

# Molecular Dynamics Simulation of a Van der Waals Gas

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## I. WRITE / ADAPT A SIMPLE MOLECULAR DYNAMICS SIMULATIONS CODE

Write down a Molecular Dynamics Simulations code for a system of  $N$  particles interacting through a Lennard-Jones potential in contact with a heat bath.

**Describe in detail the different parts of the code. How do you initialize the system of particles (and set the density)? What integrator do you use? How do you implement periodic boundary conditions? How do you control the temperature (how do you implement the thermostat)? What units do you use for the Lennard-Jones interactions? What cut-off do you use for the interactions (and why)? What truncation strategy do you choose?**

My program is divided in modules which contains all functions and subroutines, a main program that uses them for simulating the dynamics of a fluid of particles confined in a cubic box, and finally a python program to make statistics. The fortran modules are:

- **read data** The module reads the inputs and calculates the variables to initialize the simulation.
- **def var** The module declares all the global variables of the program and calculates all the real units of the simulation.
- **init**
  - **Subroutine FCC or SC** It creates a crystalline FCC or SC lattice taking as an input the number of nodes on an edge of the cube and the longitud of the edge taking care that there are no overlaps.
  - **Subroutine uniform velocity** Initialize the velocities of the system of  $N$  particles in a uniform distribution
  - **Subroutine velo rescal** Rescale them so that the kinetic energy is consistent with a given temperature
- **energy**
  - **Subroutine LJ** Compute the Lennard-Jones potential.

- **Subroutine Force** The matrix force of the system is an  $N \times N$  where  $N$  is the number of atoms. The  $i, j$ -th element holds the potential energy due to interaction of molecule  $i$  with molecule  $j$ . The diagonal elements of this matrix are 0, because the atom does not interact with itself. These interactions can be computed for  $i = 1$  to  $N-1$  and  $j = i+1$  to  $N$  and taking the advantage of the symmetry of the matrix all the interactions can be calculated.

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### Algorithm 1: Energy

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**Result:** Force, Potential, Pressure

**for**  $i = 1, N - 1$  **do**

**for**  $j = i + 1, N$  **do**

    Compute  $r_{i,j}$  Compute LJ potential;

    Compute  $F_{i,j}$ ;

  Compute Pressure

**end**

**end**

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## • integration

- **Subroutine velocity verlet** To solve the equations of motion we have used the velocity Verlet algorithm which is convenient for thermalizing.

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### Algorithm 2: Velocity Verlet

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**Result:** Velocity, Kinetic Energy

**for**  $i = 1, N$  **do**

$r(t + dt) = r(t) + v(t)dt + 0,5F(t)dt$

$v(t + \frac{dt}{2}) = v(t) + 0,5F(t)dt$

  Apply PBC

**end**

  Compute Force

**for**  $i = 1, N$  **do**

$v(t + dt) = v(t) + 0,5F(t)dt$

  Compute Kinetic energy

**end**

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- **Subroutine Andersen** In this module, the Andersen's thermostat is created, using random numbers. It uses the Box-Muller transformation to obtain a normal distribution of our velocities, adjusting them to a specific temperature.

- **gdr** Computes de radial distribution function ( in the code is explained each subroutine in detail, very large to explain in a little pseudocode)

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**Algorithm 3:** Andersen
 

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**Result:** Velocity

**for**  $i = 1, N$  **do**
 $v_x = \sqrt{-2T \log n_1} \cos 2\pi n_2;$ 
 $v_y = \sqrt{-2T \log n_1} \sin 2\pi n_2;$ 
 $v_z = \sqrt{-2T \log n_2} \cos 2\pi n_4;$ 
**end**

 Where  $n_1, n_2, n_3, n_4$  are random uniform numbers
 

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- **sample** The module calculates de statistics of the simulation and write the results.
- **statistics.py** Python program that performs the binning method to calculate the statistics of the simulation.

