Research Project: Molecular Dynamics Simulations of a Lennard-Jones System

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June 2022

Abstract

The molecular dynamics simulations predict the properties of molecular systems via the numerical solution of equations of motion for many atoms. In a box of particles, we calculate the system's Potent Energy through a pair interaction Lennard-Jones potential. Our goal is to examine the conserved quantities, the Hamiltonian and the momentum, as the distribution of particles for different simulation characteristics.

1 Introduction

1.1 N-body Problem

The N-body or Many-body Problem is an active research topic, which determines the motion of N atoms interacting with each other according to the Newton law of motion. In order to solve the N-body problem, it's important to solve numerically the Hamiltonian Equations of motion. In the atomistic level, integration of the equations of motion ascribes a trajectory, by describing the positions $\mathbf{r}$, velocities $\mathbf{v}$, and accelerations $\mathbf{a}$ of the particles as they vary by time.

The system is described by the Hamiltonian equations:

$$\dot{\mathbf{r}} = H_{\mathbf{p}}, \quad \dot{\mathbf{p}} = -H_{\mathbf{r}} \tag{1}$$

$$\frac{dr_i}{dt} = \frac{\partial H}{\partial p_i}(\mathbf{r}, \mathbf{p}), \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial r_i}(\mathbf{r}, \mathbf{p}), \quad i = 1, ...N \tag{2}$$

where $H = H(\mathbf{r}, \mathbf{p}) = K(\mathbf{p}) + U(\mathbf{r})$ the Hamiltonian and the vectors $\mathbf{r} = (r_1, ..r_N)$ and $\mathbf{p} = (p_1, ..., p_N)$ are the position and momentum vectors, respectively.

The Kinetic Energy K depends on momentum $\mathbf{p}$ and Potential Energy U on position $\mathbf{r}$ [1].

$$K(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} \tag{3}$$

So,

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}} = \frac{\partial K}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m} \tag{4}$$

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial U}{\partial \mathbf{r}} \tag{5}$$

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1.2   Molecular Dynamics Simulations

Molecular Dynamics is a technique for computing the equilibrium structural and transport properties of a classical many-body system, in which the term "classical" means that the motion, which is investigated, obeys classical mechanic's laws. Specifically, MD is a computer method for simulating the physical movements of atoms and molecules. The accuracy of the represented model is essential for obtaining the desired information [1].

In a MD simulation, we need to solve the classical equations of motion, especially Newton's equations, so that information of atoms' positions and velocities can be obtained. The procedure, which we follow for constructing a MD algorithm has several steps. The first step is the construction of a model configuration initializing each particles' position and velocities. After the calculation of the total force on each particle (intermolecular & intramolecular), the integration of motion is ensued through the equations. It is needed N_k steps until the system reaches the equilibrium. After storing the accurate positions, velocities and forces and repeating N times the central loop (see figure 1), the algorithm is terminated by calculating the averages of the measured quantities and the desired properties.

One of these algorithms, the Verlet method, is used at MD simulations for m-body problems. At this method, their equations are derived from the Taylor expansion.
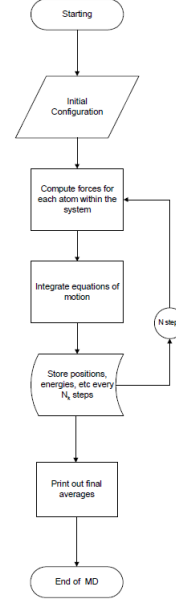

Figure 1: A Flow diagram of MD algorithm [1].

From the backward and forward Taylor expansion, we get the following equation:

$$\mathbf{r}(t + \Delta t) + \mathbf{r}(t - \Delta t) = 2\mathbf{r}(t) + \alpha(t)\Delta t^2 + O(\Delta t^4) \tag{6}$$

where $\mathbf{r} = (r_1, ..r_N), \quad r \in \mathbb{R}^{3N}$ are particles' positions and $\mathbf{a} = (a_1, .., a_N), \quad a \in \mathbb{R}^{3N}$ their accelerations.

