Study of the Dynamics of Colloidal Particles in a Lennard-Jones Potential through Verlet Integration Simulations*

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In this work, we study the evolution of the trajectories of colloidal systems due to the presence of a Lennard-Jones potential. To achieve this, simulations were performed by integrating the equations of motion using the Verlet numerical method implemented in Python. More specifically, we analyze the behavior under four different initial conditions, which include ordered and disordered particle positions, as well as zero initial velocities and random velocities. Through this, we observe that the systems always reach stability in their relative distances. The code can be found here.

I. INTRODUCTION

In simple terms, we study colloidal particles, which consist of a solid phase suspended in a liquid medium and are highly influenced by both short- and long-range forces that govern their stability. In this work, we study the evolution of this colloidal particle system under the influence of a Lennard-Jones potential, which is commonly used to describe interactions between molecules and atoms. We employ the Verlet method to numerically integrate the equations of motion. We analyze how the trajectories of the particles vary and how they reach equilibrium depending on the initial conditions.
The aim is to provide a clear view of the transition process towards equilibrium of the colloidal particles and to understand how the Lennard-Jones potential influences the particles to act either attractively or repulsively depending on their relative distances.

II. BACKGROUD

A. Colloidal Particles

In physics and chemistry, a colloid or colloidal system is a system composed of two phases, typically one fluid and the other dispersed in the form of very fine solid particles [1] with diameters ranging from 1 nanometer to 1 micrometer.
The stability of a colloidal system is defined by the particles that remain suspended in solution, and it depends on the interaction forces between the particles. These include electrostatic interactions and van der Waals forces [1].

B. Verlet Method

The Verlet method is a widely used method in the simulation of dynamic systems. It is a numerical method that integrates Newton's equations of motion to determine the evolution of the particle trajectories.

It is primarily based on the Taylor series expansion of the position function. Newton's second law is given by

$$F = ma = m\frac{d^2x}{dt^2}$$

and so the deduction of the Verlet method to approximate the trajectory is as follows.

First, we calculate the forward expansion $(t+\Delta t)$ of $x(t)$. This gives

$$x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 + \frac{1}{6}\frac{d^3x}{dt^3}\Delta t^3 + \mathcal{O}(\Delta t^4)$$

then we calculate the backward expansion $(t-\Delta t)$

$$x(t-\Delta t) = x(t) - v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 - \frac{1}{6}\frac{d^3x}{dt^3}\Delta t^3 + \mathcal{O}(\Delta t^4)$$

by summing these two results and simplifying, we obtain the Verlet method

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + a(t)\Delta t^2$$

which for our purposes can be written as

$$x(t+\Delta t) = 2x(t) - x(t-\Delta t) + \frac{F}{m}\Delta t^2 \tag{1}$$

and the error is of order $\mathcal{O}(\Delta t^4)$, indicating that it is a very good approximation.

C. Lennard-Jones Potential

The Lennard-Jones potential is one of the most widely used models in physics and chemistry to describe the dynamics and interactions between pairs of molecules and atoms. It was proposed in 1924 by the English mathematician and theoretical physicist John Lennard-Jones (1894-1954) [2]. This pair of molecules or atoms are subjected to both long-range and short-range forces. It results in a repulsive interaction at short distances and an attractive interaction at long distances. This potential has the form

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

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where ε is the depth of the potential, σ is the distance (finite) at which the potential between particles reaches a minimum, and r is the separation or distance between particles.

From basic physics courses, we know that a force is derived from a potential. This force is given by

$$\vec{F}(r) = -\frac{dV(r)}{dr}\frac{\vec{r}}{r} \tag{3}$$

This potential has a minimum, i.e., an equilibrium point, which can be obtained by knowing that it occurs where the force becomes zero. In other words,

$$\frac{dV(r)}{dr}\Big|_{r=r_{eq}} = 0$$

The solution to this equation is

$$r_{eq} = 2^{1/6}\sigma \tag{4}$$

If all the particles are separated, on average, by this distance, we can describe a system in equilibrium. This will be crucial when performing the simulations.

D. Initial Configurations and Systems to Analyze

The simulations are based on analyzing four main cases. In all of them, we arbitrarily choose $\varepsilon = 1$ and $\sigma = 1.5$.

1. We place all the particles at the corners of a square with side length L, as shown in figure 1. The initial velocities of the particles are zero. Since we have already set a value for σ, we then use equation (4) to determine that $r_{eq} \approx 1.68$. Due to the symmetry in the positions of the particles, we can approximate $r \approx L$. Thus, we analyze three subcases: when $L < r_{eq}$, $L > r_{eq}$, and finally when $L \approx r_{eq}$.

2. In the second situation, we again place the particles at the corners of a square with side length L, but this time their velocities are random, following the Maxwell-Boltzmann distribution. The velocities will depend on the temperature.

