MME 4428A Project

Molecular Simulation

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Part 1: Molecular Dynamics

a) Present a 2D plot of the (x, y) positions of all the atoms at this instant.

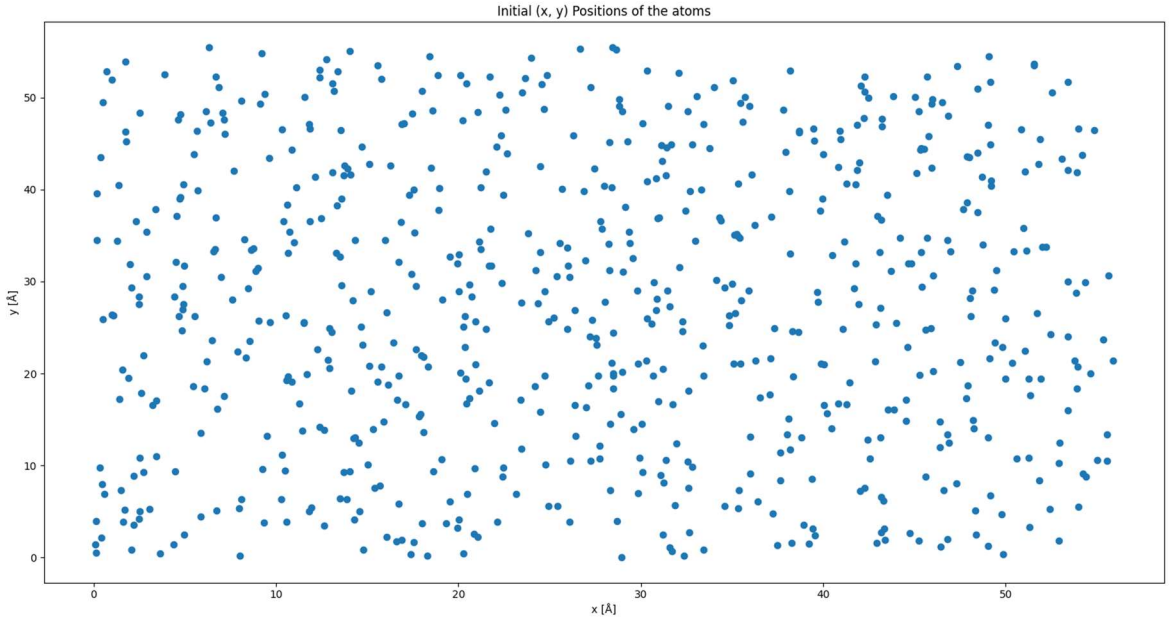

Figure 1: A scatterplot of the initial position of the atoms in the simulation

Note that for subsequent questions, units were converted to SI (for both given constants (L, ξ, and β), and all of the data in the part 1 coordinates sheet), and the mass per atom was calculated as follows:

$$m = \frac{20.18\ g}{mol} * \frac{1\ kg}{1000\ g} * \frac{1\ mol}{6.022 * 10^{23}\ atoms} = 3.351 * 10^{-26} \frac{kg}{atom}$$

b) What is the density of the fluid (molecules/m^3)?

$$\rho = \frac{N}{V}$$
$$\rho = 4.420 * 10^{27}\ molecules/m^3$$

c) Calculate the total instantaneous kinetic energy (J) of the system.

$$KE = \sum_{atoms} \frac{1}{2} m * \sqrt{{v_x}^2 + {v_y}^2 + {v_z}^2}$$
$$KE = 2.836 * 10^{-18}\ J$$

d) Based on this instantaneous kinetic energy, what is the instantaneous temperature (K) of the system?

$$\frac{KE}{N} = \langle KE \rangle = \frac{1}{2} k_B * T * 3DOF$$

$$T = \frac{2}{3} \frac{KE}{N * k_B}$$

$$T = 199.6\ K$$

e) Using the ξ and β parameters that you have been assigned, plot the Stark-Müller potential energy as a function of distance between the atoms. Ensure that you select the axis limits to illustrate important features of the function.