For the Verlet algorithm the Taylor expansion at times $t - dt$ and $t + dt$ is applied. According to the velocity-Verlet algorithm, positions are obtained through the usual Taylor expansion, whereas velocities are calculated with all accelerations computed from the forces at the configuration corresponding to the considered time

$$\mathbf{r}(t + dt) = \mathbf{r}(t) + dt\mathbf{v}(t) + \frac{dt^2}{2}\mathbf{a}(t) \tag{7}$$

$$\mathbf{v} = \frac{\mathbf{r}(t+dt) - \mathbf{r}(t-dt)}{2dt}. \tag{8}$$

1.3 Atomistic Level

Let us assume a system of N atoms in a box of volume V and at temperature T. These N particles, with position vector $r_i, \quad i = 1, ..., N$, obey Newton's second Law, that is

$$F = \mathbf{ma} \tag{9}$$

where, $\mathbf{m} \in \mathbb{R}^{N \times N}$ is the mass matrix of particles, where its diagonal elements are the values of particles' masses, $\mathbf{a} = [a_1, .., a_N], \quad a \in \mathbb{R}^{3N}$ their accelerations, and the total force $F = [F_1, .., F_N], \quad F \in \mathbb{R}^{3N}$. Obtaining the N-body equations of motion, we have

$$F(\mathbf{r}) = -\nabla_{\mathbf{r}} U(\mathbf{r}) = -(\nabla r_1 U, \dots, \nabla r_N U) \tag{10}$$

$$F(\mathbf{r}) = \mathbf{m} \frac{\partial^2 \mathbf{r}}{\partial t^2} = -\frac{\partial U(\mathbf{r})}{\partial \mathbf{r}} \tag{11}$$

where $U(\mathbf{r}) = [U_1(\mathbf{r}), .., U_N(\mathbf{r})], \quad U \in \mathbb{R}^N$ is the total potential energy.
According to eq. (6) and (11), positions are calculated by

$$\mathbf{r}(t+dt) = 2\mathbf{r}(t) - \mathbf{r}(t-dt) + \frac{Fdt^2}{\mathbf{m}} \tag{12}$$

According to statistical mechanics, the Gibbs canonical measure gives the probability of a state $\mathbf{r}$ as:

$$\mu(d\mathbf{r}) = Z^{-1} e^{-\beta U(\mathbf{r})} d\mathbf{r} \tag{13}$$

where $Z = \int_{\mathbb{R}^3} e^{-\beta U(\mathbf{r})} d\mathbf{r}$ is the partition function and $\beta = \frac{1}{K_B T}$, K_B the Boltzmann constant. [2, 3]

1.4 Coarse-Grained Level

At the atomistic level, a problem that occurs is that complex molecular systems require a large-range of time and length scales, which is an extremely time-consuming process. In order to decreace the computational cost, we need to reduce the number of degrees of freedom. At the mesoscopic level, the atoms are mapped into small batches of particles ("superatoms"), known as coarse-grained particles. Through the procedure of mapping from the atomistic level to the CG level, the degrees of freedom of the N-atoms are reduced as the new system is consisted of M-particles $(M < N)$ [2, 3]. The CG particles $\mathbf{R} = (R_1, R_2, .., R_M), \quad \mathbf{R} \in \mathbb{R}^{3M} \quad (M < N)$ are calculated by a mapping function.

The Potential Energy

The probability of a state $\mathbf{R}$ is as well given by the Gibbs measure,

$$\mu(\mathbf{R}) = \int_{A(\mathbf{R})} \mu(\mathbf{r}) d\mathbf{r}, \tag{14}$$

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Thus,

$$\mu(\mathbf{R}) = Z^{-1} \int e^{-\beta U(\mathbf{R})} d\mathbf{R} \propto e^{-\beta U(\mathbf{R})}. \tag{15}$$

Accordingly, the force $F : \mathbb{R}^{3M} \to \mathbb{R}^{3M}$ is

$$F(\mathbf{R}) = -\nabla_{\mathbf{R}} U(\mathbf{R}), \quad i = 1, 2, .., M, [3]. \tag{16}$$

1.5   Estimating the M-body Potential of Mean Force

Here, we can write the probability given by the canonical Gibbs measure of the CG state $\mathbf{R}$ using the effective potential U_{eff}

$$\mu(d\mathbf{R}) = Z^{-1} \int_{A(\mathbf{R})} e^{-\beta U_{eff}(\mathbf{R};\theta)} d\mathbf{R} \quad . \tag{17}$$