**How do you initialize the system of particles (and set the density)?**

We create a subroutine called FCC or SC that depends on the number of nodes in each dimension (M), the length of the simulation box (L), and the length of the unity cell (a). This function constructs an FCC lattice of  $N = 4M^3$  identical particles. The density  $\rho$  is set by the user in reduced units.

$$\rho = \frac{N}{L^3}; L = \left(\frac{4M^3}{\rho}\right)^{\frac{1}{3}} \quad (1)$$

We initialize the velocities of the system of N identical particles in a uniform distribution and rescale the velocities so that its kinetic energy is consistent with a given temperature T .

**How do you implement periodic boundary conditions?**

The identical particles interact through a Lennard-Jones potential (function called force). The periodic boundary conditions are implemented with the function named pbc that depends on the distance between particles and the length of the simulation box.

- Atoms that leave the simulation region at one boundary re-enter the region through the opposite face.
- Atoms interact with real and image atoms.
- No walls, reduces surface effects.
- Number density conserved.
- Size of simulation box L large compared with potential range.
- Suppress long wavelength fluctuations.
- Topology of a torus.

**What units do you use for the Lennard-Jones interactions?**

We use reduced units. Once the energies are calculated, we extract the results in kJ mol<sup>-1</sup> by multiplying the results by the depth of the potential well  $\epsilon$ .

quantity	in real units	in reduced units
density	$\rho$	$\rho^* = \rho\sigma_0^3$
temperature	T	$T^* = k_B T / \epsilon_0$
energy	U	$U^* = U / \epsilon_0$
distance	r	$r^* = r / \sigma_0$
pressure	P	$P^* = P\sigma_0^3 / \epsilon_0$
time	t	$t^* = (\epsilon_0 / m\sigma_0^2)^{1/2} t$
force	F	$F^* = F\sigma_0 / \epsilon_0$
torque	T	$T^* = T / \epsilon_0$

FIG. 1: Reduced units.

**What cut-off do you use for the interactions (and why)? What truncation strategy do you choose?**

The cut-off used is  $0,7\frac{L}{2}$ . Adding the cut-off to the calculation of the potential energy softens the cut. It is convenient to truncate the interactions because if the system has a large N, the calculation time will grow like  $N^2$  because we would have the order of  $N^2$  pairs. By truncating, the calculation time grows as N and not as  $N^2$ . Thus, the program runs faster. In this case we choose to not truncate the potential because we have a small system of particles.

The other questions have been answered by explaining the parts of the code in detail.

## II. ANALYSIS OF PROPERTIES OF XENON FLUID

Considering that the interaction between xenon atoms can be described using a Lennard-Jones potential with  $\epsilon = 1,837 \text{ kJ/mol}$  and  $\sigma = 4,1 \text{ \AA}$  (and the atomic mass of xenon is  $m = 131,29 \text{ g/mol}$ ), perform Molecular Dynamics simulations of  $N > 100$  xenon atoms in a fluid disordered state:

### A. Isolated system

We can see that at the end of the simulation, the velocities follow a normal distribution (Maxwell-Boltzmann) as expected since the system has reached the equilibrium situation which follows, when we consider a classical behaviour, the equipartition of energy principle. The

N	256
$\rho$	0,8
Equilibration steps	20000
Production steps	50000
Equilibration T	400
Production T	1,5

TABLE I: Input parameters

	X	$\bar{X}$
KE	57.99	0.024
V	9.56	0.024
E	67.56	$6.52 \cdot 10^{-5}$

TABLE II: Average and statistical error of the observables

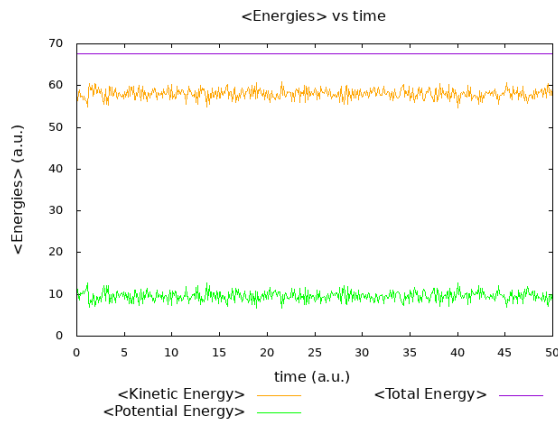


FIG. 2: Potential, kinetic and total energy per particle as a function of time.

energies and the momentums are conserved, as expected since the system is isolated and has no contact with a heat bath.

