

Molecular dynamics simulation of Argon atoms

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Abstract: The aim of this project is to create a computer code which performs the simulation of the dynamics of a system of particles. The system in this case will be a box of Argon atoms with periodic boundary conditions. We use Argon atoms because the interaction can be computed using the Lennard-Jones potential. We will set the microscopic interactions of the system using a pair interaction picture and then study the macroscopic physical observables such as pressure, specific heat and the pair correlation function to explore the different phases of the system. In the light of the results obtained we can say Lennard-Jones potential is a good approximation for the interaction between Argon atoms.

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interaction of Argon atoms.

We will be interested in computing the macroscopic observables of the system, which will allow us to explore the different phases of the material for given values of density and temperature. The macroscopic observables computed will be pressure, specific heat and the pair correlation function. We will also study the behaviour of the energy and the velocities to see if the system is behaving as expected.

In section II, we will explain the theoretical model used for the simulation. This comprises the model that we used for the interactions [1, 2] and the description of the macroscopic physical observables that will allow us to explore the different phases of the system. In Section III we will explain how this model is implemented in our code. We will review features like the initial conditions, the algorithms used to integrate the equations of motion or the units of our parameters. Section IV is devoted to present our results and compare them with other simulations or experimental data. This paper ends with a conclusion where we review the key points of the project.

II. THEORETICAL MODEL

Our system consists of a box of N particles with periodic boundary conditions, which will simulate an infinite large system. In our case, N has been chosen to be 108 so that we have a full fcc lattice. As we have already mentioned, the particles interact with each other through a Lennard-Jones potential, which will be described in the classical equations of motion. Quantum effects will not be taken into account.

The choice of Argon particles is due to the fact that Argon is a noble gas and therefore we do not have to deal with the formation of molecules or other asymmetries of the system. That is one of the reasons why there is a lot of literature focused on the study of Argon gas [1].

The interaction of Argon atoms can be successfully described by the Lennard-Jones potential. This takes into

I. INTRODUCTION

We can get insight in the interaction potential of a theory comparing computer experiments with experimental data. In article we test Lennard-Jones potential through a computational model of Argon atoms interacting in different phases.

The first step of the project is to program the microscopic interactions between the particles. To do this, we will consider a Lennard-Jones potential and repeatedly integrate the equations of motion of our system. Note that we are using a model for a classical many body system with a lot of degrees of freedom. A comparison between our computational outcome and the experimental prediction will allow us to determine whether the Lennard-Jones is a good model for the

account the Pauli Exclusion principle in the short ranges and the attraction of molecules in the large distances [3].

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

Where $\sigma = 3.405\text{\AA}$ and $\epsilon = 119.6K_B K$ for Argon [4]. The attractive term accounts for the dipole moment due to the displacement of the nucleus and the electron cloud when two atoms approach. The repulsive term becomes dominant at short distances, when the Pauli blocking prevents approach. There is no Coulomb interaction because Argon atoms are neutral. From the Lennard-Jones potential we can read off the typical distance (in order of magnitude) of separation between atoms, σ .

In our computational model we will consider only a two body interaction between atoms and then sum over all interactions to obtain the force. The force acting on particle i will be:

$$\vec{F}(r_i) = - \sum_j \frac{\partial U(r)}{\partial r_{ij}} \hat{r}_{ij} = m_i \sum_j \frac{d^2 \vec{r}_{ij}(t)}{dt^2}, \quad (2)$$

where $U(r)$ is the Lennard-Jones potential and we are summing over all the other particles j .

The evolution of the system is governed by this force. The initial conditions of the system will also play an important role to determine the behaviour of the system, which will run for a finite amount of time. The initial conditions will be a fcc lattice with a given density and a Maxwell distribution of velocities for a given temperature, which will be re-scaled until the system is properly thermalized.

