MAT 128: Project II: Molecular Dynamics

Friday, June 2nd
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Names:
[100 pts]

In this project we are going to implement a molecular dynamics (MD) simulation of Argon atoms in two dimensions (2D). The main interaction considered in this system is Van der Waals interactions. We will follow the book entitled Computational Physics by Giordano and Nakanishi. Other references are provided at the end of the assignment. As we discussed in class, in an MD simulation the evolution of the system is given by Newton's equation $\overrightarrow{F} = m\overrightarrow{a}$ which is written in the form

$$-\frac{dE}{dx} = m\frac{d^2x}{dt^2}$$

There are multiple ways to integrate this equation. Here we will use the Verlet algorithm. Next we present the steps to follow for the implementation.

1 Van der Walls interactions in a system of Argon atoms and reduced units. The energy of two atoms at a distance $r_{i,j}$ of such system is given by

$$E(r_{ij}) = 4\epsilon\left(\left(\frac{A}{r_{ij}}\right)^{12} - \left(\frac{B}{r_{ij}}\right)^{6}\right)$$

In this case $A = B = \sigma$. σ and ϵ determine the scale of the problem. σ is called the Van der Waals radius, which for Argon is 3.4 Å, and no atoms can be at a distance less than σ. ϵ is the magnitude of the energy and $\frac{\epsilon}{K_B} = 120K$. In reduced units $\sigma = \epsilon = 1$. r_{ij} is the absolute value of the distance vector between to atoms i and j. In order to solve Newton's equation we need to compute the derivative of the Energy with respect to de distance. The derivative, in reduced units, takes the form

$$f_{ij} = 24\left(\frac{2}{r_{ij}^{13}} - \frac{1}{r_{ij}^{7}}\right)$$

Furthermore it can be shown that the time step of the simulation Δt is also determined by these parameters and is approximately $2ps$.

2 Boundary conditions To avoid boundary effects on the dynamics of the system we establish periodic boundary conditions. First we set up a square region of the plane of dimensions $[0, 2L\sigma] \times [0, 2L\sigma]$ and identify the top and bottom edge and the right and left edge. In effect we obtain a torus. We need to consider how these boundary conditions will affect our simulation.

- The distance between any two atoms will have to be computed across the domain and across the identified edges

- The trajectory of a particles moving beyond the boundaries will continue across the identified edges.

3 Initialization of the system

- Choose N the number of atoms, and the size of the system L
- Fix Δt (time step)
- Set initial positions
- Set initial velocities

To set initial positions and velocities Since no atoms can be at a distance less than σ we perform the following calculation

- Define an equidistant grid of edge size σ
- Select N points of the grid at random
- Displace the N points by $2(rnd-0.5)\delta_r$ in the x and y components. With $\delta_r < \frac{\sigma}{2}$ small so atoms can never collide.
- Assign initial velocities in the x and y component $2(end-0.5)v_0$ with v_0
- Assign positions at $t=-1$ (needed by Verlet algorithm): $x_{-1} = x_0(i) - v_{x0}(i)\Delta t$ (same for y).

4 Verlet algorithm Below are the updates for the x components, the ones for the y are analogous. Notice that in this algorithm we compute the position from the acceleration without computing the velocity first.

- The new x position is given by $x_i(n+1) \approx 2x_i(n) - x_i(n-1) + a_{i,x}(n)(\Delta t)^2$
- The new x component of the velocity is $v_{i,x}(n) \approx \frac{x_i(n+1)-x_i(n-1)}{2\Delta t}$
- The acceleration $a_{i,x} = \sum_{k\neq i} f_{j,i}\cos\theta_{j,i}$ where the value of the force $f_{j,i}$ is given in the previous section and $\cos\theta_{j,i} = \frac{\Delta x}{r_{i,k}}$ with Δx the separation between atoms i,k along the x coordinate. Notice that positions can be then updated once all the forces have been calculated.

5 Reducing computational time

- Assume that atoms will not interact if their distance is greater than 3σ
- $|f_{i,j}| = |f_{j,i}|$

6 Collecting data and comparing against known results

In MD we can average measurable quantities along the trajectory of a particle and also across particles. For instance subdivide the trajectory on regular time intervals $\Delta t = 0$ and average the results for each time interval across atoms.

Since we know that the distribution of speeds is given by

$$P(v) = C\frac{v^2}{K_B T}\exp\frac{-mv^2}{2K_B T}$$

Where K_B is the Boltzman constant and T the temperature. Note that the same formula applies for the velocity distributions v_x and v_y components.

One can also estimate the temperature T at which the system is running. One approach is to use the distributions above since T can be estimated from the formula. Another approach is to use the equipartition theorem that tells us

$$K_B T = \frac{m}{2}\langle(v_x^2 + v_y^2)\rangle$$

Where the angular brackets represent the mean taken over the trajectories and particles.

7 Other references

- Schlick, T., 2010. Molecular modeling and simulation: an interdisciplinary guide: an interdisciplinary guide (Vol. 21). Springer Science & Business Media.
- Rapaport, D.C., Blumberg, R.L., McKay, S.R. and Christian, W., 1996. The art of molecular dynamics simulation. Computers in Physics, 10(5), pp.456-456.