

In brief, we are to calculate the diffusion constant in heterogeneous systems of two atom types with varying number fractions of each. The problem is straightforward, and the diffusion constant calculation is done in the same fashion as was done for Assignment 5, which dealt with the diffusion of water molecules. We have used the term ‘free diffusion’ to mean the absence of any external force or field affecting the system; the atoms still experience van der Waal’s interactions described by Lenard-Jones (LJ) potentials.

The tricky bit of the Problem was evaluating and depicting the phase space of the systems. The simulations had to be redone to output position and velocity data only for selective frames due to the inability of our laptops to extract data from the huge ensuing .dump files. Because of this, the visualizations in VMD did not offer any particular insights, and hence this report does not mention trajectory visualization anywhere. The logic behind how the phase space was depicted is explained in the report under Section 2.

Data was processed in Python3. Plots were made using Matplotlib (Python3) or MS PowerPoint.

Section 1: System descriptions

The systems are defined according to the following table:

| System | Number fraction of type 1 | Number of atoms of type 1 | Number fraction of type 2 | Number of atoms of type 1 |
|--------|---------------------------|---------------------------|---------------------------|---------------------------|
| 1 | 0.0 | 0 | 1.0 | 13125 |
| 2 | 0.2 | 2625 | 0.8 | 10500 |
| 3 | 0.4 | 5250 | 0.6 | 7875 |
| 4 | 0.6 | 7875 | 0.4 | 5250 |
| 5 | 0.8 | 10500 | 0.2 | 2625 |
| 6 | 1.0 | 13125 | 0.0 | 0 |

Common to all systems is the box size (25 x 25 x 25 units) and the number fraction 0.84, which corresponds to a total number of 13125 atoms inside 1 box.

The given Problem involves calculating the diffusion constants for the two atom types. Specifically, in all systems D_1 is to be calculated except System 1, in which case D_2 is instead reported. This distinction arises from the `compute msd` procedure performed by LAMMPS, wherein D_1 will correspond to the MSD (mean square displacement, $\langle r^2 \rangle$) of type 1 atoms and D_2 similarly for type 2 atoms. The diffusion constant D_i can be evaluated as follows:

$$D_i = \frac{1}{6} \frac{\partial \langle r^2 \rangle_i}{\partial t}$$

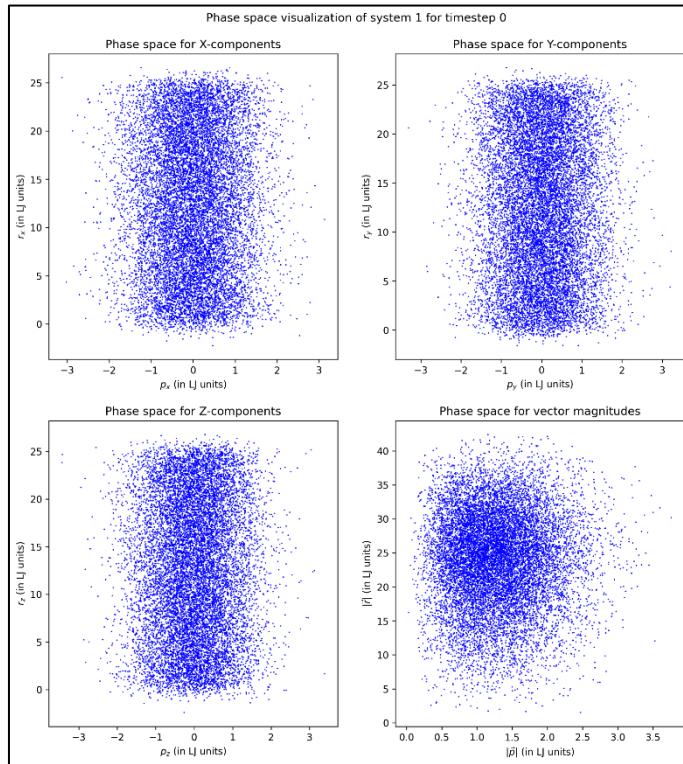
where the term on the right is the slope of the line best fitting the MSD data.

However, before we get to the diffusion constants, we need to represent the systems through their phase spaces. This is slightly tricky, since the system evolves over time, so a better descriptive graph would be a plot including the time evolution. Due to a lack of computational power, we have only included plots corresponding to specific timesteps; even then, the scripts take a non-trivial amount of time to process the data. For each selected frame, 4 plots are generated: x vs p_x , y vs p_y , z vs p_z and $|\vec{r}|$ vs $|\vec{p}|$. Ideally, each of these would be 3D plots where the third axis would be time.

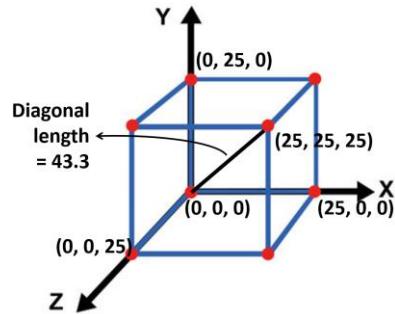
Section 3: Phase space plots

A standard color code has been followed for all plots: type 1 atoms have been colored red while type 2 atoms have been colored blue.

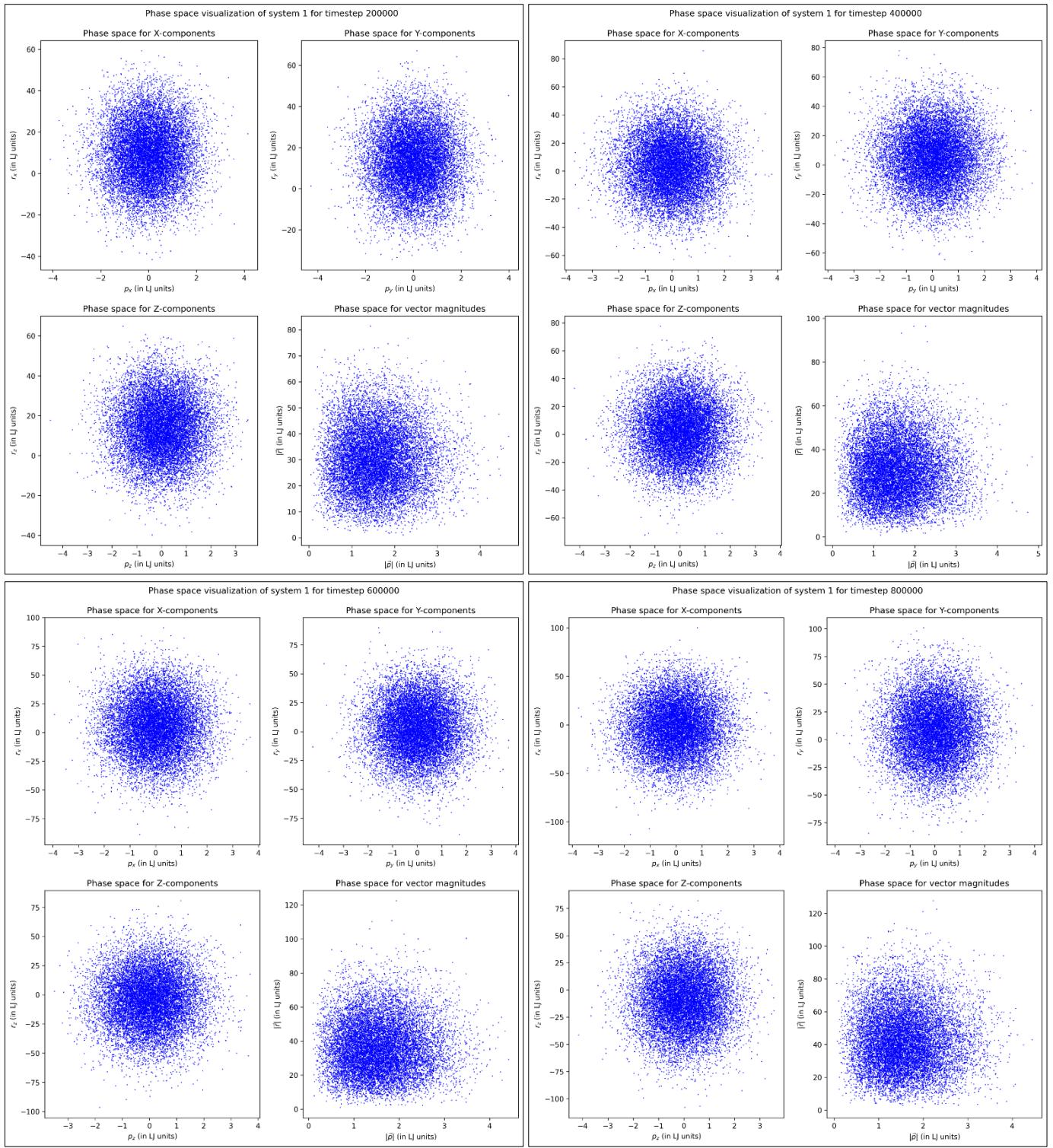
System 1 ($n_1 = 0.0, n_2 = 1.0$)

