to each other in one time-step, and this will lead to them getting unphysically large velocities. [4]

(c) Now, choose $N = 25$ and run your system for a predetermined time interval (say, `tf=100`). Plot a snapshot of the initial and final configurations. Now, using the resulting configuration, run the same code again but in the *reverse* direction. Do the particles return to their original positions? (Running the code in reverse is equivalent to changing the final velocity $\mathbf{v} \to -\mathbf{v}$. What conclusions can you draw from this?) Compare the first configuration and the time-reversed result that should bring you back to it. [2]

(d) We will now try to see what the final speed distribution of our system is, and whether it satisfies the prediction of Maxwell-Boltzmann distribution in two-dimensions:

$$\mathcal{P}(u) = \frac{1}{T} u e^{-u^2/2T} \tag{5}$$

Notice that since the temperature depends on the kinetic energy and not the total energy of the system there is no *a priori* way to figure out the temperature to which the system will settle from just the initial energy, as the kinetic energy will change with this. As a result, you will need to monitor the kinetic energy as a function of time and wait until it reaches a steady-state value (apart from fluctuations about the mean). Once it has attained this value, use Equation (3) to figure out the average temperature T.

Plot a histogram of the *speeds* of the particles after the system has attained equilibrium. Compare it to the 2D Maxwell-Boltzmann distribution (with the T determined above) and see how closely it agrees with your results. [2]

For a more detailed explanation of how best to implement this problem, consult Chapter 8 of *An Introduction to Computer Simulation Methods* by Harvey Gould, Jan Tobochnik, and Wolfgang Christian.