3. For the third case, we use zero initial velocities and random initial positions.

4. In the last case, both the velocities and positions are random.

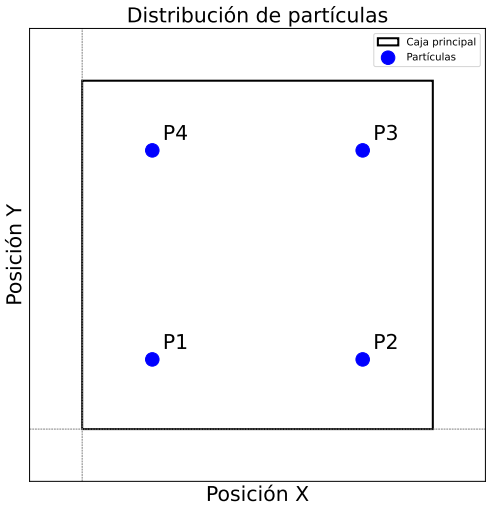


Figura 1: Configuration of particles at the corners of a square with side length L in a box of side $L+k$, with $k = 1$. The particles bounce off the walls.

For the integration, we used a $\Delta t = 0.001$ and iterations ranging from 1000 steps to 20000 steps, depending on the initial conditions employed.

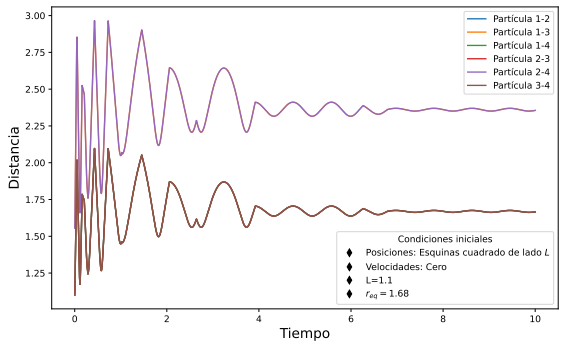
III. RESULTS

The results are divided into the four cases discussed in the theoretical framework.

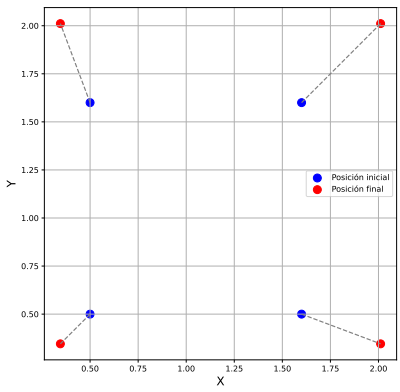
A. Case 1

For this first case, with zero velocities and positions at the corners of a square, we obtain three relevant results.

The first situation is illustrated in figure 2, where we consider $L = 1.1 < r_{eq}$. In figure 2a, we observe that the initial behavior is chaotic; however, over time, the distances between particles become almost constant, indicating that equilibrium is reached. In figure 2b, we observe the final position of the particles (in red), which have tended to move away from their initial position. This was expected since the initial distance between them was, on average, better than the equilibrium distance. This led to a repulsion between them, as predicted by the Lennard-Jones potential. It is important to note that only two curves are observed in the graphs due to the symmetry of the problem, with the other curves overlapping. The two curves shown belong to the particles that are at distance L (the lower one) and the particles at distance $\sqrt{2}L$ (the upper one). This is because particle 1 and 3 (as well as 2 and 4) are at a diagonal distance that is greater than the others (figure 1).

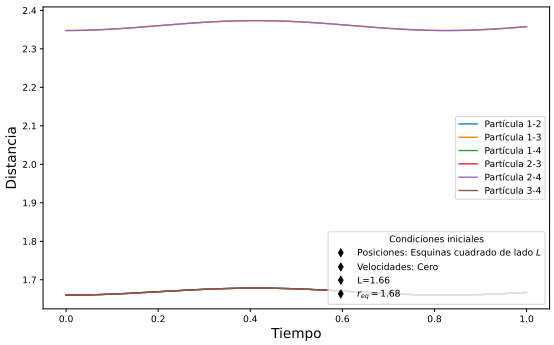


(a) Relative distances between particles over time. Due to the symmetry in the initial conditions, overlapping graphs occur.

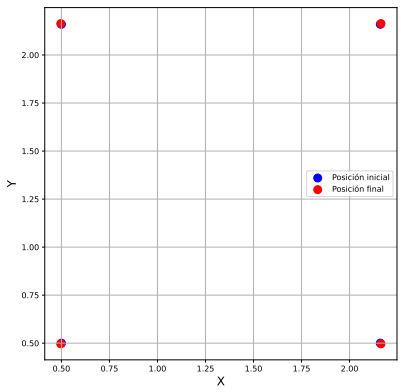


(b) Comparison between initial and final positions of the particles after reaching equilibrium. The animation can be viewed here.