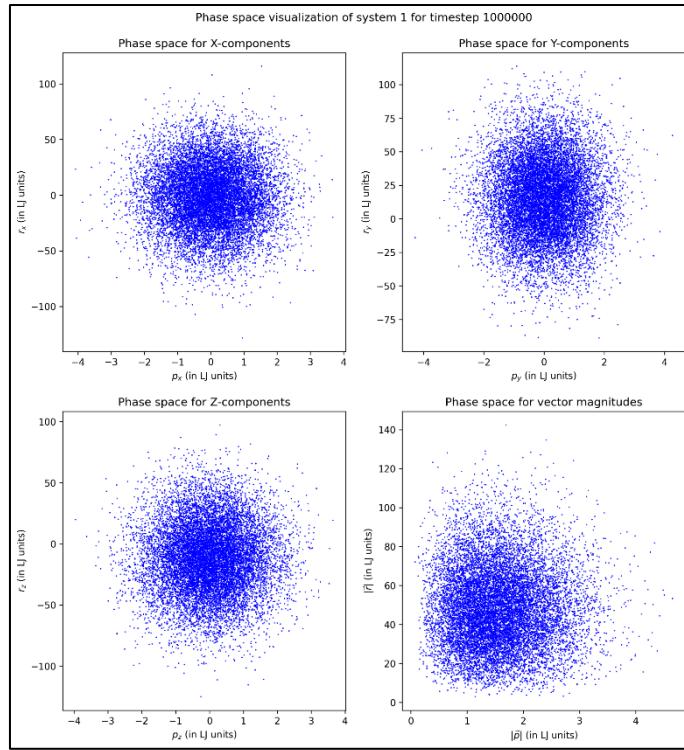


At the start of the simulation, we see that the ‘spread’ along momentum is consistent with our expectations from a Maxwell velocity distribution centred around $p_i = 0$ for $i = x, y, z$. The net momentum magnitude looks skewed but we emphasize that only the magnitude has been taken. There seems to be a uniform spread across the position axis – this too is consistent with our expectations of the atoms being positioned randomly within the box post-minimization and equilibration. It might be helpful to illustrate how our coordinate system is defined, so the fourth subplot above makes sense:



According to our coordinate axes, the maximum distance can be ~ 43.3 units. This corresponds with what we see in the 4th subplot. The distribution seems to be centred about $|\vec{r}| \sim 24-25$; this is near the midpoint of the diagonal, so this makes sense as well. We can now say that our system has been established correctly, and safely move on to the analysis of the production run.





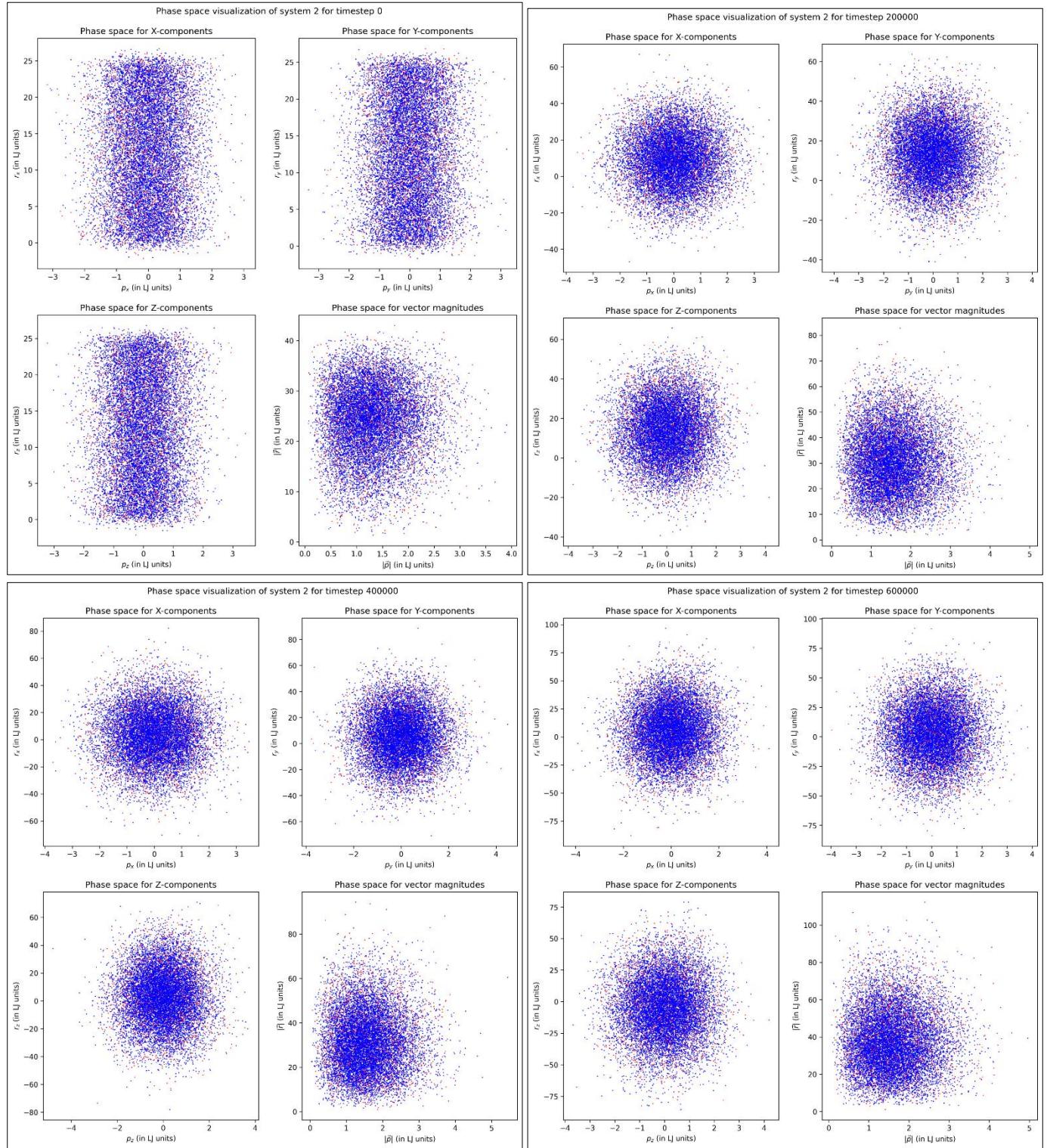
As the simulation progresses, the i vs p_i plots take on a 2D-radial distribution. There are a few key features here:

