
Evaluating Diffusion Coefficients in LAMMPS

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TCCM
2024

1 MSD plot and D_{self}

The self-diffusion coefficient D_{self} can be calculated from the slope of the mean squared displacement (MSD) plot as per the equation:

$$D_{self} = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle |r_{i,\alpha}(t + \tau) - r_{i,\alpha}(t)|^2 \rangle}{\tau}$$

For the calculation, we use the linear fit of the MSD plot where the slope represents $2d \times D_{self}$, given that d is the dimensionality of the system. Thus, for a 2-dimensional system, the self-diffusion coefficient D_{self} is calculated from the slope of the linear fit as:

$$D_{self} = \frac{\text{slope}}{2 \times 2}$$

Since we have already determined the slope of the MSD plot (1.28), we can use that value to calculate D_{self} directly. Let's proceed with this calculation. The self-diffusion coefficient D_{self} calculated from the slope of the mean squared displacement (MSD) plot is approximately 0.32, using the provided equation for a two-dimensional system.

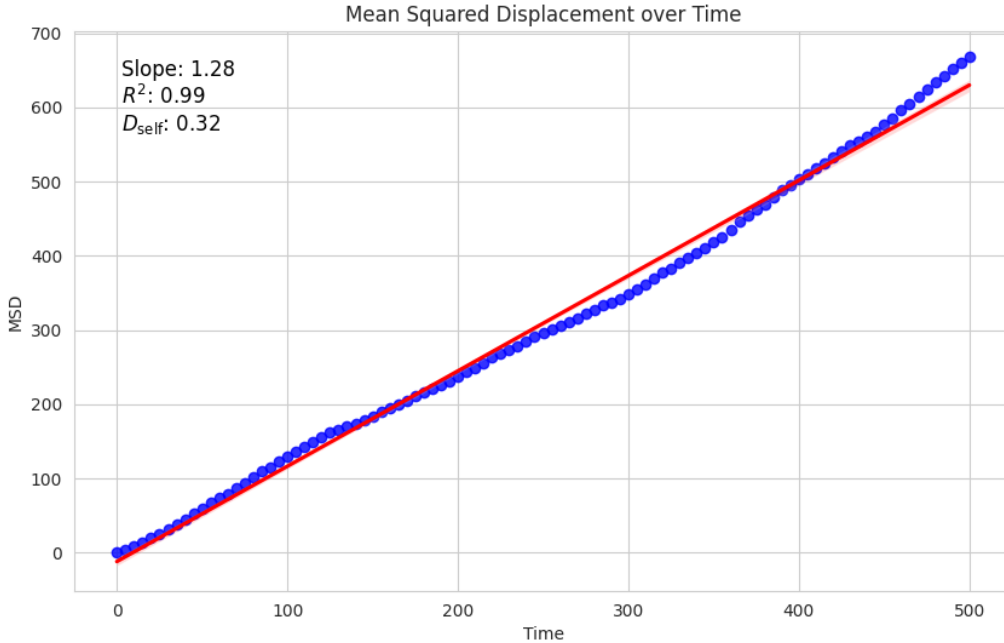


Figure 1: MSD vs Timestep

This plot is linear, which is proved by the value of $R^2 > 0.99$. The calculated D_{self} is the same with what was obtained in the output (`v_fitslope`, last value =

0.32053858). The value from README is 0.36, which is a bit higher, but still close.