Figura 2: Results for particles separated by a distance smaller than the equilibrium distance.



(a) Relative distances between particles over time. Due to the symmetry in the initial conditions, overlapping graphs occur.



(b) Comparison between initial and final positions of the particles that remained in equilibrium. The animation can be viewed here.

Figura 3: Results for particles separated by a distance very close to the equilibrium distance.

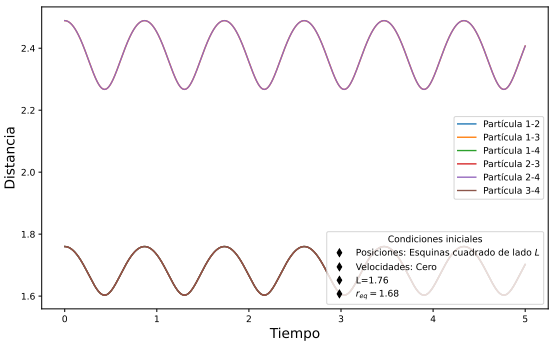
In the following situation, figure 3, we use $L = 1.66 \approx r_{eq}$. The graphs in 3a and 3b show that the particles remain in equilibrium at those positions. This behavior is also expected since we placed the particles at a distance such that the force between them (equation 3) is approximately zero.

Finally, we analyze the situation where $L = 1.76 > r_{eq}$, figure 4. The graph 4a shows oscillations in the distances. This indicates that the particles are moving closer and farther apart in a synchronized manner, as shown in figure 4b. This is also due to the symmetry in the initial conditions. Moreover, this behavior was anticipated since $L > r_{eq}$ places us in the domain where the interaction force between particles is attractive. Thus, the particles move closer to each other, only to move apart again when they enter the repulsive domain, oscillating around the equilibrium point.

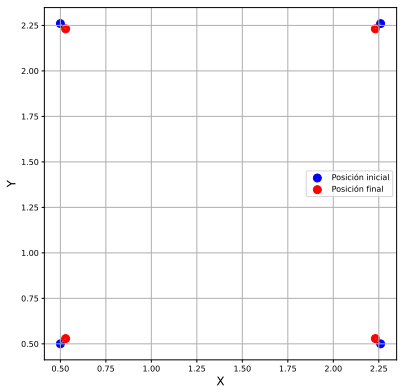
In all three situations, the curves are superimposed because the particles are in a symmetric configuration. Only two characteristic curves remain: the larger distances correspond to the distances between diagonal particles, while the shorter distances correspond to the distances between adjacent particles.

B. Case 2

Now we consider initial velocities for the particles different from zero and random. However, the positions still remain at the corners of a square of side L. This makes the configuration no longer symmetric as in the previous cases. As a result, we observe in 5a that the curves no longer follow the same behavior. They change independently. Initially, the behavior is chaotic, but eventually, the system reaches equilibrium. The relative distances between particles vary around the same value, except for the distance between particles 1 and 3, which has a greater separation that helps maintain equilibrium, as shown in figure 5b.

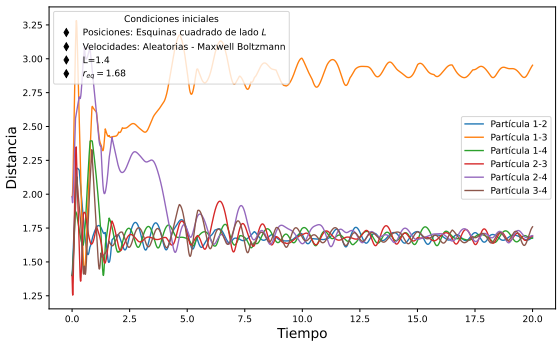


(a) Relative distances between particles over time. Due to the symmetry in the initial conditions, overlapping graphs occur.

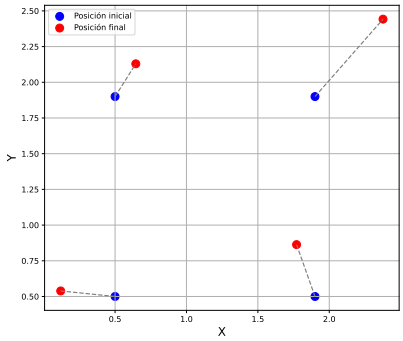


(b) Comparison between initial and final positions of the particles when the simulation is cut. The animation can be viewed here.

Figura 4: Results for particles separated by a distance greater than the equilibrium distance.



(a) Relative distances between particles over time.



(b) Comparison between initial and final positions of the particles after reaching equilibrium.

Figura 5: Results for particles with random initial velocities and initial positions at the corners of a square with side L. The animation can be viewed here.

