Homework2

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1 Molecular dynamics simulations of Lennard-Jones argon

The experimental data for Lennard-Jones argon:

$$\frac{\epsilon}{k_B} = 119.8K, \sigma = 3.405\mathring{A}, M = 0.03994kg/mol \tag{1}$$

Use the md.py code provided here to run a MD simulation at the temperature $T = 202K$ and the density $\rho = 1460kg/m^3$. The simulation time after equilibrium should be at least 12 picoseconds.

1.1

In the reduced units $\epsilon = k_B = 1$, so we know that the $T_0 = \epsilon/k_B = 119.7K$ in this units is equal to 1. Then we could get:

$$T^{(ru)} = \frac{T}{T_0} T_0^{(ru)} = 202/119.8 \approx 1.686 \tag{2}$$

In the reduced units $\sigma = 1$, $mass = M/N_A = 1$. We can get the ρ_0 which is 1 in the units firstly.

$$\rho_0 = \frac{M}{N_A \sigma^3} \approx 1679.9864kg/m^3 \tag{3}$$

$$\rho^{ru} = \frac{\rho}{\rho_0} \rho_0^{ru} \approx 0.869 \tag{4}$$

1.2

In the reduced unit we could get the t_0 which is connected to the $t_0^{ru} = 1$. As we know:

$$t_0^{ru} = \frac{\sigma^{(ru)}}{v_0^{(ru)}} = \frac{\sigma^{(ru)}}{\sqrt{\frac{k_B^{(ru)} T_0^{(ru)}}{m}}} = \sigma^{(ru)} \sqrt{m/\epsilon^{(ru)}} = 1 \tag{5}$$

So we can get:

$$t_0 = \sigma \sqrt{M/\epsilon N_A} \approx 2.156 \times 10^{-12} s \tag{6}$$

The least simulation time after equilibrium is 12 picoseconds, in the reduced units is about 5.57 seconds. I choose 6 seconds to satisfy the requirement and set the number of iterations is 12000. Then the time step is equal to $dt = 6/iterations = 6/12000 = 5 \times 10^{-4}$. I done the simulations 12000 iterations for equilibrium run and another 12000 iterations for production run, then I got the figure which is about the kinetic energy, potential energy and total energy along with the time.

We can see that the total energy is stable and the kinetic energy and potential energy are changing with the time.

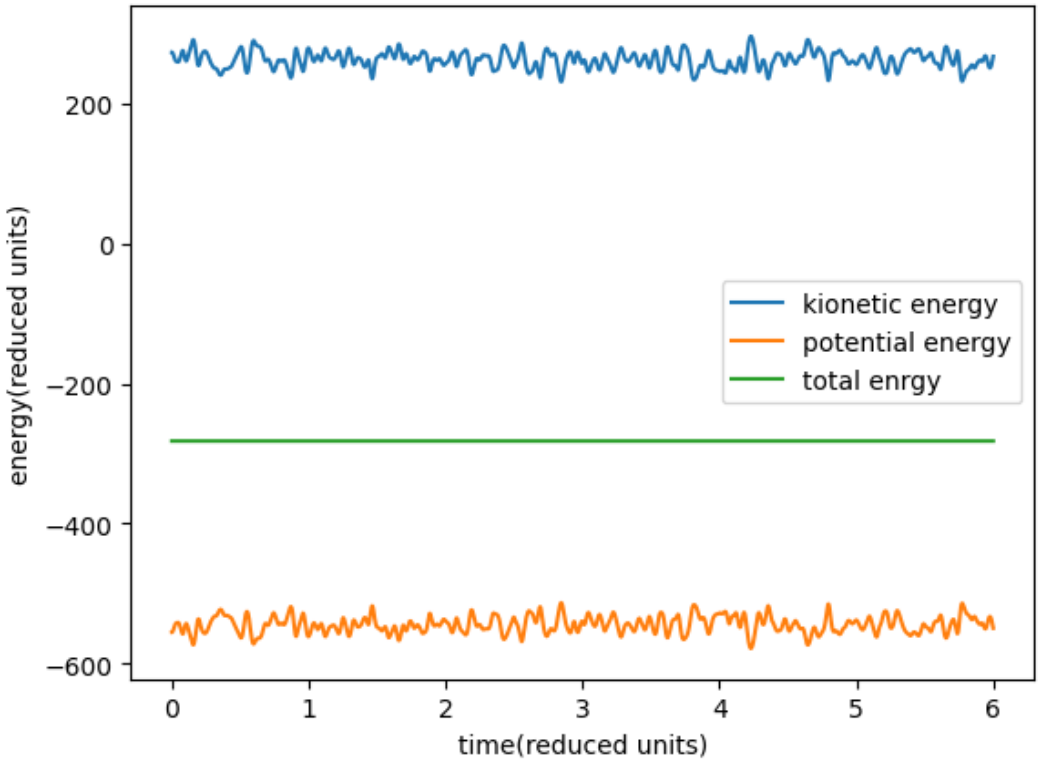

Figure 1: The change of energy with time in 6 seconds after a 6 seconds equilibrium run. $N\_cell = 3$