In principal, the M-body potential energy is consisted of the contributions of two-body, three-body e.t.c interactions. Let the term $r_{ij} = \|R_j - R_i\|, \quad i,j = 1, 2, ..., M$ denote the distance between the particle i and j. Thus,

$$U(\mathbf{R}) = \sum_{i,j} u_2(r_{ij}) + \sum_{i,j,k} u_3(r_{ij}, r_{ik}, r_{jk}) + ... \quad . \tag{18}$$

It is common to estimate the energy with the two-body contributions.

$$U(\mathbf{R}) \approx \sum_{i,j} u(r_{ij}) \tag{19}$$

Lennard-Jones Potential

The Lennard-Jones potential is an intermolecular pair potential and is applied to calculate the potential energy of the CG particles. The two molecules have both attractive and repulsive forces between them.
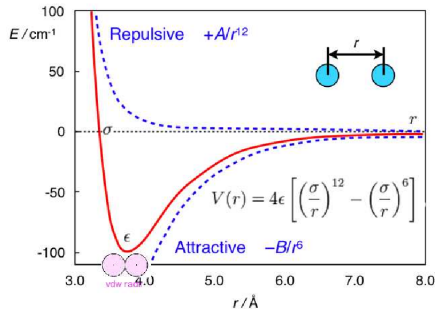

Figure 2: The Lennard-Jone Potential [4]

Form of the L-J potential:

$$U_{LJ}(r_{ij}) = 4\epsilon\left((\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6}\right) \tag{20}$$

where r_{ij} is the distance between two particles with positions r_i and r_j , ϵ is the depth of the potential well and σ is the atom diameter. The term $(\frac{\sigma}{r_{ij}})^{12}$ describes repulsion and the $(\frac{\sigma}{r_{ij}})^{6}$ term describes attraction [4].

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2 Implementation of the Molecular Dynamics Algorithm

2.1 Analysis of the Molecular Dynamics Algorithm

Let us assume a system N particles in a box that interact via a pair interaction Lennard-Jones potential. The CG energies depend on the local chemical environment of the particles, according to a cut-off radius r_c of choice. This means that each particle's contribution is dependent on a number of neighboring particles that interact with the central particle examined. The outside-of-the-cut-off-radius particles do not interact with the central molecule. Otherwise, their contribution is minor, as it is shown at the figure 3.

The number of particles in systems can be very large. So, in order to overcome this problem, we need to specify the simulation box and the periodic boundary conditions. fig 3 illustrates the use of periodic boundary conditions in two dimensions. The central simulation box is surrounded by its periodic images. When a moving particle leaves the simulation box at one boundary, one of its images simultaneously enters the simulation box at the opposite boundary. Therefore, the total number of particles in the system is conserved. In order to prevent incorporating spurious interactions between the periodic images of the particles into the force calculation, the interaction range must be less than the half length of the simulation box — the so-called minimum-image convention [5].
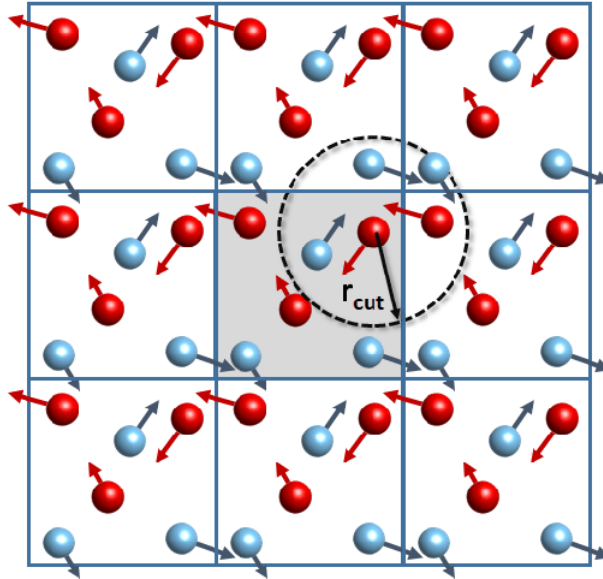

Figure 3: A two-dimensional periodic system with the minimum image convention. [6]

Instead of **R** *for the CG positions, we use* **r**.