2 No equilibration MSD calculation

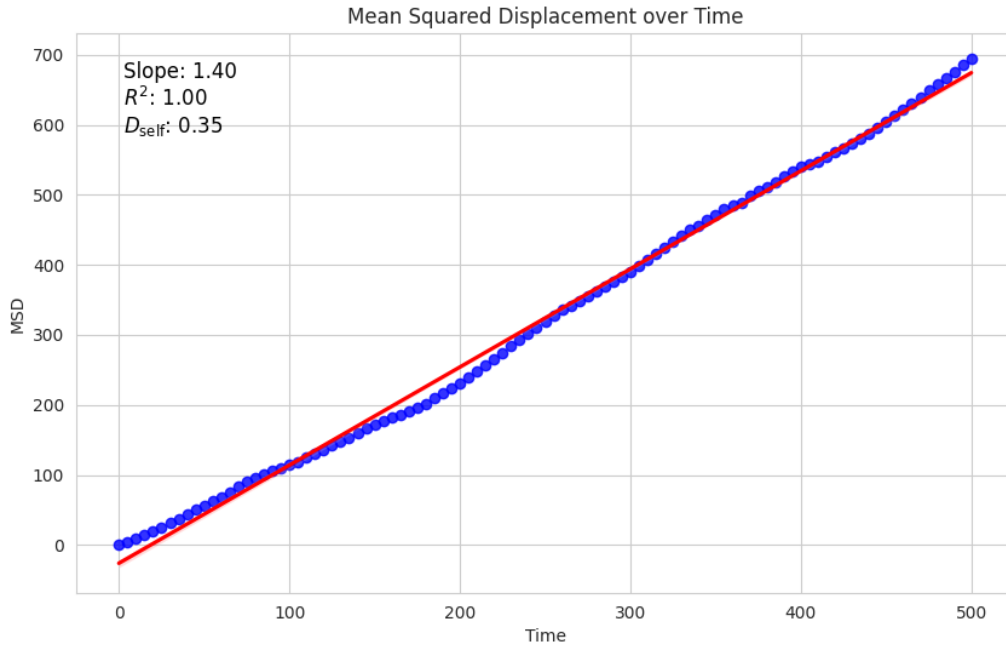


Figure 2: MSD vs Timestep without equilibration (run = 1)

$$D_{self} = 0.35$$

More or less the obtained value is close to the previous with equilibration, but slightly higher. The plot is still linear. This value is closer to that one which was written in the README file.

3 VACF

The other way to obtain the D_{self} value is by integrating the velocity auto-correlation function (VACF):

$$D_{self} = \frac{1}{d} \langle v_{i,\alpha}(t + \tau) v_{i,\alpha}(t) \rangle d\tau$$