The standard deviation with respect to the bin size, we can appreciate how both the potential and the kinetics present the same values, this is because the system is in equilibrium, therefore the fluctuations will be equal in magnitude but opposite.

A plateau regime is reached, the maximum value of  $m$  has been chosen according to the correlation presented by the data.

### B. System in contact with heat bath

Consider now a system of ( $N > 100$ ) xenon atoms in a fluid state in contact with a heat bath at  $kBT = 1,5\epsilon$ .

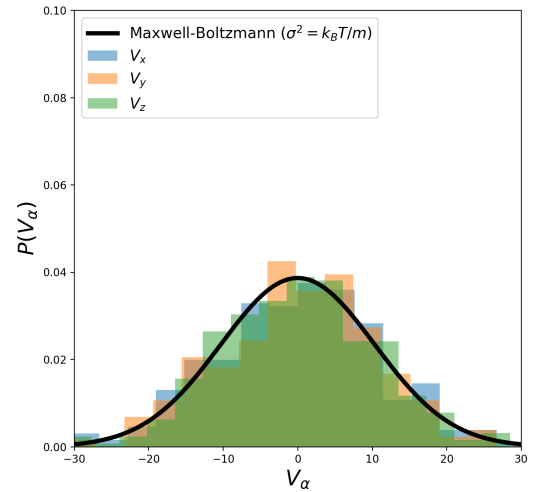


FIG. 3: Final distribution of the velocities

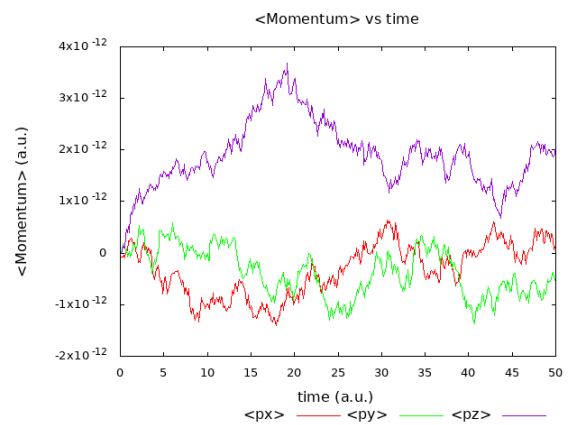


FIG. 4: Momentum as a function of time.