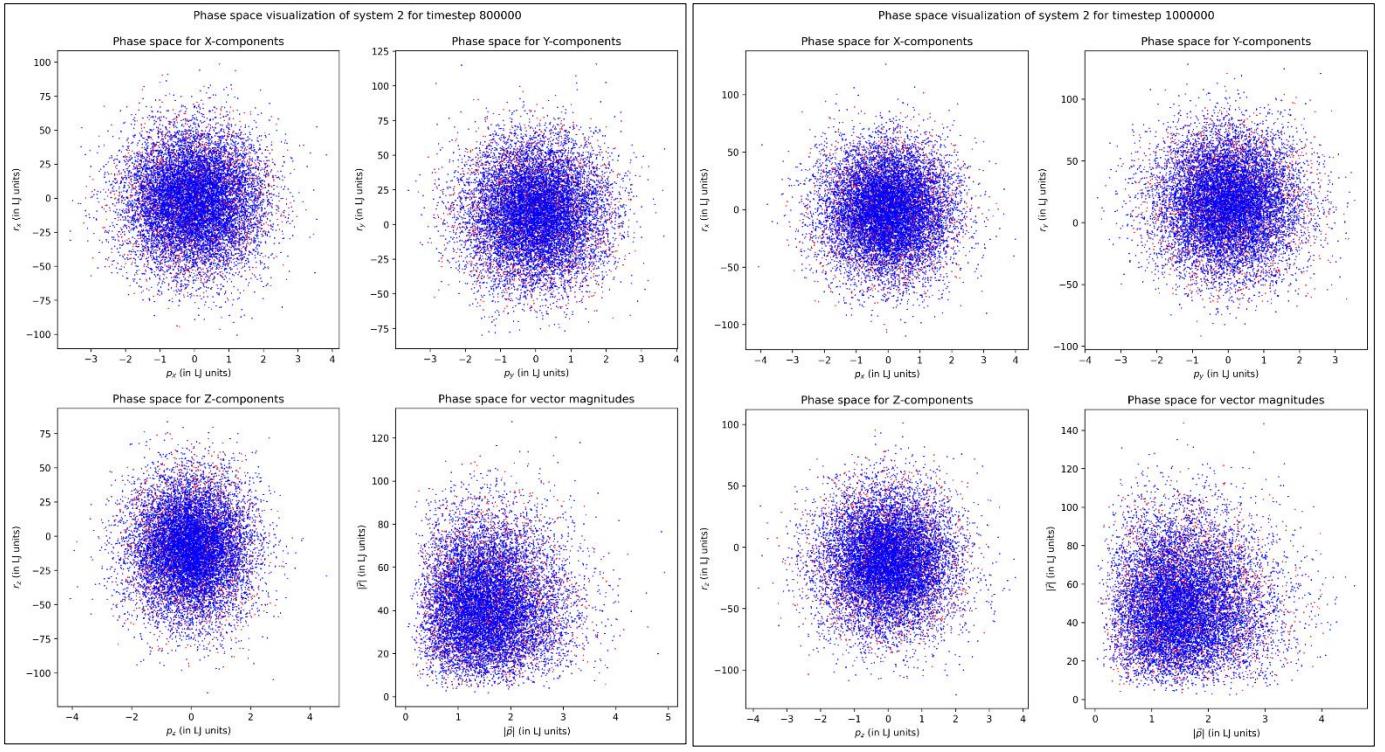
1. The distribution is centred on $(0, 0)$ i.e. there is no system bias with respect to position or velocity. This is consistent with our simulation of freely diffusing particles.
2. From timestep = 0 to timestep = 200,000, the position distribution changes from being uniform along $(0, 25)$ to a normal-like distribution from $(-40, 60)$. This is because the particles now begin to diffuse radially outwards, so negative values of position are allowed.
3. The position axis grows larger as simulation time increases. Since our particles diffuse primarily outwards over time, this is also expected.
4. Velocity distribution remains centred along $p_i = 0$, which is expected for free diffusion.

In one line, we can say that the phase space is changing from a normal distribution uniform along the position axis to a 2D normal distribution – and this is what we expect.

Now we will look at corresponding plots for systems where atom 1 is also in the picture. The common characteristics listed above will not be reiterated.

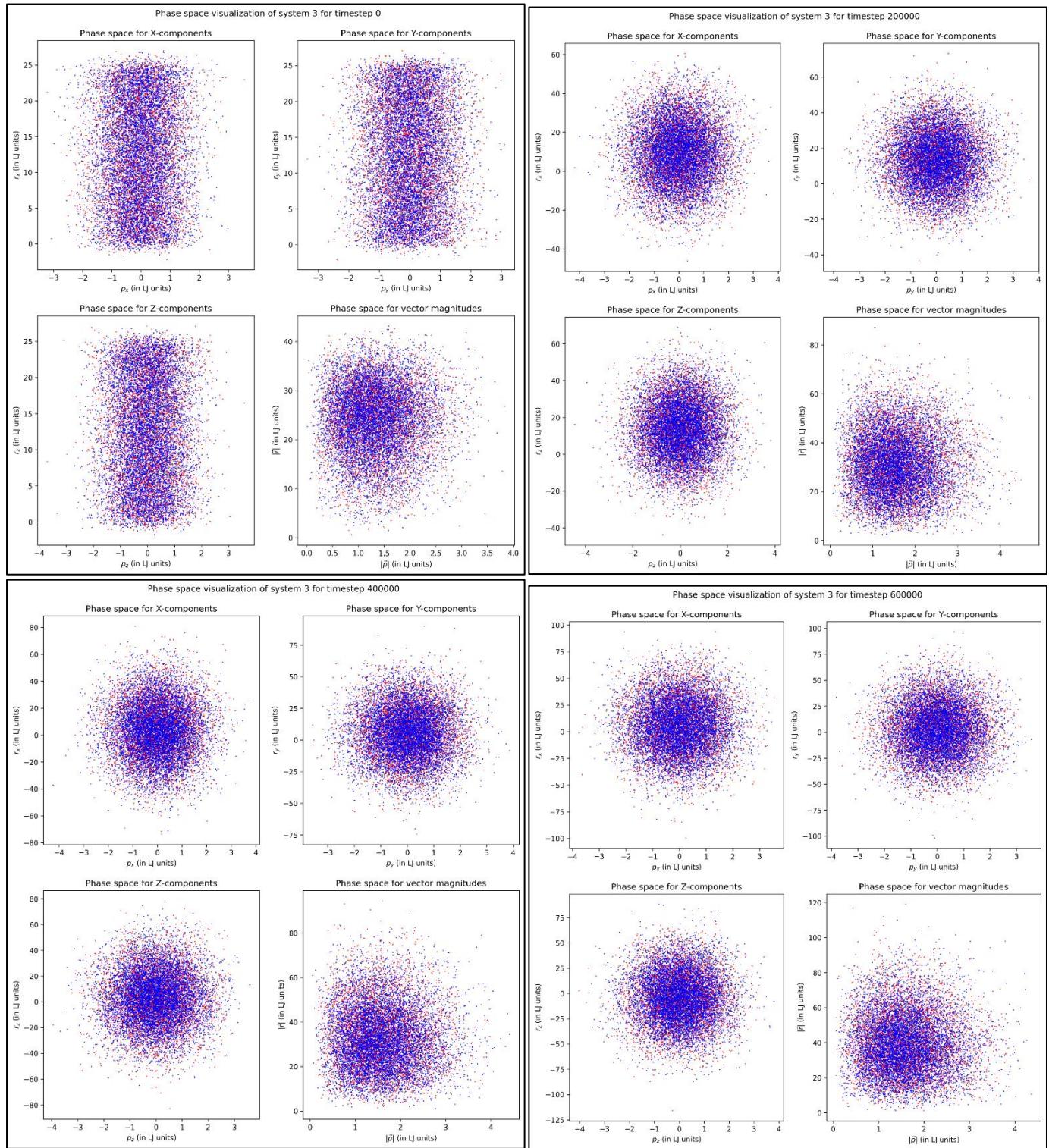
System 2 ($n_1 = 0.2, n_2 = 0.8$)