1.3

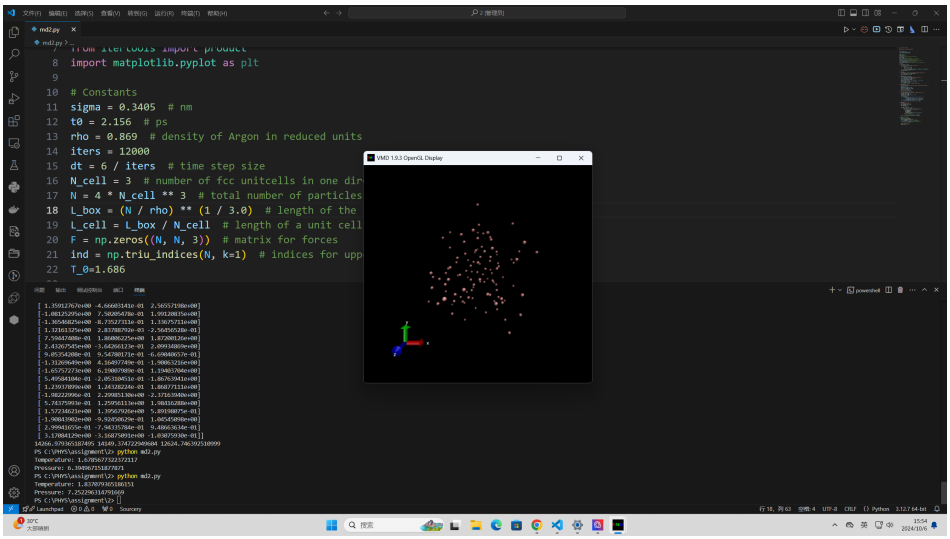

Figure 2: the screenshot of using VMD

As I claimed before, I chose the iterations after equilibrium run is 12000, and the output.gro file as the simulation result is attached. We use the argon atoms which is consistent with the question 4. The screenshot I using VMD software to observe the result is given in 2.

As the question said, there is no need for us to write down every MD simulation step if the time step is very small. As the time step is very small, the velocity and position are changing lightly. In this situation writing down all the steps will cause a lot of redundant data. These data contribute

little help to the Accuracy of simulation but could let the read and write operations cost a lot of time. These will cause the time of running the code and the time for the software that display the simulation to read the data will be much longer.

1.4

The definition of the radial distribution function is:

$$g(r+\frac{1}{2}dr) = \frac{n(r)}{\frac{4}{3}\pi((r+dr)^2 - r^2)\rho(r)} = \frac{n(r)}{4\pi r^2 dr\rho(r)} \tag{7}$$

where $n(r) = \frac{h(r)}{N_{atom}N_{frame}}$, the $h(r)$ is the histogram of the particle number in the distance $r->r+dr$, ρ is the number density of the simulation box. Usually $r < L_{box}/2$. I modified the code and defined some functions to calculate the radial distribution function, the result is showed in 3. It is a result for the number of cells in each direction is 3 and I just simulate for $r < L_{box}/2$. If you what to calculate the $r > L_{box}/2$ situation, I think you need to modify the representation for dV, I think it is a trivial work.

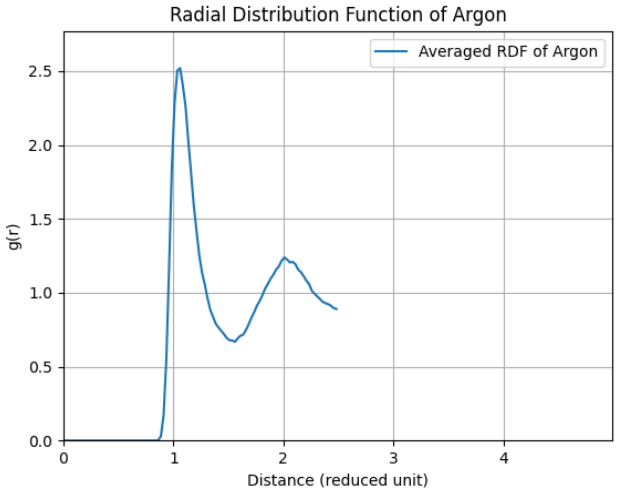

Figure 3: radial distribution function at $\mathrm{N}_P cell = 3, T = 1.686, \rho = 0.869$.