The initial coordinates of the system are given via a periodic crystal structure, a Simple Cubic fig 4, and the velocities randomly, where they follow a Boltzmann distribution, $v \sim N(0, \sqrt{(k_b/\mathbf{m})})$,

where $\mathbf{m} = 1$ and $k_b = 1$. For the first integration step, we use a first order scheme,

$$\mathbf{r}(t + dt) = \mathbf{r}(t) - dt\mathbf{v}(t) + 0.5F(t)dt^2 \tag{21}$$

and for the next integration steps the eq.(12). For each simulation, we consider a fixed amount of particles within a box and a fixed number density $\rho = N/V$. The volume of the simulation box is given by $V = N/\rho$ and the length L of each side of the box is given by $L = V^{1/3}$.
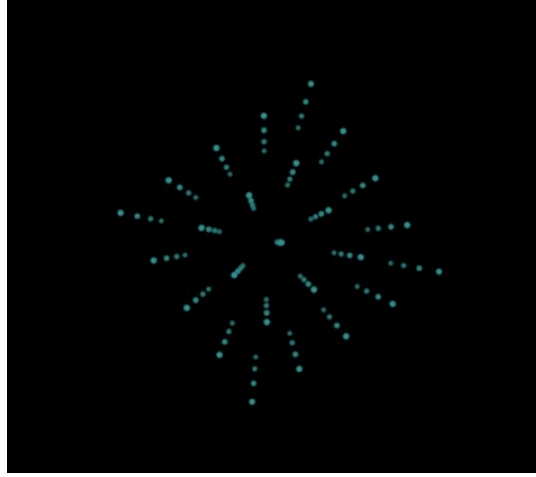

Figure 4: Configuration of the initial positions particles ($N = 100$). Density= 0.1, Temperature= 2.0

To summarize the above analysis, a Molecular Dynamics algorithm for the microcanonical ensemble could be defined as the following:

Set N, ρ, T, dt
Set number of steps $nsteps$
Initialize $\mathbf{r}(t_0), \mathbf{v}(t_0)$ and compute $\mathbf{r}(t_1)$ with equation (15)
for $j=1,\ldots,nsteps$ **do**
    $t = jdt$
    for $i=1,\ldots,N$ **do**
        $\mathbf{r}_i(t + dt) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - dt) + \frac{\mathbf{F}_i}{m_i}(t)$
        $\mathbf{v}_i = \frac{\mathbf{r}_i(t+dt)-\mathbf{r}_i(t-dt)}{2dt}$
    end
    Compute forces $\mathbf{F}(\mathbf{r}(t + dt))$
    Implement periodic Boundary Conditions
end

Figure 5: MD algorithm

## 2.2   Results of the Molecular Dynamics Algorithm

Our first goal is to calculate particles properties, like the kinetic energy, the potential energy and the Hamiltonian. These quantities are evaluated at every step and they are averaged every ksteps. A key concept in the microcanonical ensemble is that the Hamiltonian must be conserved. Another conserved quantity is the total momentum P, which should be close to zero (within the statistical fluctuation of the initial velocities that follow the Boltzman distribution). The total momentum has calculated every k steps.

Another goal is to compute the distribution distances between all particles in the box and the pair distribution function $G(r)$. In order to calculate the $G(r)$, we count the number of particles, that lie in a thin spherical shell of thickness dr at a distance r from each of the other particles, then we divide with the volume of the spherical shell $V_{shell} = 4\pi r^2 dr$ and then normalize with the number density ρ. The pair distribution function is averaged at the end of the molecular dynamics simulation, over n times, where $n = Nstep$, and $Nstep$ is the total number of configurations.

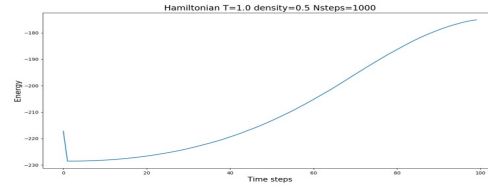- Nstep= $10^3, 10^4$

- Density= $0.1, 0.5, 0.7$
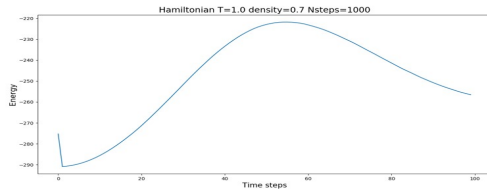
- Temperature= $0.5, 1.0, 2.0$