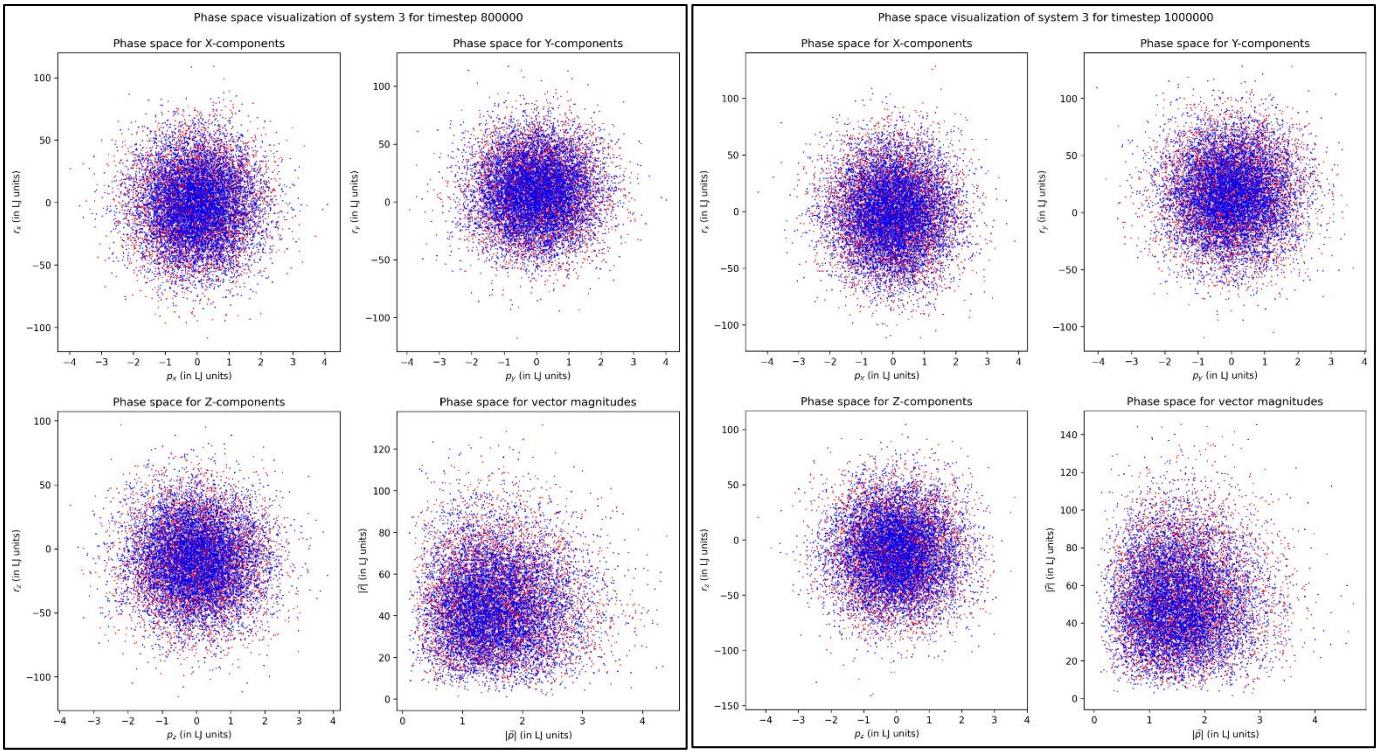




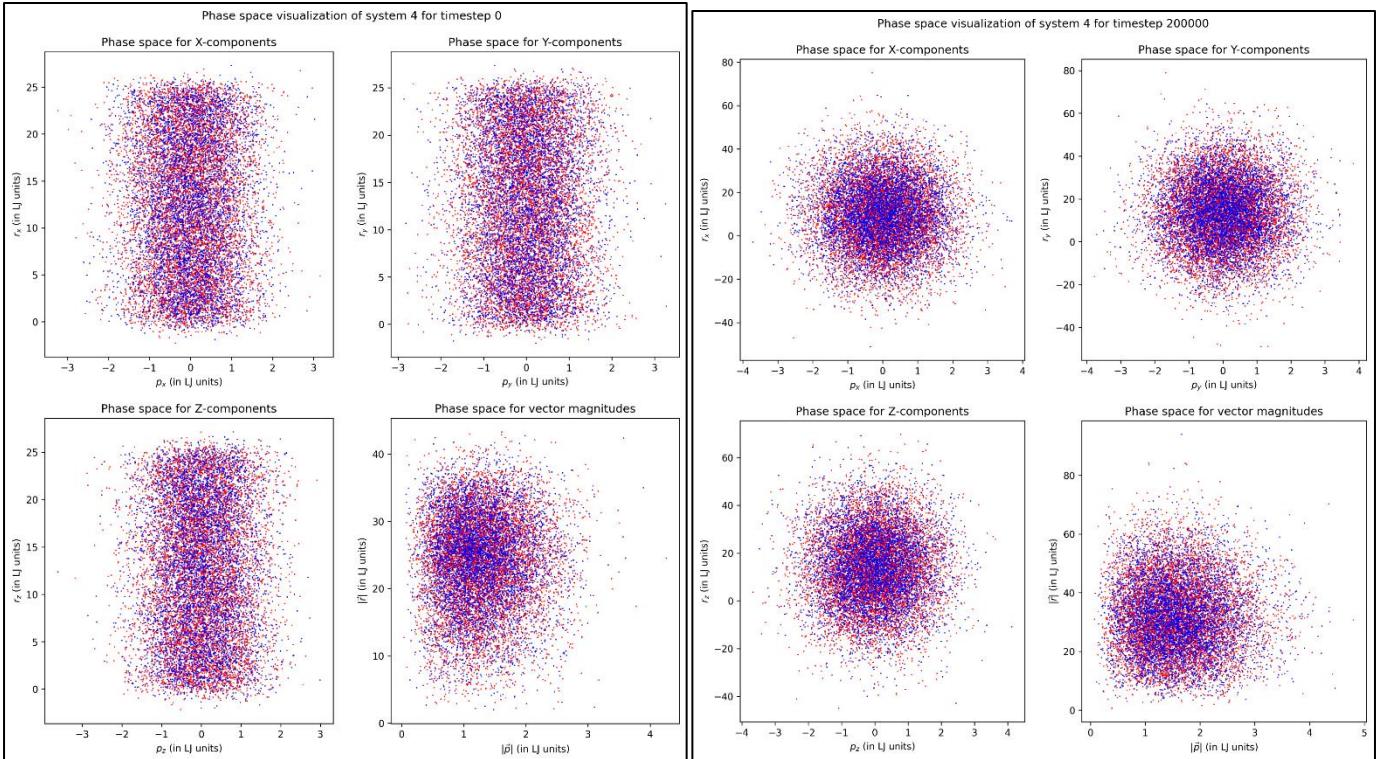
Since atom 2 is the majority, the blue dots seem to mask the red dots. However, on closer inspection, the distributions for each of the atoms share the common features pointed out for System 1.

System 3 ($n_1 = 0.4, n_2 = 0.6$)