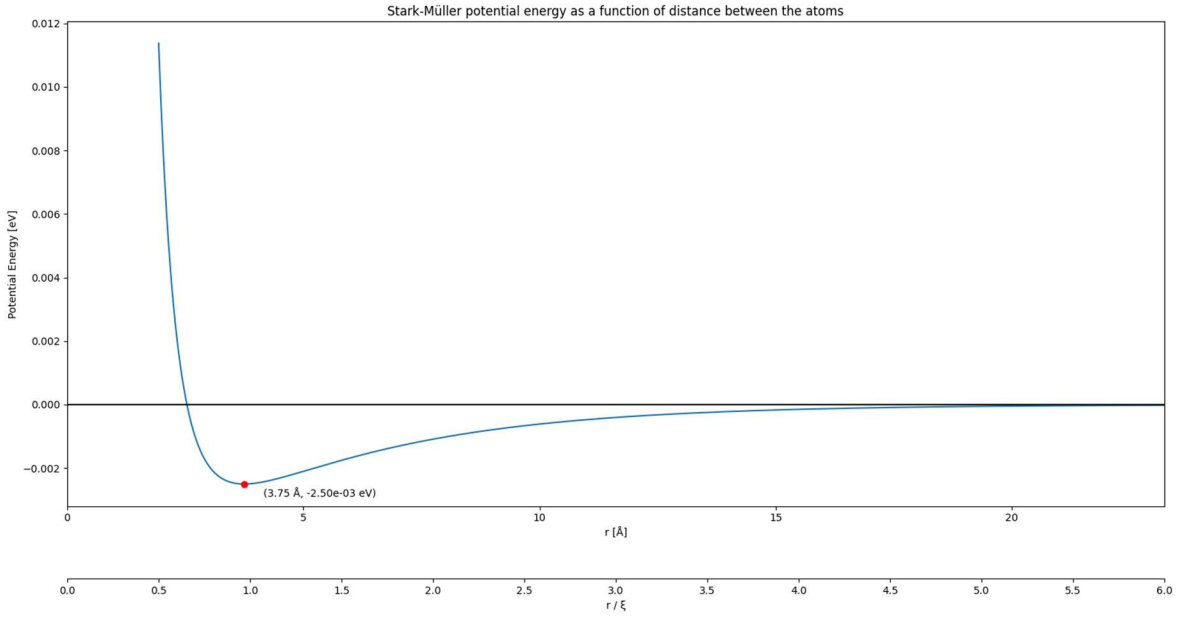

Figure 2: Stark-Müller potential energy as a function of distance between atoms

f) Using a Lennard-Jones cut-off radius of 15 Å, calculate the total potential energy (J) in interactions between atom M and all other atoms.

1. For each atom other than M, find the distance between it and atom M:

$$r = \sqrt{(x - x_M)^2 + (y - y_M)^2 + (z - z_M)^2}$$

2. For each atom whose calculated r to atom M is less than 15 Å, calculate the PE according to the Stark- Müller PE equation, and sum them all:

$$PE = \sum_{atoms\ |\ r < 15\ Å} \beta \left(\frac{1}{16} \left(\frac{\xi}{r} \right)^5 - e^{-\frac{r}{\xi}} \right)$$

$$PE = -6.788 * 10^{-21}\ J$$

g) Again using the snapshot data in the "Part 1 Coordinates" sheet and a cut-off radius of 15 Å, calculate the total potential energy of the system at this instant, ignoring the periodic boundary conditions.

1. Initiate a variable for the sum of potential energy and set it to 0
2. Create an outer for loop whose index i goes through as many numbers as there are atoms
3. Create an inner for loop whose index j goes through the numbers ranging from i+1 to the total number of atoms
4. In the inner for loop, calculate r between atom i and atom j (equation from question f, but with (x, y, z) replaced with (x_i, y_i, z_i), and (x_M, y_M, z_M) replaced with (x_j, y_j, z_j))
5. If the calculated r is less than 15 Å, substitute the calculated r into the term inside the sum in the second equation from part f, and add the result to the variable holding the sum of potential energy

$$PE = -1.391 * 10^{-18}\, J$$

h) Derive an expression for the Stark-Müller force exerted by one atom on another.

$$F = -\frac{dV}{dr}$$
$$F = -\frac{d}{dr}\left(\beta\left(\frac{1}{16}\left(\frac{\xi}{r}\right)^5 - e^{-\frac{r}{\xi}}\right)\right)$$
$$F = -\beta * \frac{d}{dr}\left(\frac{1}{16}\xi^5 r^{-5} - e^{-\frac{r}{\xi}}\right)$$
$$F = -\beta\left(-\frac{5}{16}\xi^5 r^{-6} + \frac{1}{\xi}e^{-\frac{r}{\xi}}\right)$$
$$F = \frac{\beta}{\xi}\left(\frac{5}{16}\left(\frac{\xi}{r}\right)^6 - e^{-\frac{r}{\xi}}\right)$$

i) What is the force (N) vector on atom M at this instant, again, using a cut-off radius of 15 Å?