Hamiltonian

For Nstep= 10^3 and $dt = 0.0001$:
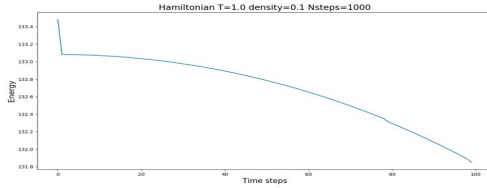
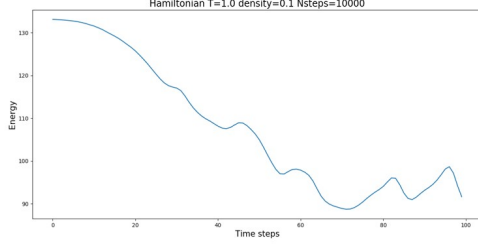(a) Hamiltonian for $\rho = 0.1, T = 1.0$
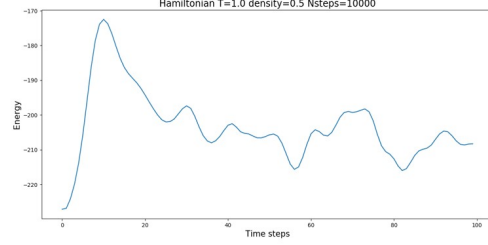

(b) Hamiltonian for $\rho = 0.5, T = 1.0$

(c) Hamiltonian for $\rho = 0.7, T = 1.0$

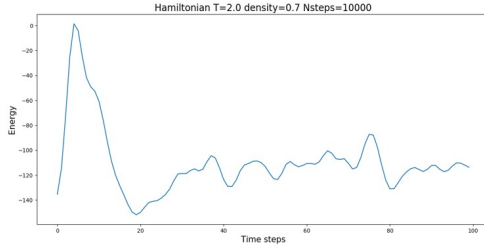Figure 6: Hamiltonian figures for $Nstep = 1000$ with $dt = 0.0001$

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For Nstep= 10^4 and $dt = 0.0001$:

(a) Hamiltonian for $\rho = 0.1, T = 1.0$
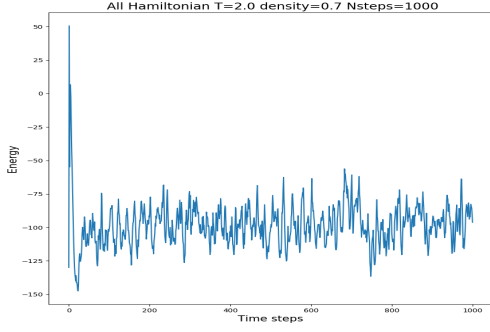

(b) Hamiltonian for $\rho = 0.5, T = 1.0$

(c) Hamiltonian for $\rho = 0.7, T = 2.0$

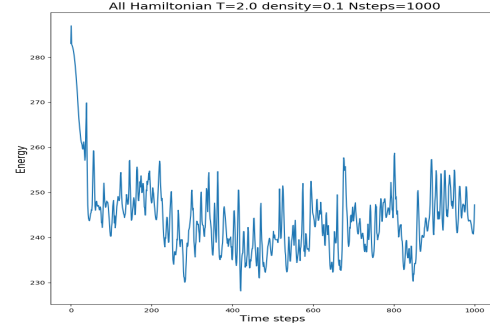Figure 7: Hamiltonian figures for $Nstep = 1000$ with $dt = 0.01$

At fig. 7, we presented the Hamiltonian in only temperature $T = 1.0$, since the behaviour of the Hamiltonian does not change at any temperature. From these figures, we can see that the Hamiltonian can not be well conserved with a small number of time steps ($dt = 0.0001$). Only in the fig 13 seems the Hamiltonian to start getting stabilized after big number of steps. In fig 8 the results are characteristically better, because the Hamiltonian stabilizes after a few steps ($dt = 0.01$). That means that the systems with larger time step can reach the equilibrium state more quickly. Also for systems with lower density (see fig 8b, the Hamiltonian is more unstable than the systems with higher density (see fig 8a and 8d).
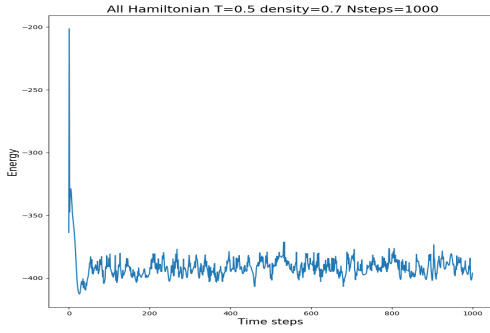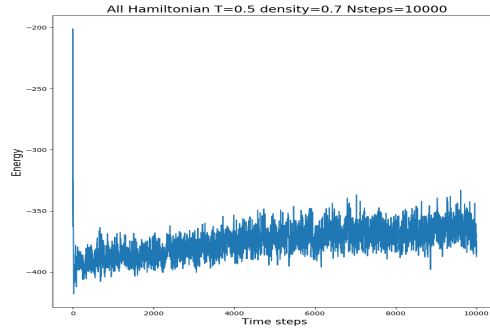
For $dt = 0.01$:

(a) Hamiltonian for $\rho = 0.7, T = 2.0, Nstep = 1000$

(b) Hamiltonian for $\rho = 0.1, T = 2.0, Nstep = 1000$
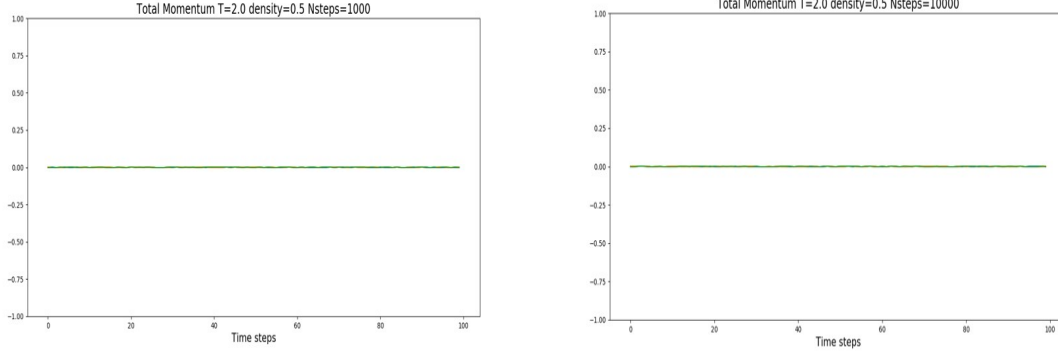

(c) Hamiltonian for $\rho = 0.7, T = 0.5, Nstep = 1000$

(d) Hamiltonian for $\rho = 0.7, T = 0.5, Nstep = 10000$

Figure 8: Hamiltonian figures for $Nstep = 100$ and $Nstep = 100$ with $dt = 0.01$

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Momentum

(a) Momentum for $\rho = 0.5, T = 2.0, Nstep = 1000$ (b) Momentum for $\rho = 0.5, T = 2.0, Nstep = 10000$

Figure 9: Momentum for different Nstep

Momentum is a conserved quantity at any value of temperature or density and remains equal to zero for all configurations (see fig 9a and 9b).

Pair Distribution function

At the following figures, the pair distribution function $G(r)$ has been calculated only for $dt = 0.01$.
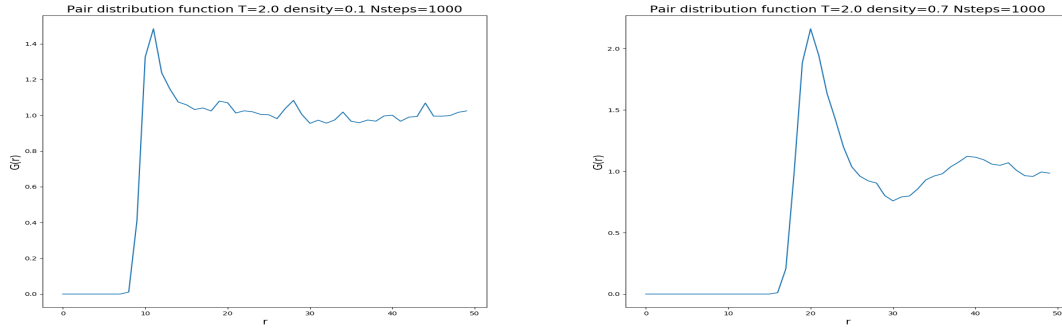
(a) Momentum for $\rho = 0.1, T = 2.0, Nstep = 1000$ (b) Momentum for $\rho = 0.7, T = 2.0, Nstep = 1000$

Figure 10: Figures of Pair distribution function with different densities

The fig. 13a and 13b shows that we have a radial distribution function of liquids. At short distances, the value of $G(r)$ is equal to zero. This is due to the strong repulsive forces. When the first peak occurs, shows that there is a high probability of finding more molecules at this distance. After the peak, the probability to find molecules decreases and at some point the $G(r)$ approximates one, conclusively this means that the probability to find molecules is equal to zero. Fig. 13a shows