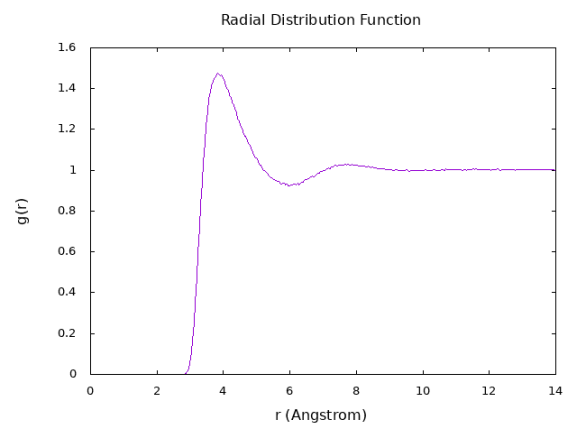


FIG. 5: Radial Distribution Function

To determine the simulation time, short time simulations

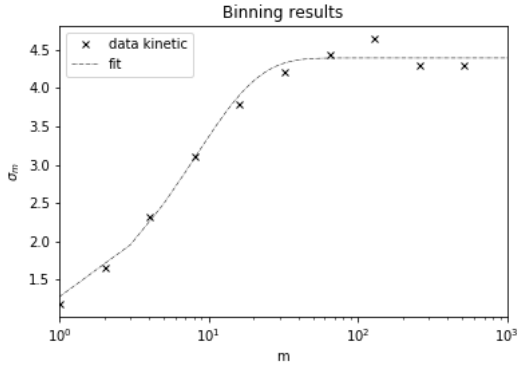


FIG. 6: Standard deviation of the Kinetic energy as a function of bin size

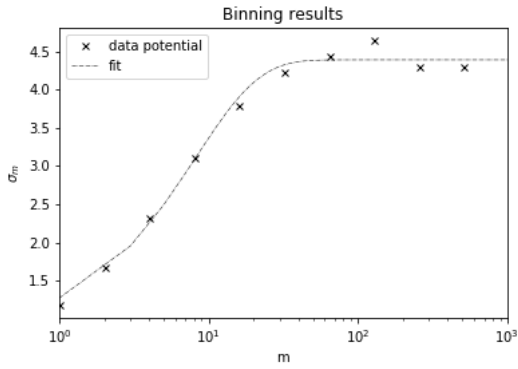


FIG. 7: Standard deviation of the Potential energy as a function of bin size

are carried out and we appreciate when equilibrium is assumed. It can also be done through dimensional analysis with the units. First we perform an NVT equilibration to disorder correctly the system to measure the observables in the production run.

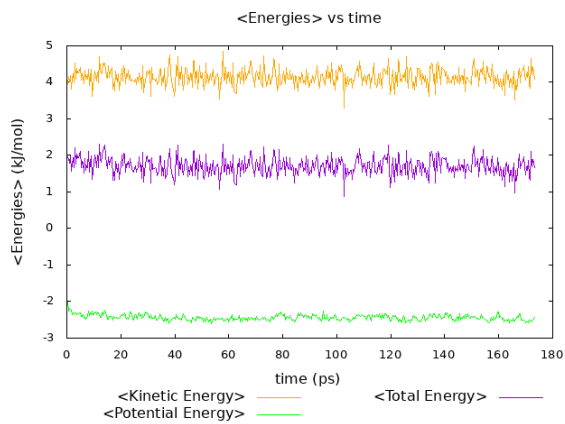


FIG. 8: Potential, kinetic and total energy per particle as a function of time.

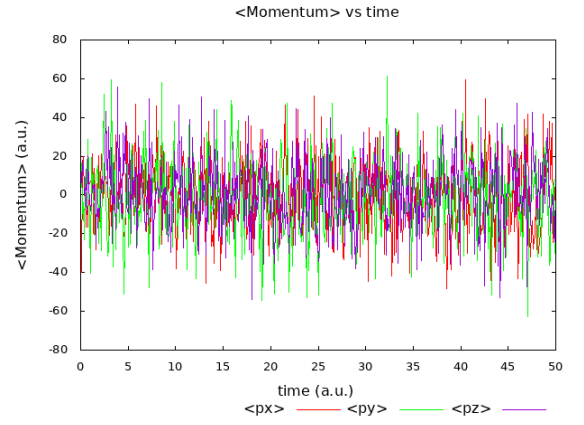


FIG. 9: Momentum as a function of time.

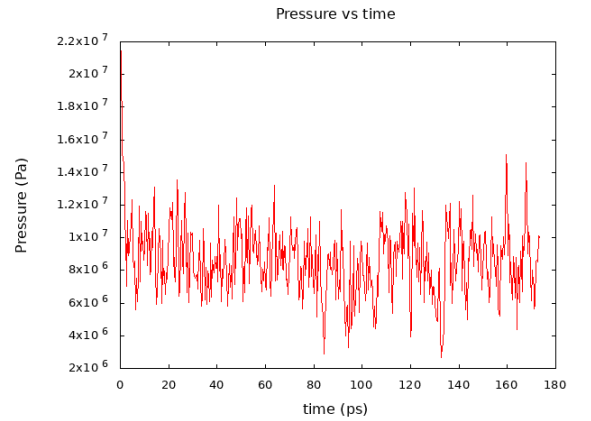


FIG. 10: Momentum as a function of time.