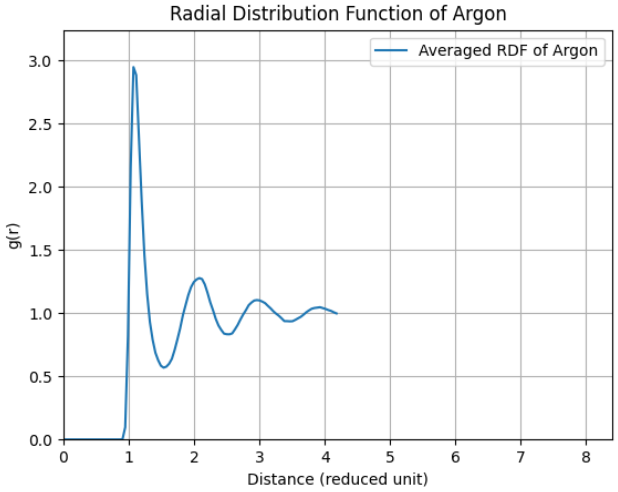

Figure 4: radial distribution function at $\mathrm{N}_{cell} = 5, T = 0.71, \rho = 0.844$.

To evaluate the calculation progress is correct, I also done the calculate at $T = 0.71$ and $\rho = 0.844$(all in reduced unit), then I got the radial distribution function at this situation like 4.

1.5

The Einstein relation is:

$$D = \frac{1}{6} \lim_{t->\infty} \frac{d < [\vec{r}(t) - \vec{r}(0)]^2 >}{dt} \tag{8}$$

After the equilibrium run, I add a function to output the mean MSD of the system. The result is like that:

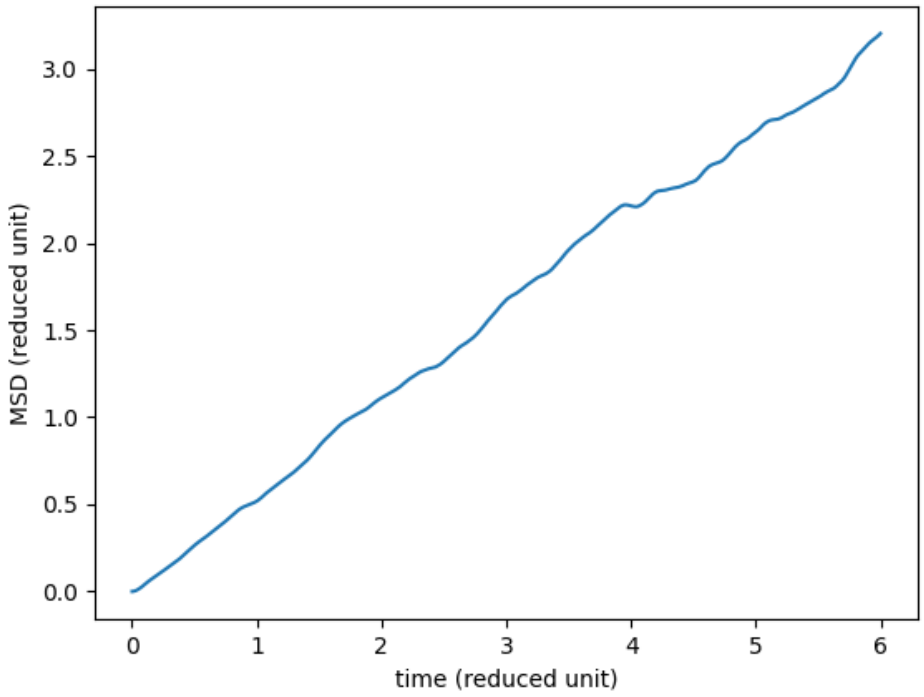

Figure 5: The MSD of all the atoms(reduced unit)

Then I use polyfit to get D from the MSD distribution.

$$D \approx 0.52 \tag{9}$$

The Green-kubo equation is:

$$D = \frac{1}{3N_{atom}} \int_0^\infty \sum_i^{N_{atom}} < \vec{v_i}(\tau) \cdot \vec{v_i}(0) > d\tau \tag{10}$$

Noted that I run it in a long time to make sure the conmstant could be converged. I also add a function to write it and I just treat the integration as a sum. I also set the ∞ in the equation be t so I could calculate the diffusion constant for every t. The result is showed in 6 and 7.