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that we have fewer particles around the central particle due to the low density. In contrast fig. 13b, with density equal to 0.7, presents a lot of particles around the central one.
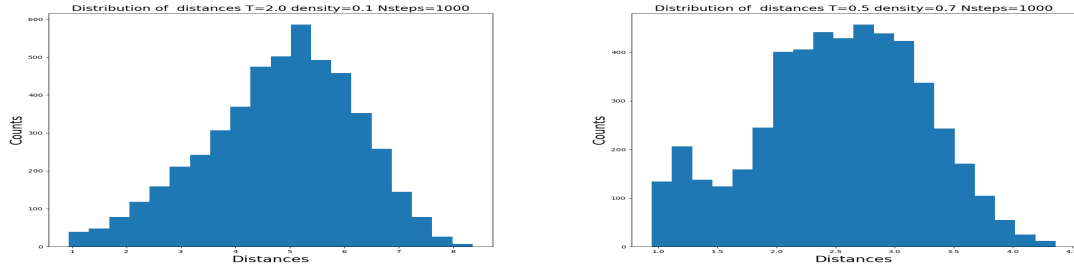
Distribution of Distances

For Nstep= 10^3 :
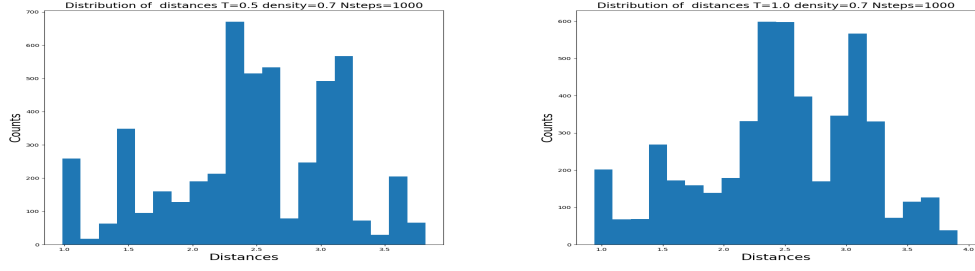
(a) Distribution of Distances for $\rho = 0.7, T = 0.5$ (b) Distribution of Distances for $\rho = 0.7, T = 1.0$
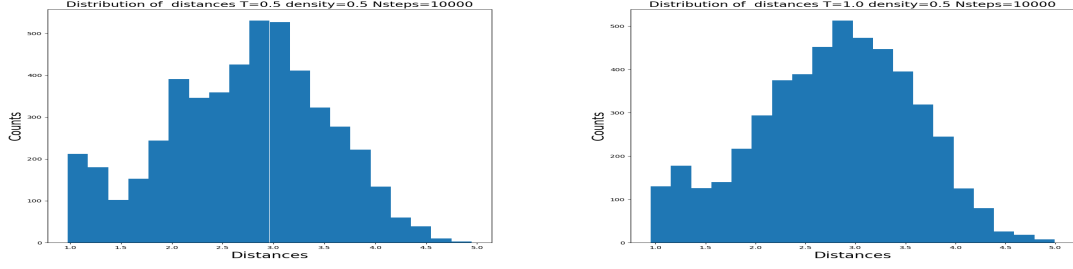
Figure 11: Distribution of Distances for $Nstep = 1000 and dt = 0.0001$

(a) Distribution of Distances for $\rho = 0.1, T = 2.0$ (b) Distribution of Distances for $\rho = 0.7, T = 0.5$

Figure 12: Distribution of Distances for $Nstep = 1000 and dt = 0.01$

For Nstep= 10^4 :

(a) Distribution of Distances for $\rho = 0.5, T = 0.5$ (b) Distribution of Distances for $\rho = 0.5, T = 1.0$

Figure 13: Distribution of Distances for $Nstep = 10000$

At fig 11, 12 and 13, we notice that the distribution of pair distances approximates the normal distribution $N(3, \sigma)$. This is more clear when the Nstep increases and the time step decreases.

3   Conclusions

Our system of liquid particles can reach the equilibrium state more quickly with larger time steps or more configurations. It works better though when we choose a larger time step and a small number of configurations, in order to reach the equilibrium state, because the results are already satisfactory in earlier time. Also, the Hamiltonian of low density systems is more unstable, since these systems can not reach that well the equilibrium state.

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