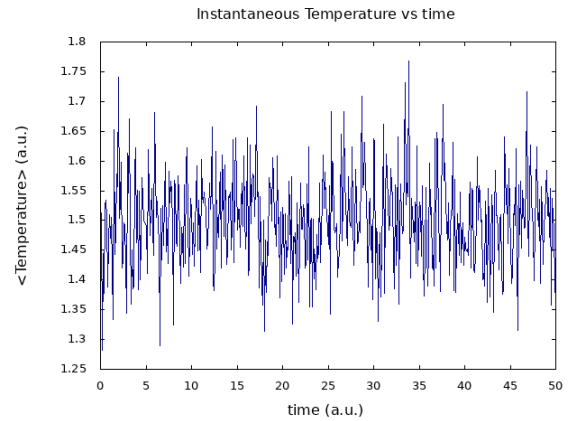


FIG. 11: Temperature as a function of time.

At first, the energies undergo an abrupt change due to melting, but they stabilize quickly upon reaching equilibrium. We can see that the momentums show more fluctuations than in the case of Figure 6, as expected since the system is in contact with a heat bath. Also, can be seen that the Temperature oscillates around  $1.5\epsilon$ ,

so can be concluded that the Andersen thermostat it works correct.

### 1. Kinetic Energy

The error of kinetic energy has to do with temperature fluctuations that must occur. It is also related to the size of the system. The larger the system, the smaller will be the relative fluctuations. As in our case the system is not very large, there are large fluctuations that are normal to be present. The kinetic energy does not only change with the density since its value is equal to  $\frac{3}{2} K_b T$ . As we have fixed  $K_b T$ , the kinetic energy will be the same whatever the density value is, because the number of particles does not change.

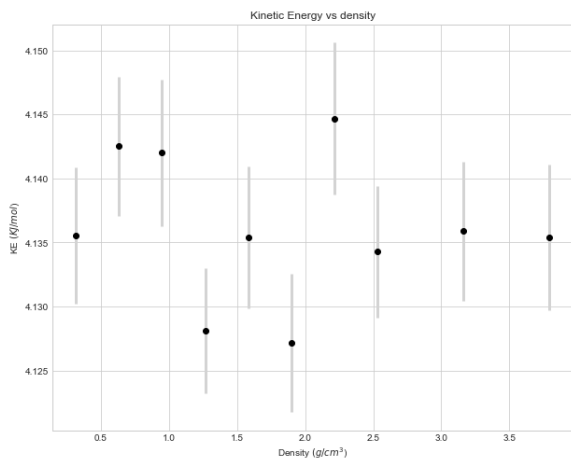


FIG. 12: Kinetic energy as a function of density.

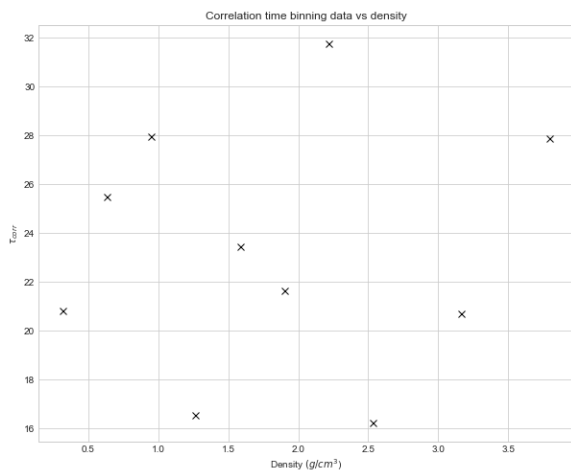


FIG. 13: Correlation time of the binning kinetic energy as a function of density .

$\rho(g/cm^3)$	KE (kJ/mol)	$\tilde{KE}$
0.32	4.13	0.0053
0.63	4.14	0.0054
0.95	4.14	0.0057
1.26	4.13	0.0048
1.58	4.14	0.0055
1.89	4.13	0.0053
2.21	4.14	0.0054
2.53	4.13	0.0051
3.16	4.14	0.0053
3.79	4.14	0.0057

TABLE III: Average and statistical error of the Kinetic energy

### 2. Potential Energy

If we think that the particles are uniformly distributed, we will have a characteristic distance between particles. At the lowest density value, the distance between particles is quite large. The energy between particles in this case is negative but not much. When the density increases a little, the energy is getting smaller as the attractions begin to become noticeable. When the density continues to increase, the distance between particles becomes so small that the energy begins to increase again because the repulsions become more noticeable than the attractions. The results are agreed with the Lennard-Jones behaviour.