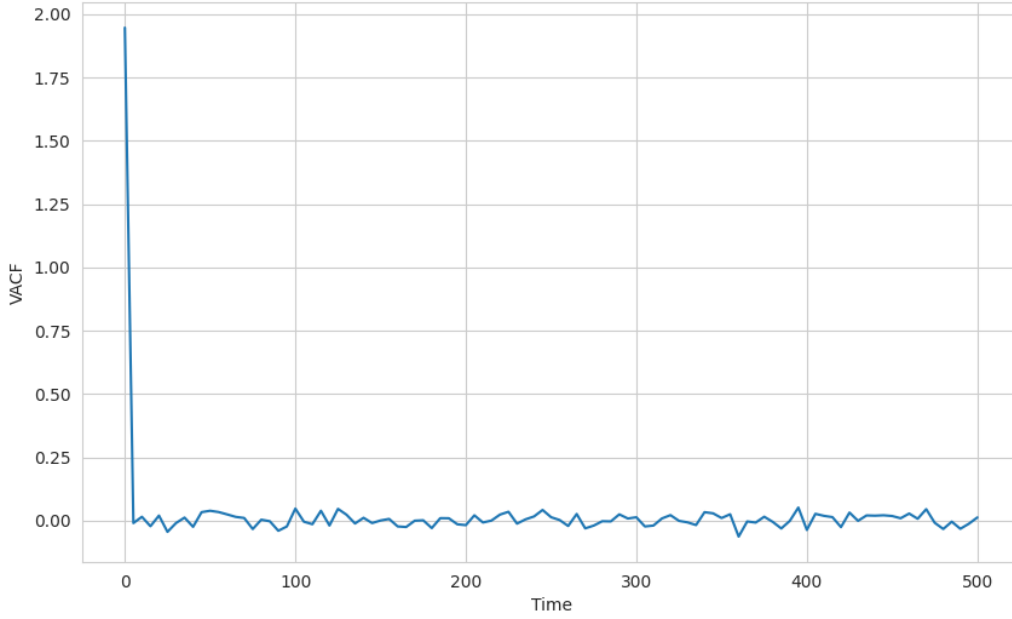


Figure 3: VACF over time

The plot 3 represents the VACF. It is converged, The values fluctuate between -0.05 and 0.05.

In the LAMMPS example input, the 4th column is the time-integration of the VACF (for every timestep), integrated up to that point in time, converted into the diffusion coefficient.

Without changing the input file, I got the following result in the fig. 4-5.

Obviously, it is not converged and taking the mean value is pointless. To get things better, I changed the timestep to 0.0001 and increased the run time.

In general, we can't assert that reducing the timestep and increasing the runtime have significantly aided in achieving convergence. However, it's noteworthy that the self-diffusion coefficient, D_{self} , fluctuates around 0.30 between 1500 and 2900, with overall values ranging from 0.20 to 0.35. This is more specific than the initial range of 0.3 to 0.7. The choice of the microcanonical ensemble, which generally poses more challenges in achieving convergence compared to the canonical ensemble, might partially attribute to this pattern.