1. Initialize an array of 3 zeros to store the total force acting on atom M
2. Looping through all atoms within 15 Å of atom M:
    a. Determine the value given by the equation derived in part h for the r between that atom and atom M
    b. Find the unit vector pointing from that atom to atom M by subtracting the coordinates of that atom from those of atom M and dividing by the distance between them (r)
    c. Multiply the unit vector by the value determined in (a) to determine the force on atom M from the atom in question
    d. Add the force contribution from that atom to the array with the total force acting on atom M

$$\vec{F} = \left(-9.174\,\hat{\imath} + 4.143\,\hat{\jmath} - 19.71\hat{k}\right) * 10^{-13}\, N$$

j) Using a timestep of Δt in a modified Verlet scheme, calculate the position (m) and velocity (m/s) of atom M one timestep in the future. (For this part, assume that the velocity data in the "Part 1 Coordinates" sheet are actually one half timestep behind the position data. Calculate the new velocity and position one timestep in the future, though still offset one half timestep from one another).

1. Add the initial velocity and the product of the instantaneous acceleration (the quotient of the instantaneous force and mass) and the timestep to the to determine the new velocity:

$$\overrightarrow{v_{new}} = \overrightarrow{v_{old}} + \frac{\vec{F}}{m} * \Delta t$$
$$\overrightarrow{v_{new}} = \left(-166.2\,\hat{\imath} + 228.7\,\hat{\jmath} - 221.7\,\hat{k}\right) m/s$$

2. Sum the old position, the product of the new velocity and the timestep, and half the product of the instantaneous acceleration and the square of the timestep to determine the new position:

$$\overrightarrow{r_{new}} = \overrightarrow{r_{old}} + \overrightarrow{v_{new}} * \Delta t + \frac{1}{2}\vec{a} * \Delta t^2$$
$$\overrightarrow{r_{new}} = \left(2.967\,\hat{\imath} + 2.130\,\hat{\jmath} + 3.786\,\hat{k}\right) * 10^{-9}\ m$$

Part 2: Metropolis Monte Carlo

k) Using a 0.1 Å bin size, plot a histogram of the position of Atom B. Discuss the results.

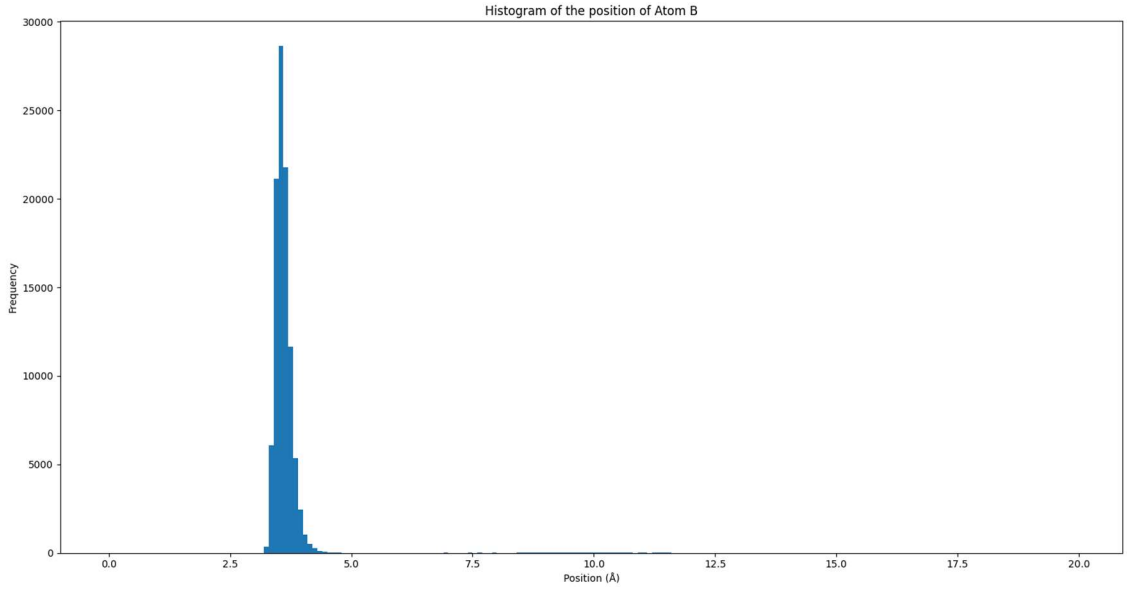

Figure 3: Histogram of the position of atom B during the simulation

The results are as expected. The atom spends most of its time near a specific distance away from atom A, likely due to that position being the largest potential well where it gets stuck, and which it is very

unlikely to get far away from. There seems to be another local minimum (or possibly several of them) near about 10 Å, where it may spend some smaller amount of time before being drawn back to the absolute minimum (which, as expected, is on the order of σ. More specifically, $\sigma * \sqrt[6]{2}$ as derived in question q below).

m) Based on your simulation results, calculate the average distance (m) between the two atoms, $\langle x \rangle$.