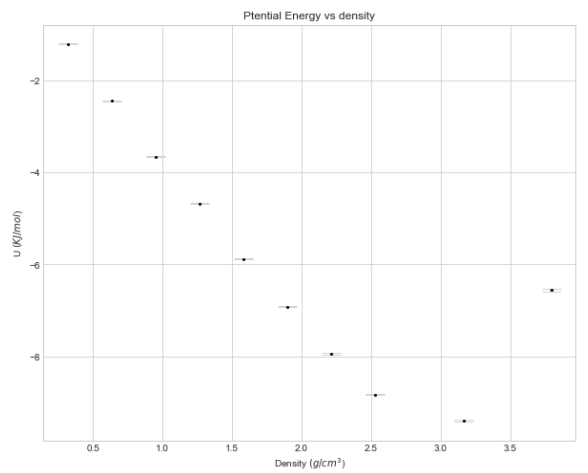


FIG. 14: Potential energy as a function of density.

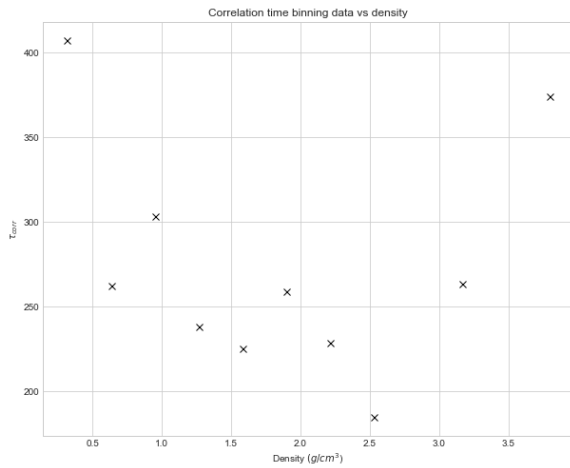


FIG. 15: Correlation time of the binning potential energy as a function of density .

$\rho(g/cm^3)$	U (kJ/mol)	$\bar{U}$
0.32	-1.20	0.008
0.63	-2.44	0.005
0.95	-3.65	0.008
1.26	-4.67	0.007
1.58	-5.87	0.008
1.89	-6.92	0.01
2.21	-7.94	0.01
2.53	-8.83	0.01
3.16	-9.40	0.017
3.79	-6.5	0.034

TABLE IV: Average and statistical error of the Potential energy

### 3. Total Energy

Same behaviour as the potential energy because the kinetic energy is constant.

### 4. Pressure

Pressure increases as the density increases as expected.

When performing the binning method, we observe that the error increases with the density, without taking into account the kinetic that do not depend on it. The binning correlation times have also been obtained, where we see that for kinetics we have low correlations, because it's independent of the density, but in the case of potential and pressure, we obtain high correlations. One reason may be for choosing a high cutoff for all densities, making the force calculation take into account all interactions, no matter how small, and leading to statistically non-

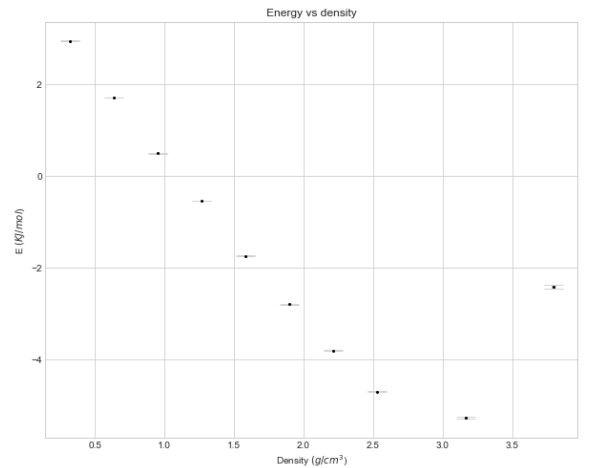


FIG. 16: Total energy as a function of density.