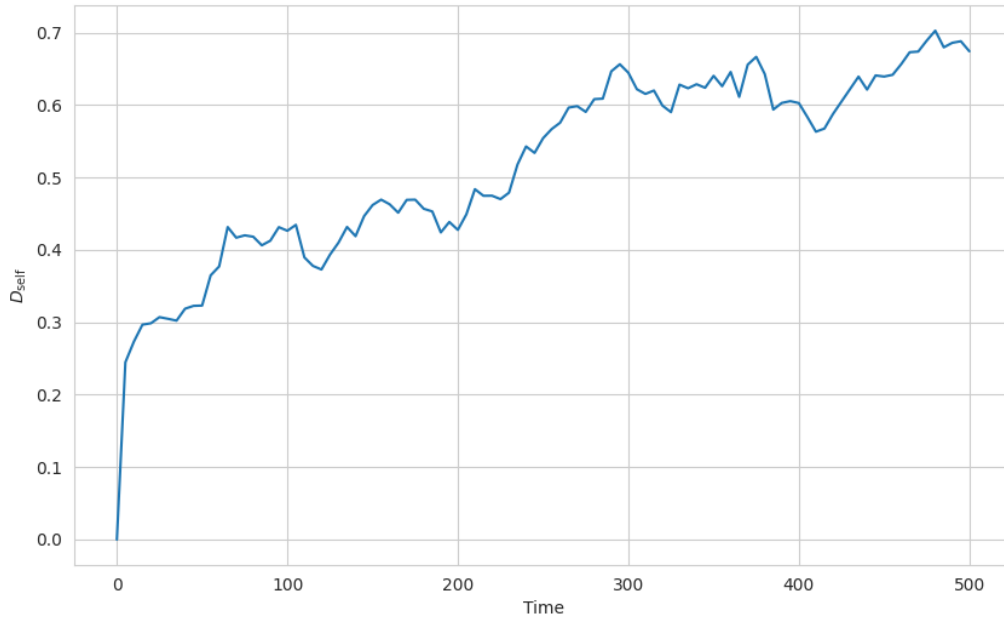


Figure 4: D_{self} derived from the VACF with the initial input parameters

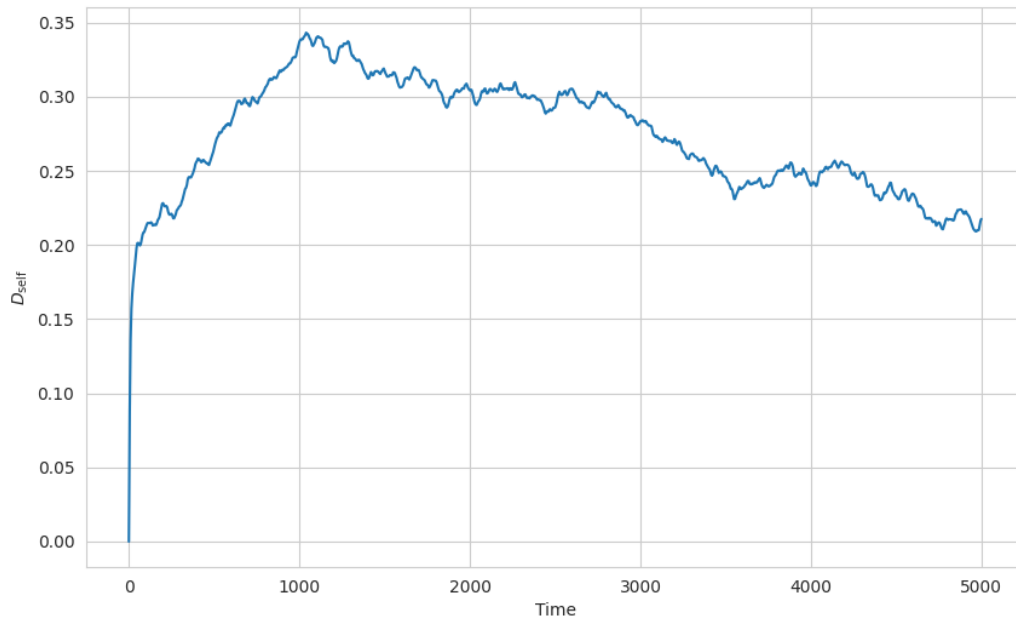


Figure 5: D_{self} derived from the VACF with timestep = 0.0001 and increased run

In a very rough approximation, these values are close to what was obtained with the MSD method, but the data obtained is much noisier.

4 Increasing the box size

With increasing box size, D_{self} slightly decreased from 0.32 up to 0.30.

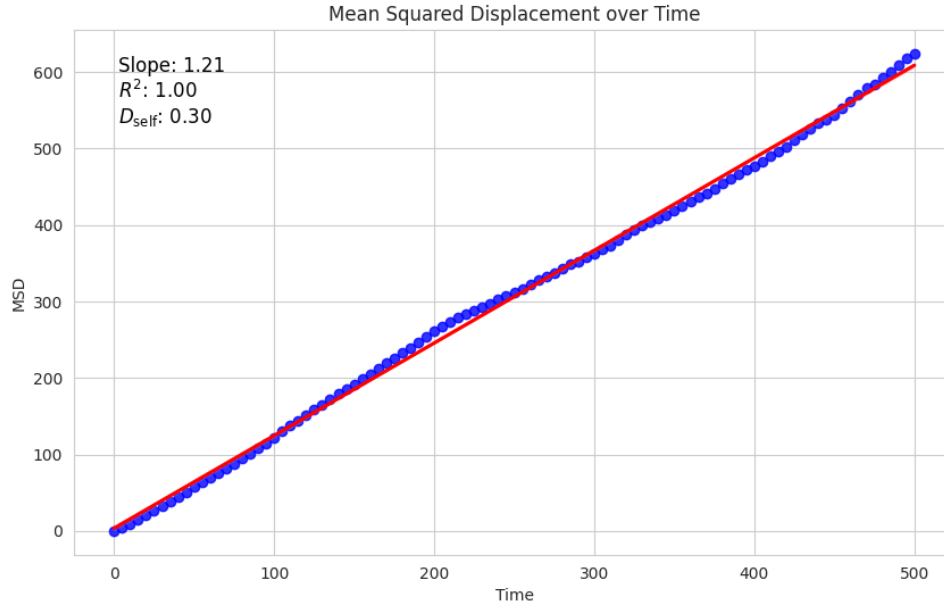


Figure 6: MSD vs Timestep with box size = 50

With the number of steps of the equilibration run increased to 10000, D_{self} increased to 0.39.