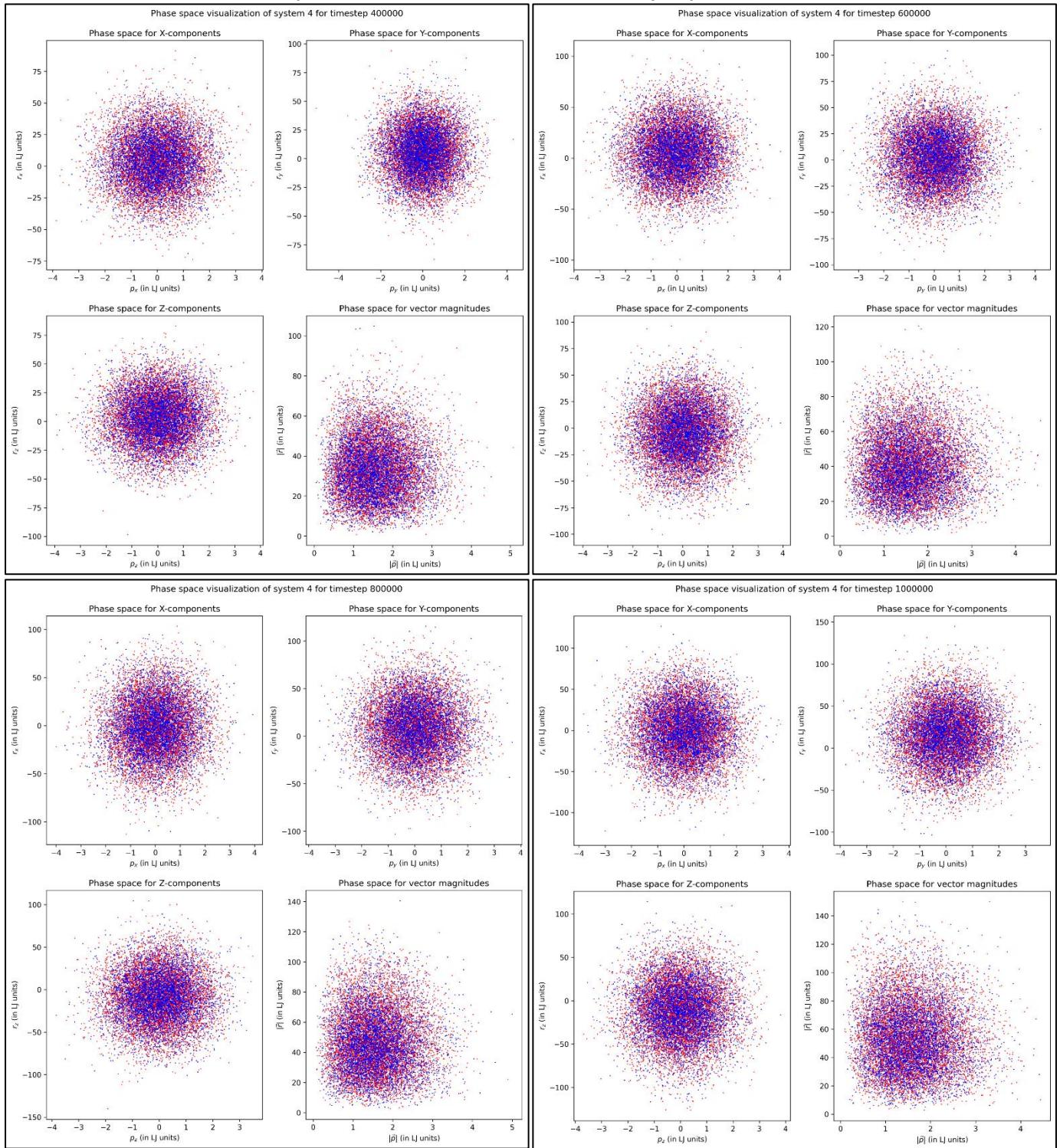




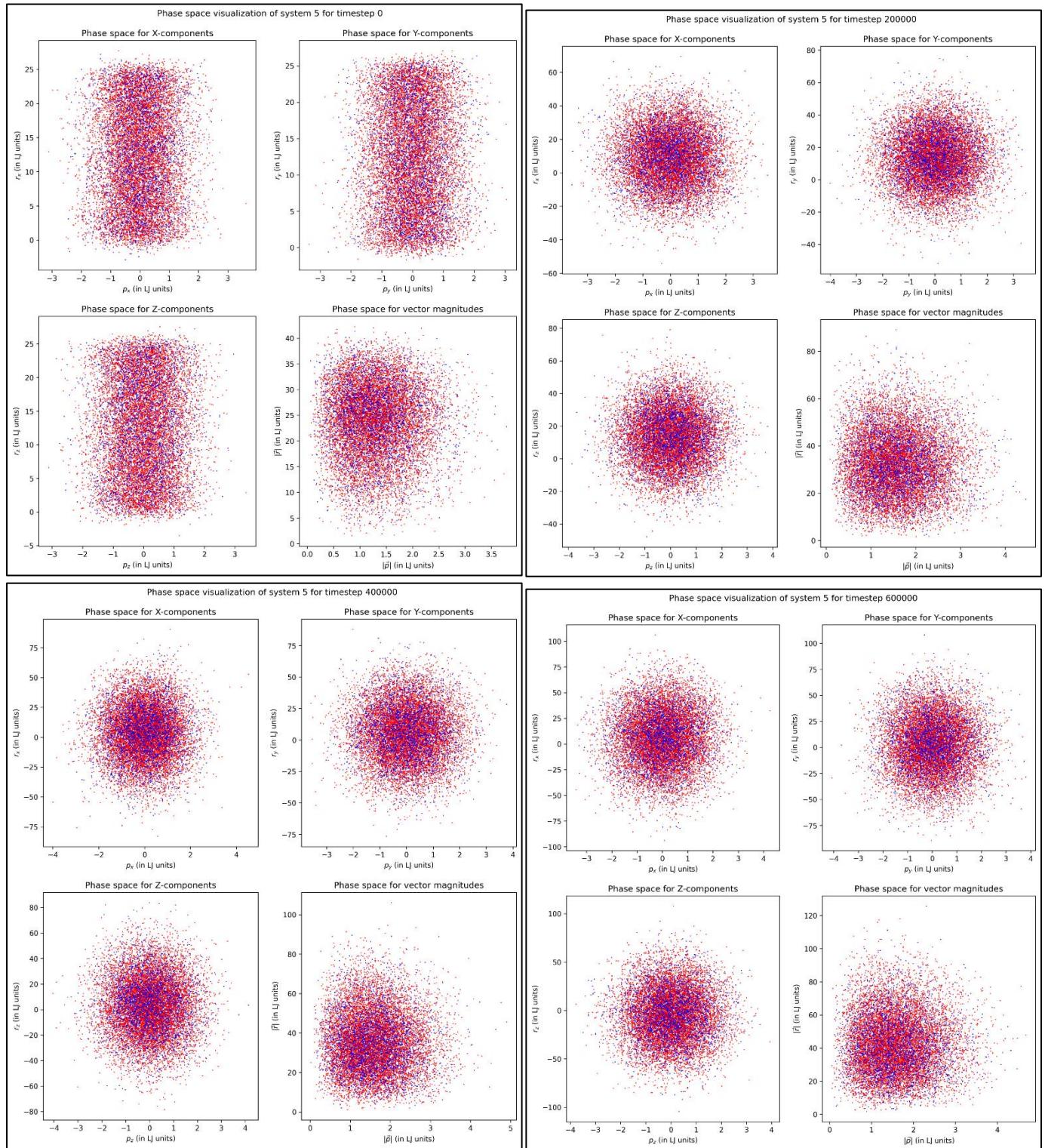
System 4 ($n_1 = 0.6, n_2 = 0.4$)