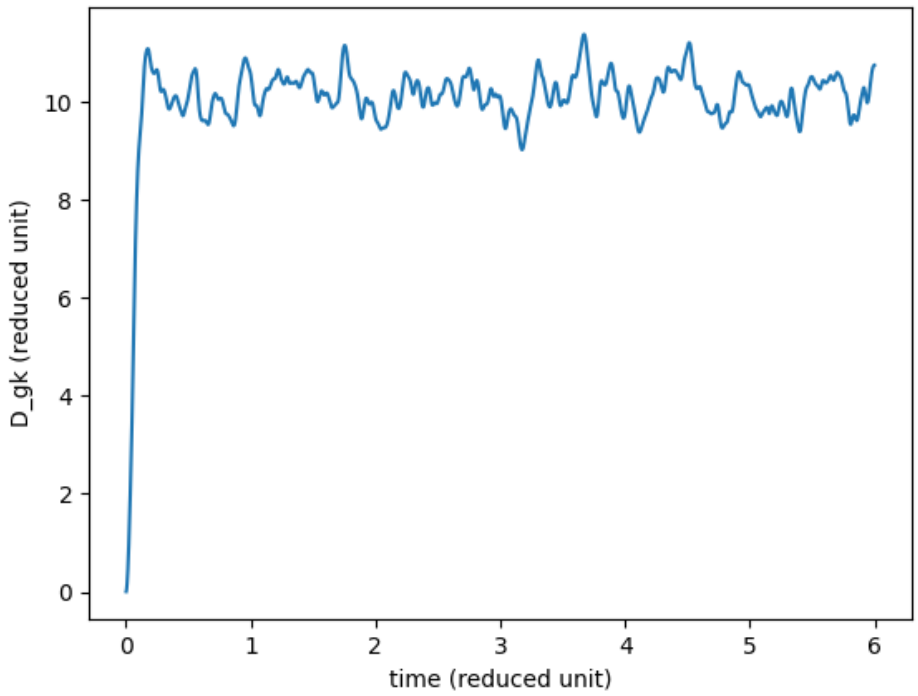

Figure 6: The D gotten from Green-Kubo relationship(in reduced unit)

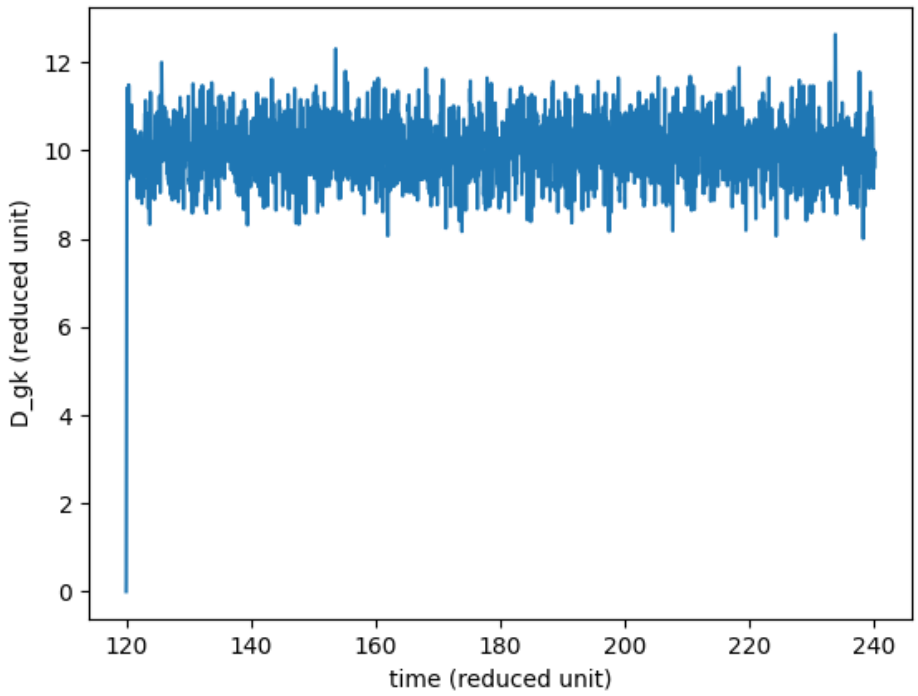

Figure 7: The D gotten from Green-Kubo relationship(in reduced unit). Have run a long time.

You can see that the D driven from Green-Kubo equation is

$$D \approx 10.06 \tag{11}$$

This two result is not consistent and the difference between them is pretty large. I have changed the T and found that the D got from Green-Kubo relationship always about 20 times bigger than the D got from the Einstein relationship. I also changed the number of cells in each coordinate but I found after $N_{cell} = 3$, there is no bigger change of the result. I could not found the reason.

And for the use of folded position? I think we need to use the position which is unfolded, because the Einstein relationship need the position change should be consistent. Only that could we get a consist result of the MSD.