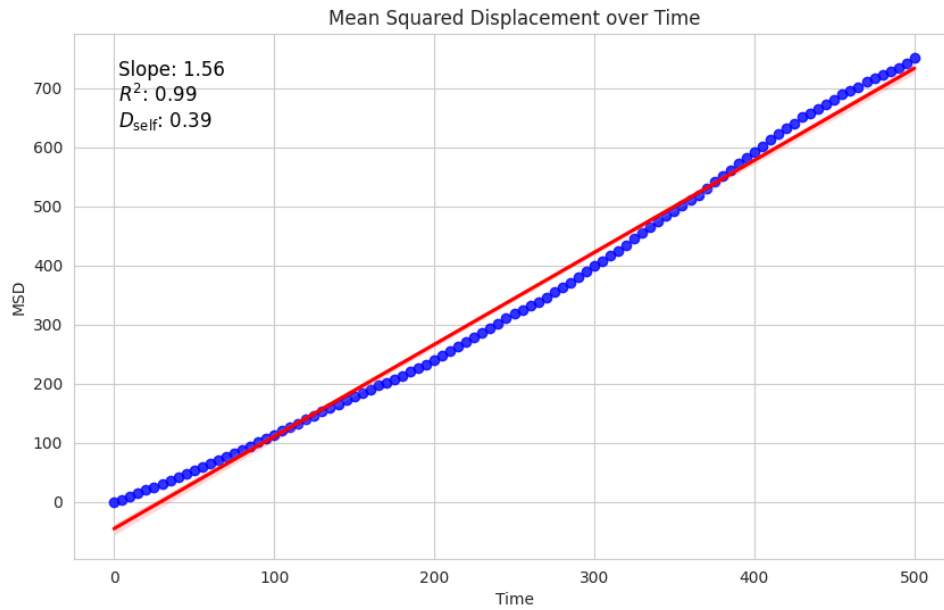


Figure 7: MSD vs Timestep with box size = 50, equilibration run = 10000

In principle, as the volume of the box increases and the number of particles remains constant, one should expect an increase in the self-diffusion coefficient, since the distance between particles increases and the self-diffusion process should be easier. In general, we observe this picture if we compare the results from question 1 and the calculation with a box of size 50 angstroms with an increased time of equilibration of runs. However, it is interesting that with fewer steps in the equilibrium run, the diffusion coefficient dropped slightly compared to the original calculations. I can assume that this is due to the fact that the system has not reached equilibrium. Although at the same time this will contradict the results obtained in the second question, where running calculations without equilibrium preliminary calculations gave a slightly higher value of the self-diffusion coefficient.