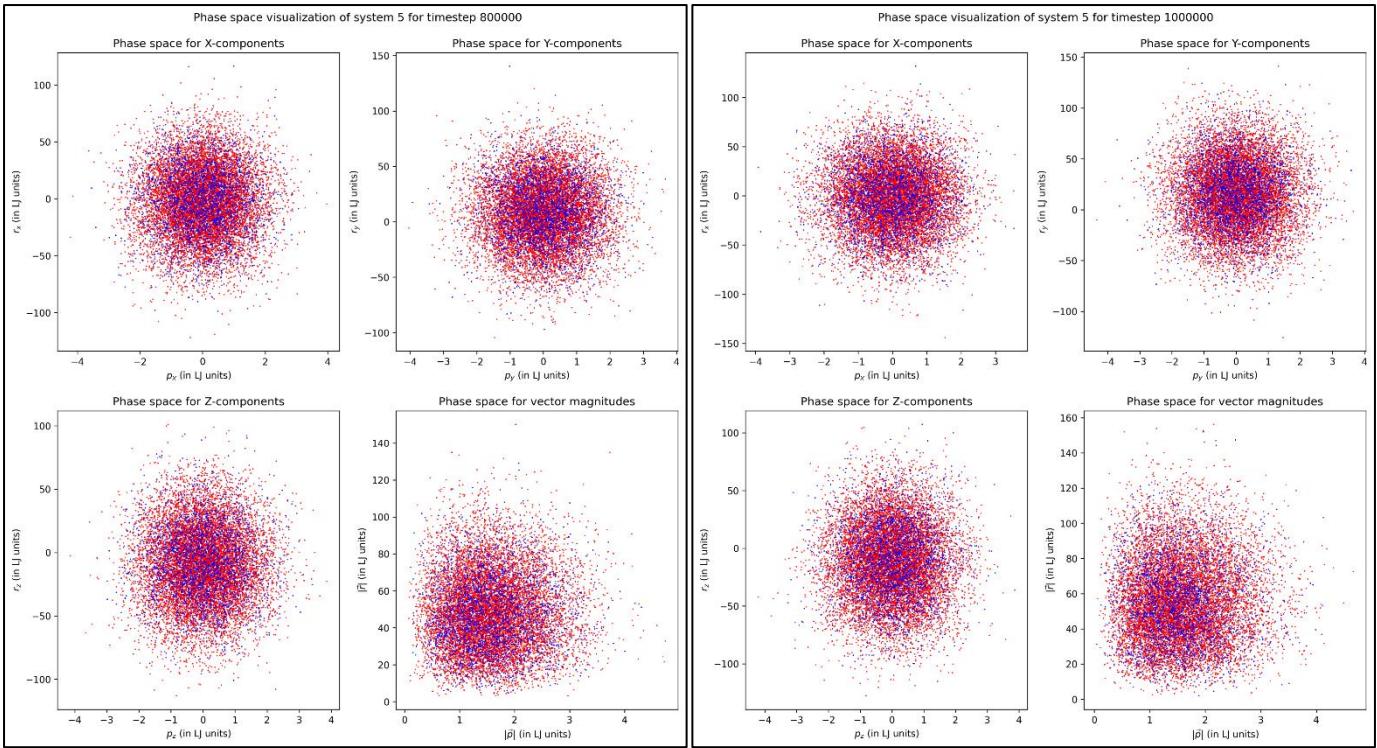


Now, we can see a dominantly 'red' plot since atom 1 is in the majority.

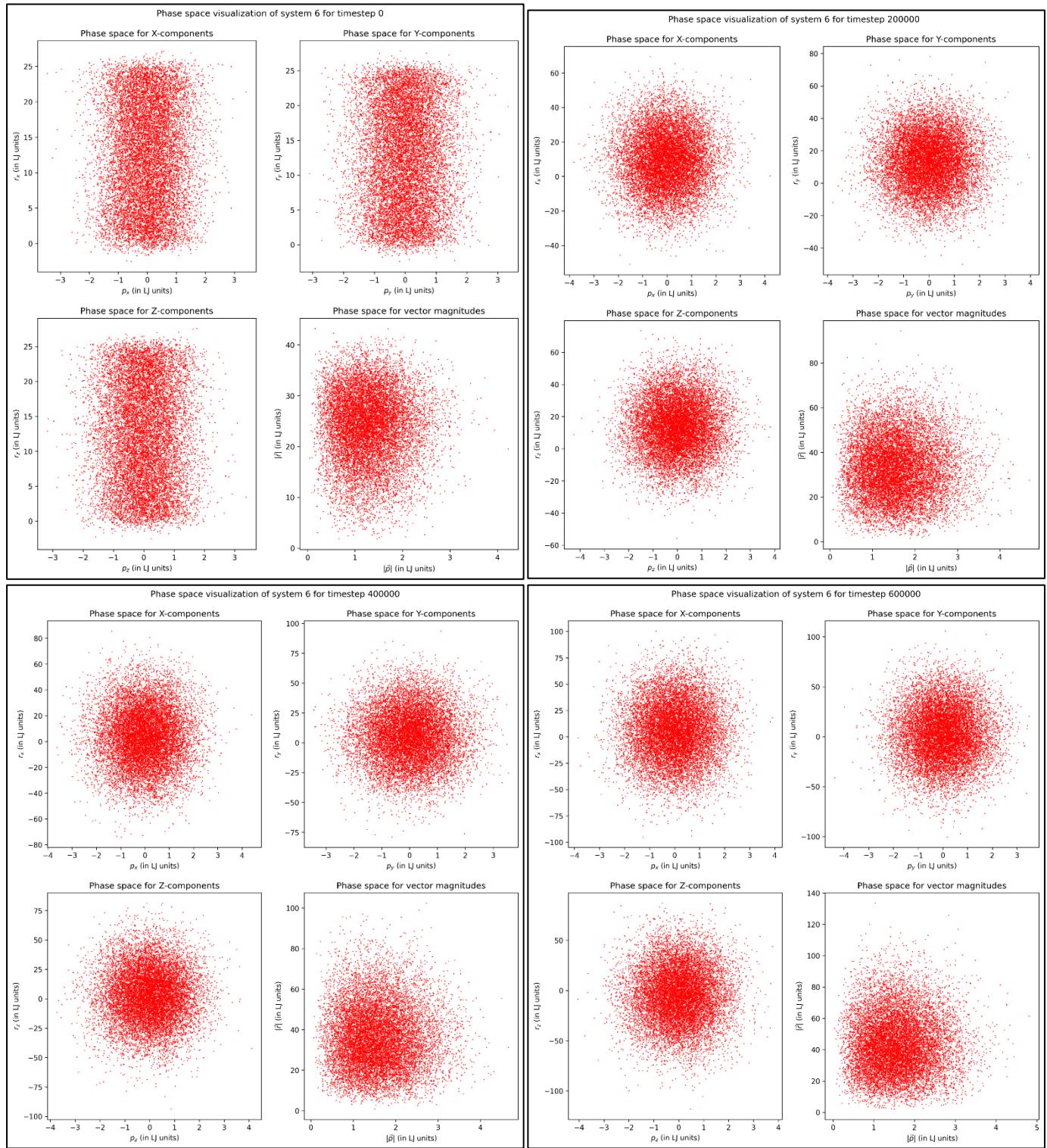


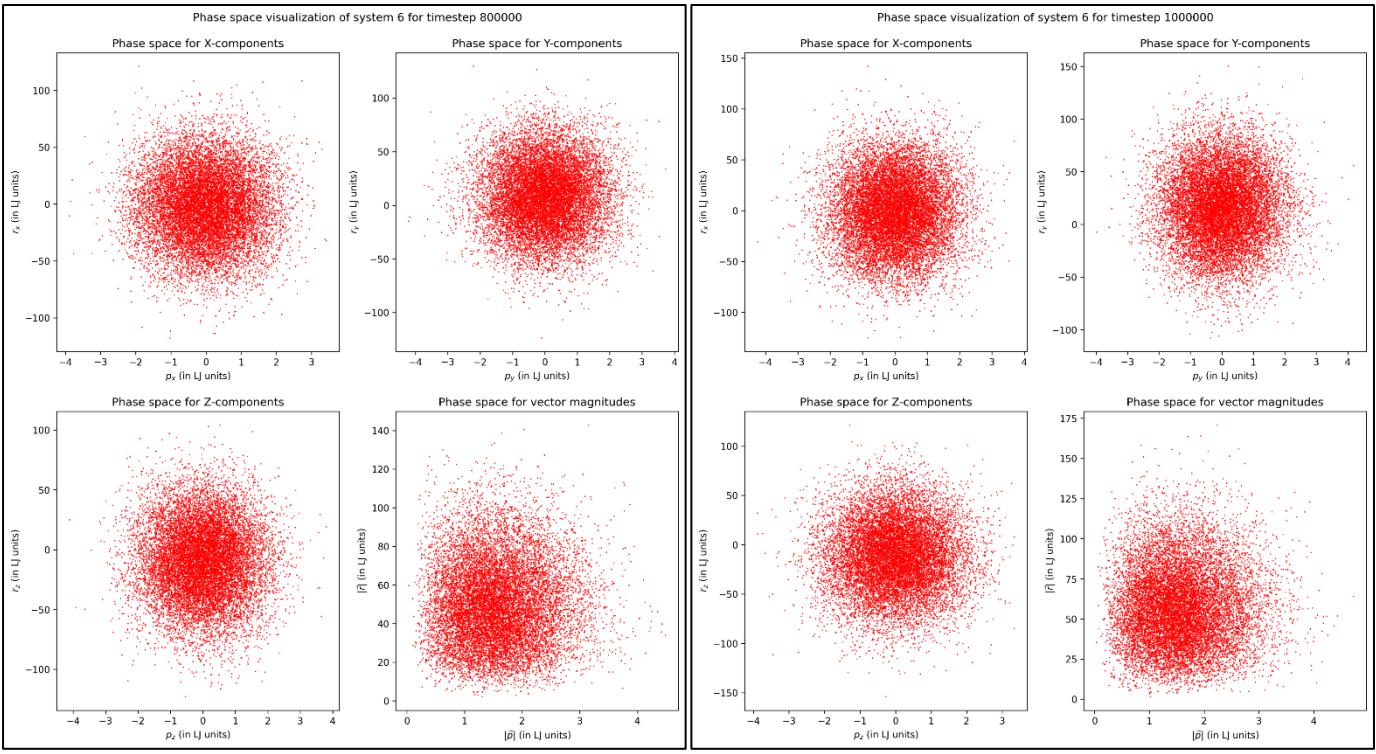
System 5 ($n_1 = 0.8, n_2 = 0.2$)