Average the values obtained from the simulation to determine the average distance between the atoms:

$$\langle x \rangle = 3.601 * 10^{-10}$$

Note that it's technically possible for B to end up on the other side of A if the simulation is run for long enough. This did not happen in 1000 runs of the simulation (as can be seen in Figure 4 below), but in the odd chance that it had, the average distance between them would need to be calculated as the sum of the absolute values divided by the number of attempted moves, rather than the average position.

n) Based on your simulation results, calculate the average potential energy (J) of interaction between the atoms, $\langle E \rangle$. Discuss the reliability of this calculation and how that can be assessed.

Average the values obtained from the simulation to determine the average potential energy:

$$\langle E \rangle = -3.966 * 10^{-2}\ J$$

Some of the ways in which the reliability of the results can be assessed are:

1. By running the simulation multiple times and comparing the results to determine reliability
    a. Note that having run it a couple of thousand times, the atom was observed to occasionally spend most of the simulation in wells other than the global minimum. See the histograms below (Figures 4 and 5) for the average position and average energy of atom B in 1000 runs of the simulation (with 100 000 attempted moves in each run).
    b. Even when the average stayed around the global minimum, there is some variation between each run. Given that the Metropolis Monte Carlo method is stochastic, averaging the results of many simulation runs can improve the reliability of the results.
2. By running the simulation for more steps
3. By running the simulation with different step sizes
4. Using a different energy model than Lennard-Jones
5. Combinations of the above
6. By comparing the order of magnitude of the results to the value that the equipartition theorem gives (the amount of potential and kinetic energy likely aren't many orders of magnitude different from each other, touched on further in question p)
7. By comparing the results to experimental data (likely having to see what happens in a slightly larger system and scale it down to see what two atoms would behave like)