5 Increasing density

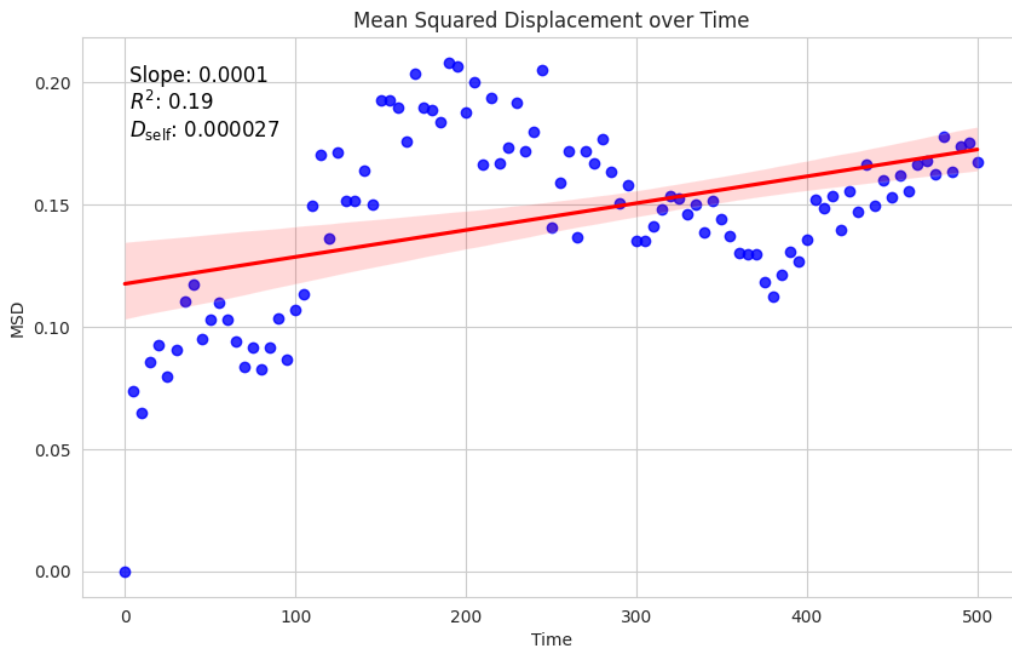


Figure 8: MSD vs Timestep with a density of 1 and a equilibration 100000 steps

The graph for calculations with increased density is not linear at all, and, in principle, it is impossible to calculate the self-diffusion coefficient from it. I would venture to suggest that a phase transition occurred, and therefore the value of the coefficient collapsed. According to the plot in the given pdf file (Figure 2. Phase diagram of the Lennard-Jones substance), we should observe a mixed phase solid+liquid, which aligns with the obtained result.

6 Decreasing temperature

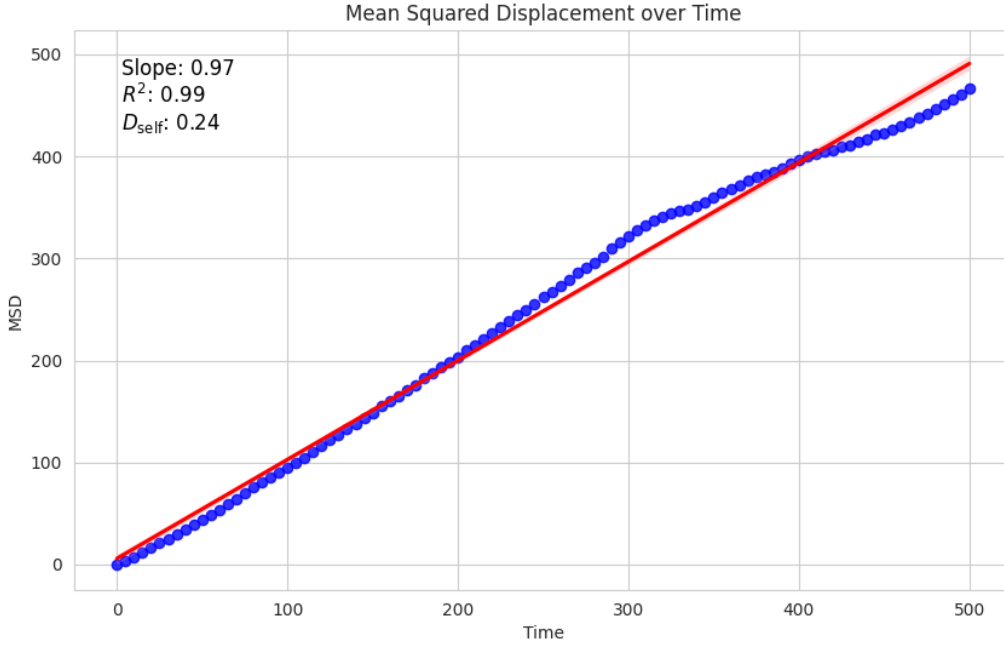


Figure 9: MSD vs Timestep with temperature of 0.7 and an equilibration of 10000 steps

At a qualitative level, everything is clear with temperature - the lower the speed of movement, the lower the mean square displacement and the self-diffusion coefficient. So it makes sense that D_{self} decreased from 0.32 to 0.24.