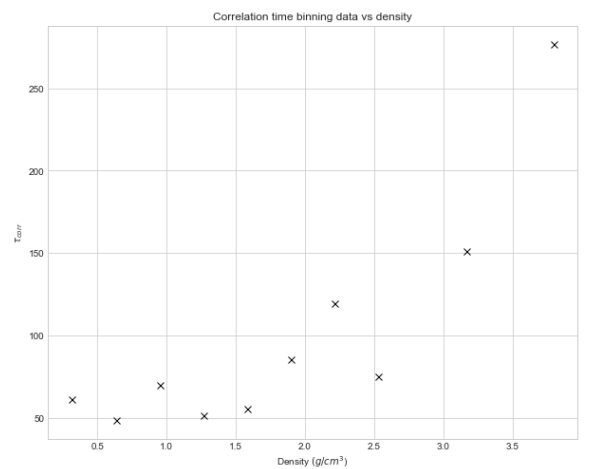


FIG. 17: Correlation time of the binning energy as a function of density .

$\rho(g/cm^3)$	E (kJ/mol)	$\bar{E}$
0.32	2.93	0.008
0.63	1.70	0.007
0.95	0.49	0.009
1.26	-0.54	0.008
1.58	-1.74	0.009
1.89	-2.79	0.011
2.21	-3.80	0.014
2.53	-4.69	0.012
3.16	-5.26	0.019
3.79	-2.42	0.035

TABLE V: Average and statistical error of the total energy

independent results.

For the potential we see two maxima in the correlation

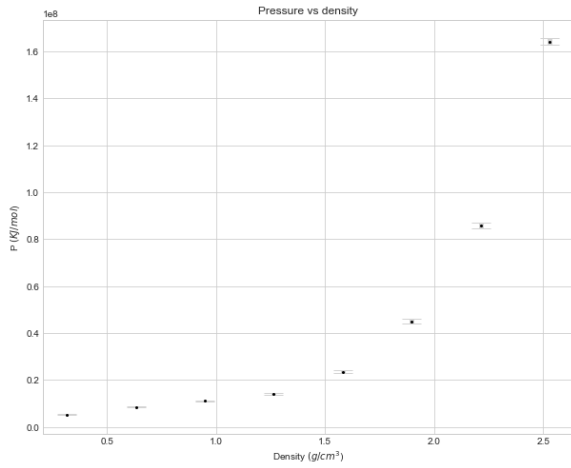


FIG. 18: Pressure as a function of density.

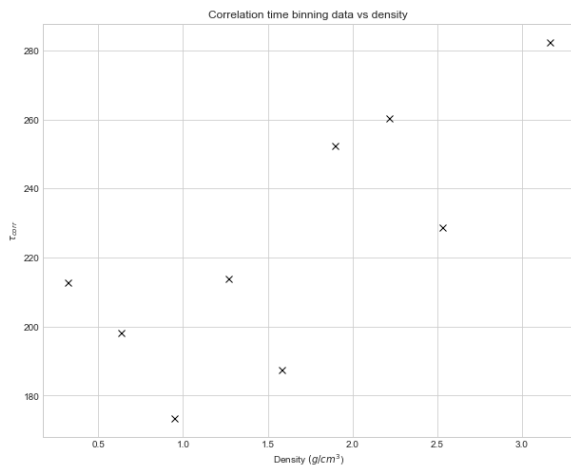


FIG. 19: Correlation time of the binning pressure as a function of density .