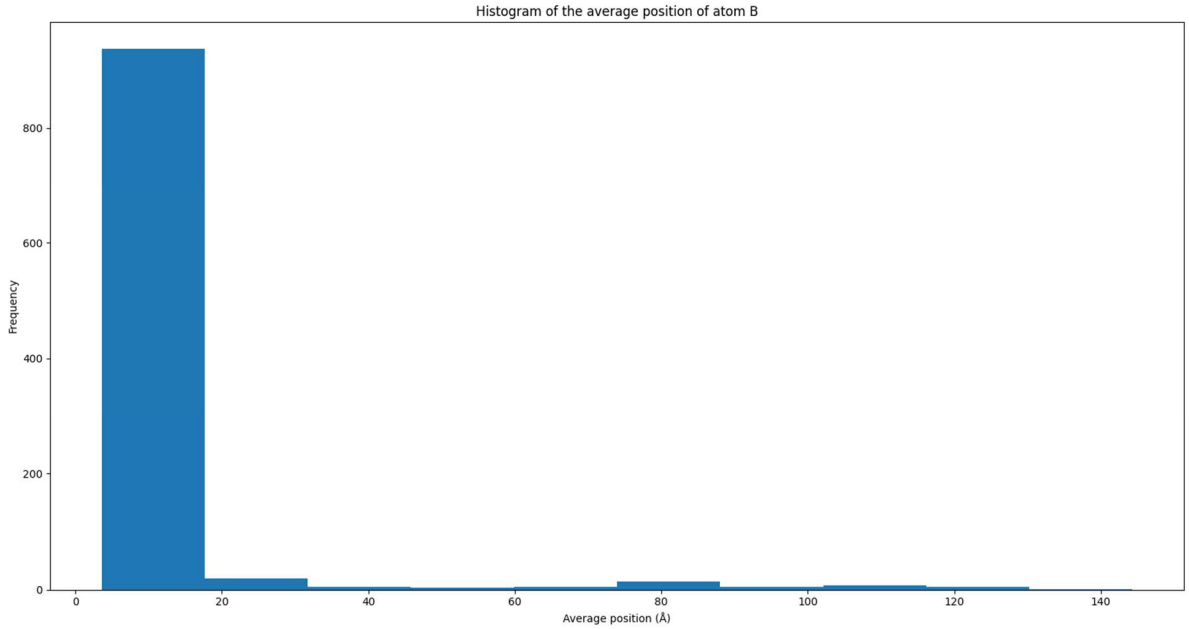

Figure 4: Average position of atom B in 1000 simulations

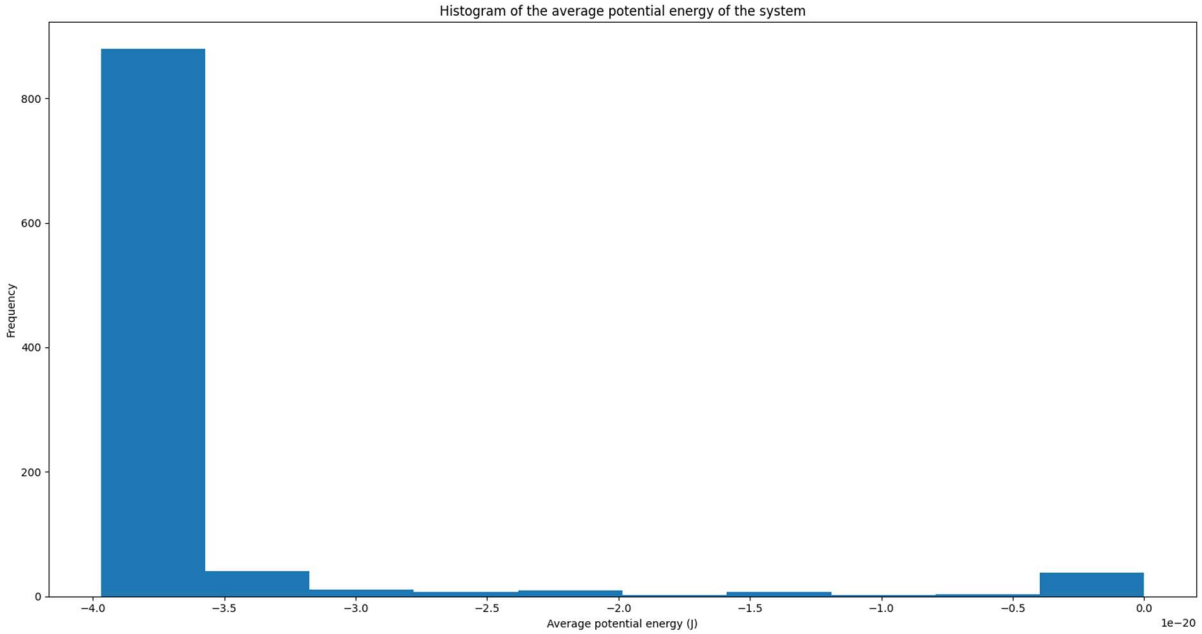

Figure 5: Average potential energy in 1000 simulations

p) Compare your calculated average potential energy to the predictions of equipartition theorem and discuss the results.

The equipartition theorem yields an average kinetic energy according to:

$$\langle KE \rangle = \frac{1}{2} k_B * T * 1DOF$$
$$\langle KE \rangle = 1.897 * 10^{-21}\, J$$

The average kinetic energy according to the equipartition theorem is near the same order of magnitude (10^{-21}) as the magnitude of the average potential energy as determined by the simulation (10^{-20}). It seems reasonable that they're approximately the same order of magnitude, because as atom B moves through and around the potential well, it repeatedly transfers a large portion of its kinetic energy to potential energy and back again. The exact relationship between the two is determined by a number of factors, including the specific dynamics of the system, the accuracy of the simulation, and how close the Leonard-Jones potential models the true interatomic potentials created by the interactions between the two atoms.

q) If the system temperature were slowly lowered to 0 K, what would be the average potential energy (J) of interaction between the atoms, $\langle E \rangle$, and average distance (m) between the two atoms, $\langle x \rangle$?

1. Find the value of r for which the derivative of potential energy with respect to distance is zero:

$$0 = \frac{d}{dr} V$$
$$0 = \frac{d}{dr} 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$
$$0 = \frac{d}{dr} (\sigma^{12} r^{-12} - \sigma^{6} r^{-6})$$
$$0 = \frac{d}{dr} (\sigma^{6} r^{-12} - r^{-6})$$
$$0 = -12\sigma^{6} r^{-1} + 6r^{-7}$$
$$r^{6} = 2\sigma^{6}$$
$$r = \sigma * \sqrt[6]{2}$$
$$r = 3.540 * 10^{-1}\ \ m$$

2. Plug the value of r into the Leonard-Jones potential energy equation:

$$V = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$
$$V = -4.187 * 10^{-20}\, J$$