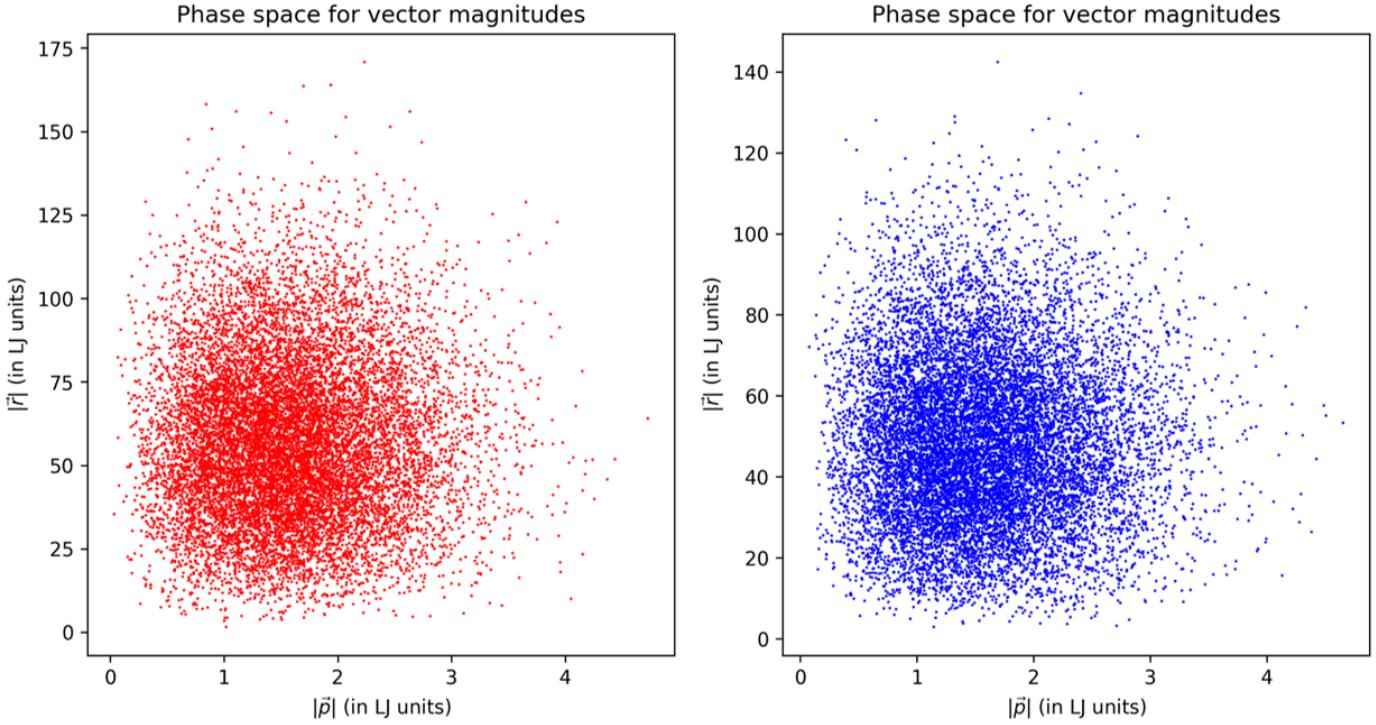


System 6 ($n_1 = 1.0, n_2 = 0.0$)





To visualize how differently atoms 1 and 2 behave, I have used the 4th subplot of each at the 1,000,000th timestep as representative images:



Here, we see that atoms 1 seem to diffuse a further distance than atoms 2. From their LJ potential parameters, we know that there is a stronger interatomic interaction between type 2 atoms than type 1 atoms. This might limit the distance moved by type 2 atoms, as a larger separation (when compared to the distance at the potential minimum) is energetically less favorable. This will impact the diffusion constant as well: we hence expect that type 1 atoms will have a higher diffusion constant than type 2 atoms in homogeneous systems. The value of D_1 in heterogeneous systems might be in-between the two values of $D_{1,homogeneous}$ and $D_{2,homogeneous}$. Section 4 covers this aspect.