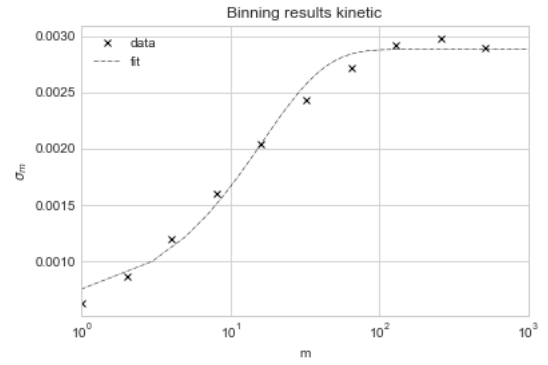
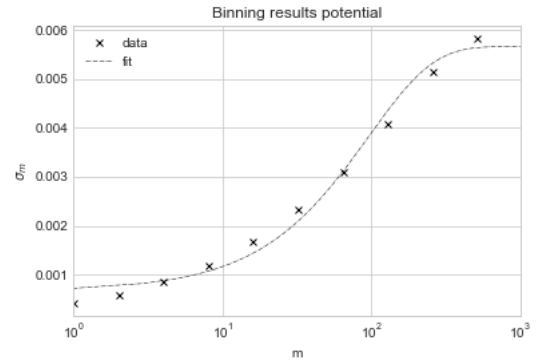
$\rho(g/cm^3)$	P (Pa)	$\bar{P}$
0.32	5315130.724	61083.06
0.63	8557073.504	142441.76
0.95	11077446.47	222325.44
1.26	14075504.4	399680.52
1.58	23567691.92	501778.35
1.89	45035049.64	894110.55
2.21	85917071.19	1248890.4
2.53	164119919.6	1304351.95
3.16	563889573.3	2354875.98

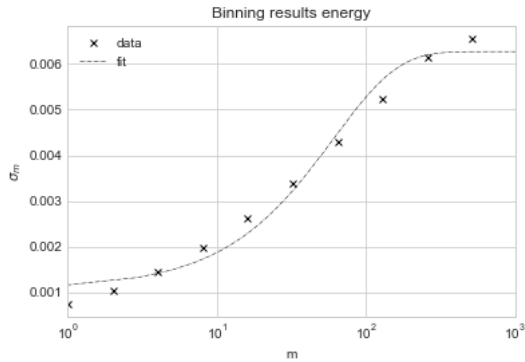
TABLE VI: Average and statistical error of the total energy

time, the first case for very low density, when the distance between particles is high and there are no strong interactions. In the second case, when the distance is low and

repulsions increase. Therefore, clearly the correlations are due to the cutoff, since in both cases the interactions would have to have been truncated at smaller distances, so that only the most relevant interactions are taken into account.

Therefore, to obtain statistically independent results, the cutoff is an important parameter to take into account. For all observables it can be seen that the correlation increases with density, therefore, to obtain statistically correct results we will have to increase the number of time steps for higher densities.

FIG. 20: Binning analysis Kinetic Energy for  $\rho = 0.8$ .FIG. 21: Binning analysis Potential Energy for  $\rho = 0.8$ .

FIG. 22: Binning analysis Energy for  $\rho = 0.8$ .

All the binning plots are in reduced units for better visualization.

### III. RADIAL DISTRIBUTION FUNCTION

It can be seen that for high densities we obtain higher peaks, we also see how they take longer to stabilize around the unit value, since at higher densities the system will be more compacted. Therefore, for high densities we see a behavior of the RDF as a liquid, as the

density decreases the behavior of the RDF becomes similar to that of a gas.

It can be seen how the RDF peak is located just at a distance equal to the sigma of the gas, therefore, we can conclude that the results obtained are correct.

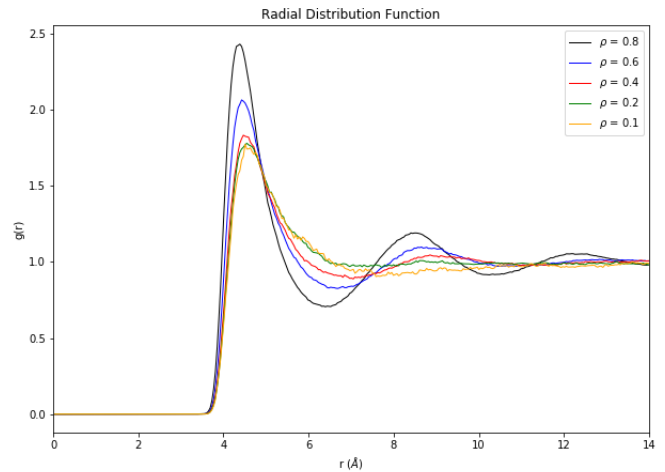


FIG. 23: RDF as a function of density.