7 Changing LJ parameters

Table 1: Self-diffusion coefficients (D_{self}) for various Lennard-Jones potential parameters (σ and ϵ)

ϵ	σ	D_{self}
1	1	0.32
0.8	1.2	0.07
1	1.2	0.05
1	0.8	0.62
0.8	1	0.40
1.2	1	0.28
1.2	1.2	0.02
0.8	0.8	0.57
1.2	0.8	0.50

According to the results in the table 1, we can extract following general trends:

- Smaller σ tends to increase the self-diffusion coefficient as particles can move more freely.
- Lower ϵ can also increase diffusion, as particles are less bound to each other, facilitating movement.

The balance between these two parameters determines the overall diffusion behavior in a system modeled by the Lennard-Jones potential.

Table 2: Comparison of D_{self} for different simulation parameters

N _o	x	y	Method	equilibration run	ρ	T	σ	ϵ	D_{self}
1	40	40	MSD	5000	0.6	1	1	1	0.32
2	40	40	MSD	1	0.6	1	1	1	0.35
3	40	40	VACF	5000	0.6	1	1	1	≈ 0.30
4	50	50	MSD	5000	0.6	1	1	1	0.30
4	50	50	MSD	10000	0.6	1	1	1	0.39
5	40	40	MSD	100000	1	1	1	1	≈ 0
6	40	40	MSD	10000	1	0.7	1	1	0.24
7	40	40	MSD	5000	0.6	1	0.8	1.2	0.07
7	40	40	MSD	5000	0.6	1	1	1.2	0.05
7	40	40	MSD	5000	0.6	1	1	0.8	0.62
7	40	40	MSD	5000	0.6	1	0.8	1	0.40
7	40	40	MSD	5000	0.6	1	1.2	1	0.28
7	40	40	MSD	5000	0.6	1	1.2	1.2	0.02
7	40	40	MSD	5000	0.6	1	0.8	0.8	0.57
7	40	40	MSD	5000	0.6	1	1.2	0.8	0.50

Appendix: LJ units

mass = mass or m

distance = σ , where $x^* = \frac{x}{\sigma}$

time = τ , where $t^* = t \left(\frac{\epsilon}{m\sigma^2} \right)^{1/2}$

energy = ϵ , where $E^* = \frac{E}{\epsilon}$

velocity = $\frac{\sigma}{\tau}$, where $v^* = \frac{v\tau}{\sigma}$

force = $\frac{\epsilon}{\sigma}$, where $f^* = \frac{f\sigma}{\epsilon}$

torque = ϵ , where $t^* = \frac{t}{\epsilon}$

temperature = reduced LJ temperature, where $T^* = \frac{TKb}{\epsilon}$

pressure = reduced LJ pressure, where $P^* = \frac{P\sigma^3}{\epsilon}$

dynamic viscosity = reduced LJ viscosity, where $\eta^* = \frac{\eta\sigma^3}{\epsilon\tau}$

charge = reduced LJ charge, where $q^* = \frac{q}{(4\pi\epsilon_0\sigma\epsilon)^{1/2}}$

dipole = reduced LJ dipole, moment where $\mu^* = \frac{\mu}{(4\pi\epsilon_0\sigma^3\epsilon)^{1/2}}$

electric field = force/charge, where $E^* = E(4\pi\epsilon_0\sigma\epsilon)^{1/2}\sigma/\epsilon$

density = mass/volume, where $\rho^* = \rho\sigma^{\text{dim}}$