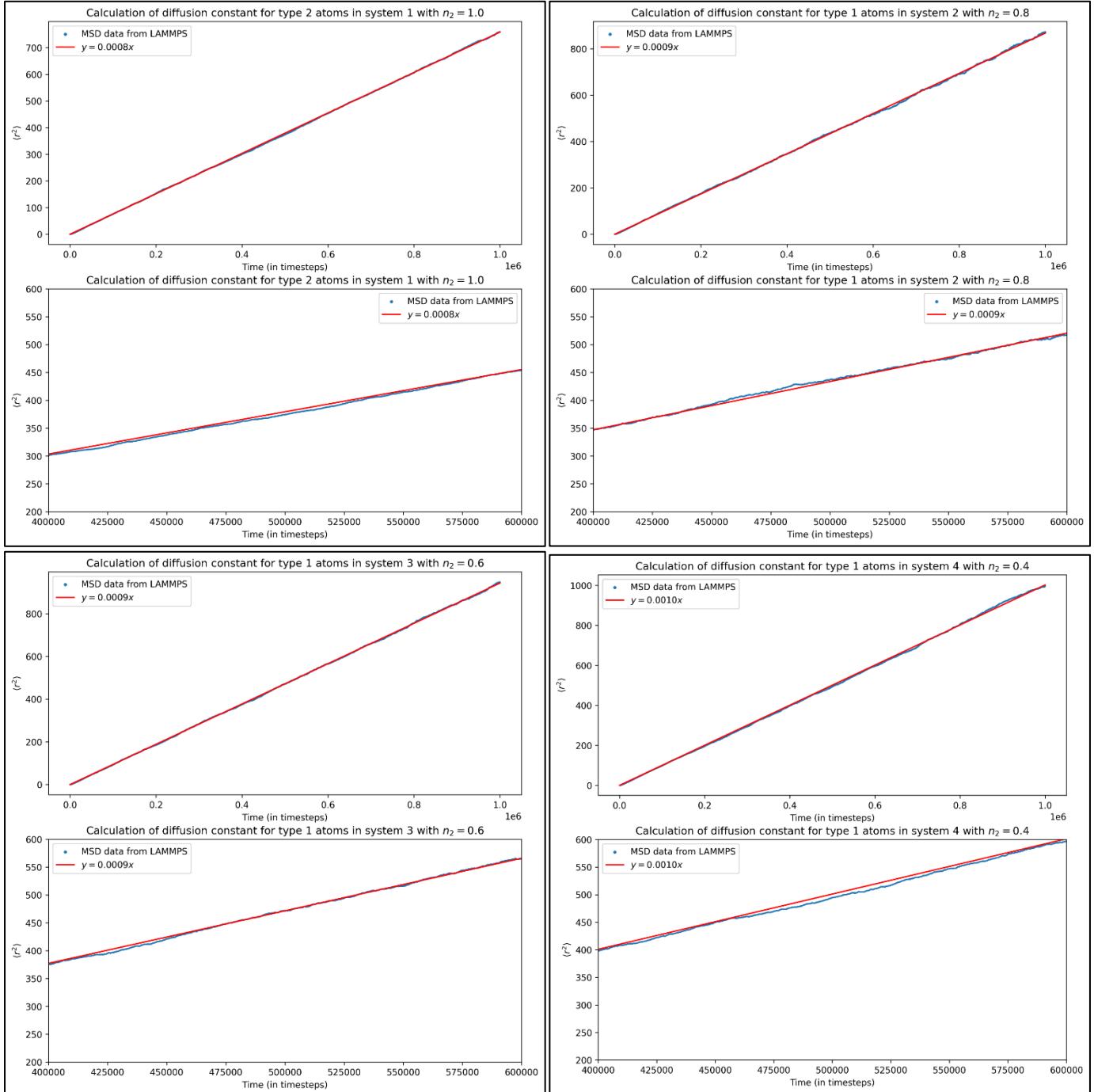
Section 4: Diffusion constant plots

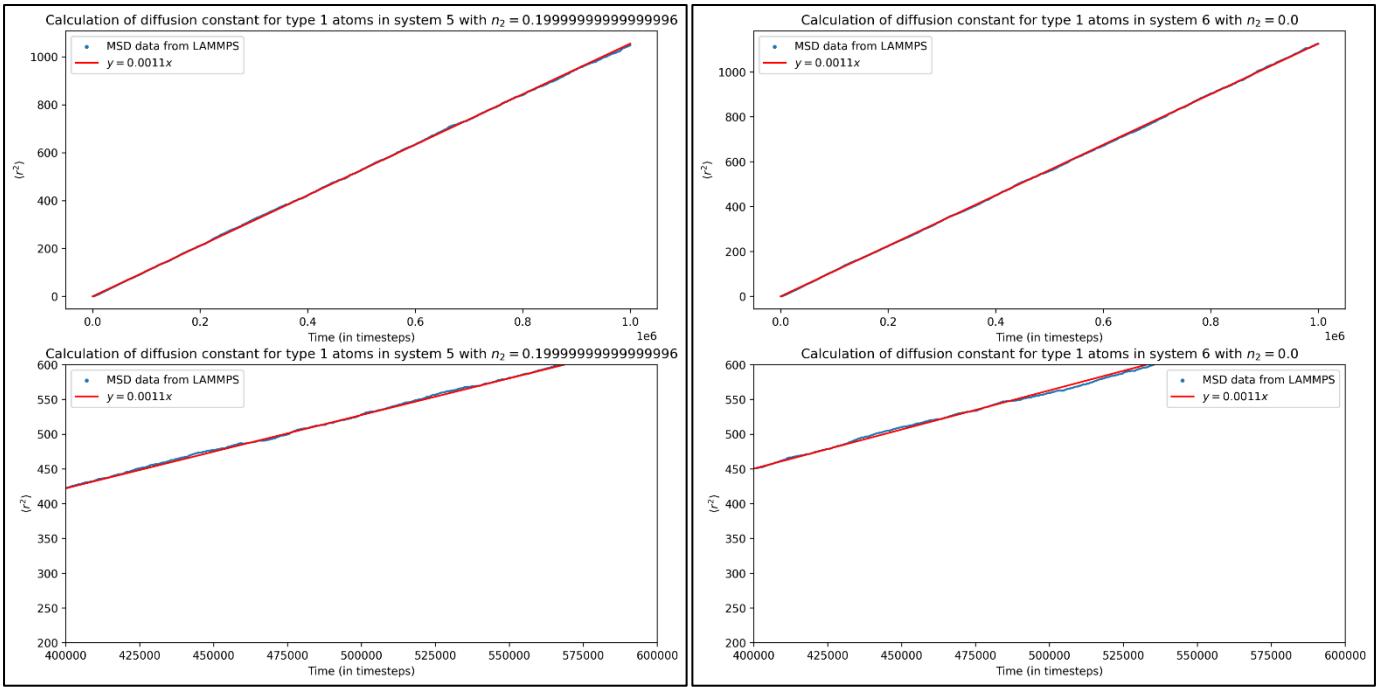
To reiterate the procedure explained in Section 1, the MSD data as outputted from LAMMPS is taken and plotted against time. A linear fit of profile $y = mx$ was calculated. The slope m of the curve relates to the diffusion constant as:

$$D_i = \frac{m_i \text{ (in units of length}^2 \text{ timestep}^{-1})}{6} = \frac{100 \times m_i \text{ (in units of length}^2 \text{ time}^{-1})}{6}$$

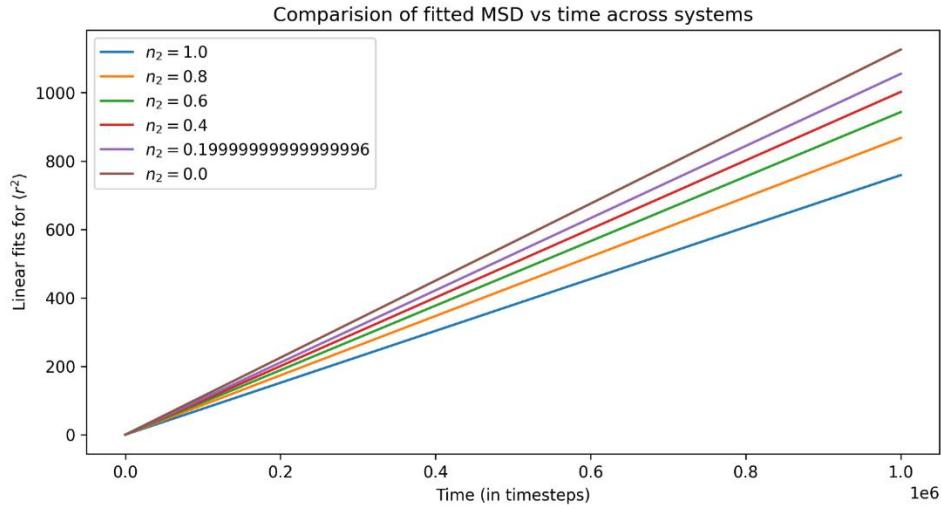
The following plots include a plot over the entire simulation time and a zoomed-in section to illustrate how the data actually looks (since the complete plot obscures the data points slightly).

One can point out that, for $n_2 = 0.2$, we see a value with multiple decimals instead of a nice round figure. This is unimportant and is only a visual bug due to Python.

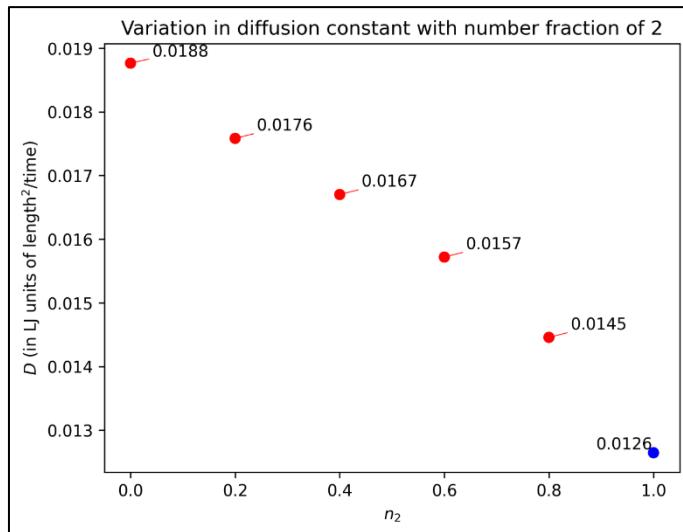




I have also included a combined plot of all linear fits for a direct comparison:



Finally, after calculating the diffusion constant as mentioned above, we can make the following plot:



Here, as we hypothesized earlier, the diffusion constant of type 1 atoms is higher than that of type 2. It is important to note that the values of diffusion constant are for type 1 atoms except for the case of $n_2 = 1.0$, and this is illustrated by the same color coding as for the phase space plots.

To summarize:

| System | n_1 | n_2 | Diffusion constant of type 1 atoms |
|--------|-------|-------|------------------------------------|
| 1 | 0.0 | 1.0 | 0.0126 (type 2) |
| 2 | 0.2 | 0.8 | 0.0145 |
| 3 | 0.4 | 0.6 | 0.0157 |
| 4 | 0.6 | 0.4 | 0.0167 |
| 5 | 0.8 | 0.2 | 0.0176 |
| 6 | 1.0 | 0.0 | 0.0188 |

It seems as if D_i varies linearly with n_i . For a heterogeneous mixture, the diffusion constant is a function of the partition function, which relates to the number fraction. So this observation is supported by theory as well.