C. Case 3

Now the initial velocities are zero, but the particle positions are random. This also introduces a chaotic behavior initially, as shown in figure 6a, which later stabilizes at an equilibrium point. The final equilibrium positions are shown in figure 6b.

D. Case 4

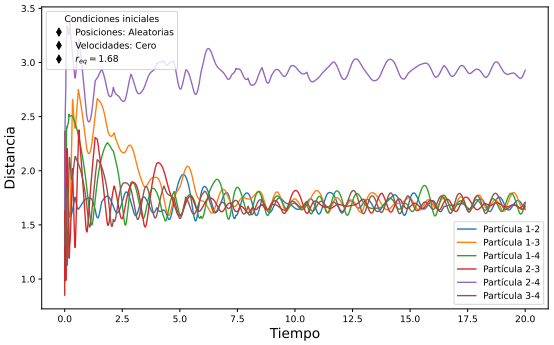
In this last situation, both velocities and positions are random. This case takes a longer time to reach equilibrium, as the initial behavior is much more chaotic, as shown in figure 7a. However, after waiting for the necessary time, the relative distances between particles stop varying significantly, and equilibrium is reached.

IV. CONCLUSIONS

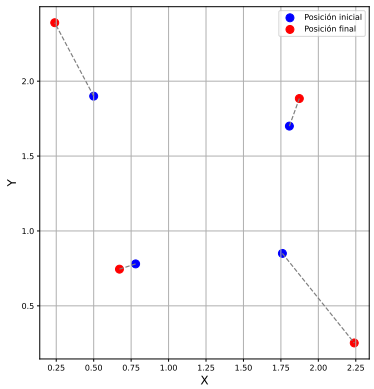
Throughout this work, we have analyzed different configurations of colloidal particles subjected to a Lennard-Jones potential with $\varepsilon = 1$ and $\sigma = 1.5$. For the simulations, we employed the Verlet method to integrate the equations. These simulations allowed us to observe the behavior of the particles under different initial conditions, including both random and organized positions and velocities.

In the first case, where the particles were placed at the corners of a square with zero initial velocities, it was confirmed that the system reached equilibrium when the distance between the particles approached the equilibrium value of the Lennard-Jones potential. This result is consistent with the nature of the potential, which tells us that the force becomes zero at the equilibrium point.

In the next case, where the velocities were random, a chaotic behavior was observed at first, which then stabilized at an equilibrium point corresponding to an average particle distance close to r_{eq}. The same results were obtained with random



(a) Relative distances between particles over time.

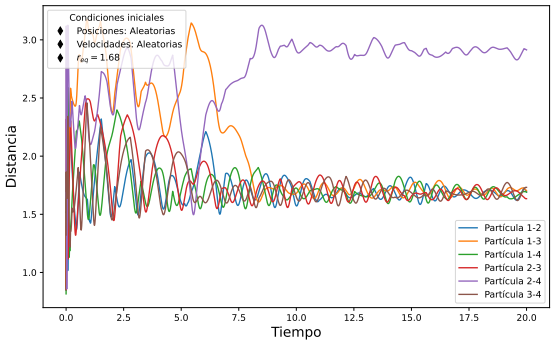


(b) Comparison between initial and final positions of the particles after reaching equilibrium.

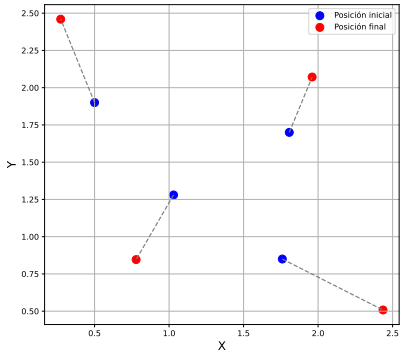
Figura 6: Results for particles with zero initial velocities and random initial positions. The animation can be viewed here.

initial positions.
After enough time, all configurations reached equilibrium, at which point the particles formed a sort of parallelogram. In this configuration, all particles were approximately at the same distance from each other, except for the largest diagonal. The graphs show at least one distance between two particles greater than the others.

These results reflect the expected behavior discussed regarding the Lennard-Jones potential. Particles at close distances behave repulsively, while those at farther distances attract each other. As a consequence, they tend to reach equilibrium through a combination of these two behaviors.



(a) Relative distances between particles over time.



(b) Comparison between initial and final positions of the particles after reaching equilibrium.

Figura 7: Results for particles with random initial velocities and random initial positions. The animation can be viewed here.

[1] Wikipedia contributors. Coloide — wikipedia, la enciclopedia libre, 2024. Accedido: 24 de noviembre de 2024.

[2] Wikipedia contributors. Potencial de lennard-jones — wikipedia, la enciclopedia libre, 2024. Accedido: 23 de noviembre de 2024.