A. Physical observables

Computing macroscopic physical properties gives us a description of the behaviour of the system and will determine the state of the material. By defining specific initial conditions, we can observe phase transitions to other states of the material. Here we present the observables that will be computed.

a. Temperature. From the equipartition theorem we know that the relation between the temperature and the kinetic energy is the following:

$$E_{kin} = (N - 1) \frac{3}{2} k_B T. \quad (3)$$

If we fix the temperature of the system we should obtain the corresponding kinetic energy.

b. Pressure. The average pressure can be computed using:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \frac{1}{2} \sum_{i,j} r_{i,j} \frac{\partial U(r)}{\partial r_{ij}} \right\rangle, \quad (4)$$

where $\beta = \frac{1}{K_B T}$, ρ is the density of the system, N is the number of particles and U is the Lennard-Jones potential. We use relative distances because we consider a two body interaction and periodic boundary conditions of our system. In [1] some values are computed for the compressibility factor ($\frac{\beta P}{\rho}$). For a system with $\rho = 0.88$ and $T = 1.095$, which would correspond to the liquid phase, the value they obtained is 3.48.

c. Specific heat. The specific heat $c_v = \frac{C_v}{N}$ can be calculated from:

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} \left(1 - \frac{3N}{2C_v} \right), \quad (5)$$

where $\langle \delta K^2 \rangle$ are the kinetic energy fluctuations. When the kinetic energy fluctuations are large, the specific heat diverges and can become negative, so we will be interested in having a thermalized system for which the kinetic energy remains almost constant.

d. Pair correlation function. The pair correlation function gives the probability for a given reference particle to find another particle at a certain distance r :

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}, \quad (6)$$

where V is the volume of the box, N the number of particles and $\langle n(r) \rangle$ is the number of particles that can be found inside a shell with inner radius r and outer radius $r + \Delta r$.

One way to look at the phase transitions is through the pair correlation function. We expect that for a solid material there will be certain distances for which it is more likely to find particles. These distances will be related to the crystal structure of the lattice. However, for a liquid state this correlation should start disappearing since the atoms will not be bounded. This feature would be even more obvious in a gas state where there should not be any preferred distances at all.

III. IMPLEMENTATION

In this Section we will explain the implementation of the theoretical ideas in our code and the approximations that were done throughout the process.

A. Periodic boundary conditions

It is not possible to simulate an infinite system. A way to obtain a good approximation for it is to consider a box of particles with a given size and then apply periodic boundary conditions both in the positions and when computing the iterations. That is implemented by the minimal image convention, i.e. considering the distance between the particles to be the closest distance possible within the periodic boundary conditions.

This approximation has to be taken into account when computing some of the observables. For example, when computing the pair correlation function we need to consider distances up to half of the size of the box, since otherwise we would be over counting particles.

B. Units

In order to make coding simpler and for the values of physical quantities to be more clear we will use dimensionless parameters.

Since the typical distance is in the order of σ , the dimensionless position can be expressed in terms of that quantity. In the same way we can take ϵ as the energy unit (both for kinetic and potential energy).

$$\tilde{r} = \frac{r}{\sigma}, \quad \tilde{U} = \frac{U}{\epsilon}, \quad \tilde{T} = \frac{T}{\epsilon}.$$

Thus, the Lennard-Jones potential becomes:

$$\tilde{U}(\tilde{r}) = 4(\tilde{r}^{-12} - \tilde{r}^{-6}).$$

Regarding the time unit, we can arrange the mass of the atom, σ and ϵ so that:

$$\tilde{t} = \frac{t}{\sqrt{\frac{m\sigma^2}{\epsilon}}}$$

We will define the dimensionless temperature as the energy by taking the Boltzmann constant in natural units, so that it is defined as:

$$\tilde{T} = \frac{k_B T}{\epsilon}.$$

It is interesting to check which time step value would be adequate for the simulation. By the equipartition theorem, $v = \sqrt{\frac{3K_B T}{m}}$, where the natural unit for velocity is $\sqrt{\frac{\epsilon}{m}}$. Therefore, in dimensionless units and around room temperature (100 K):

$$\frac{v}{\sqrt{\frac{\epsilon}{m}}} = \sqrt{\frac{3K_B T}{\epsilon}} \sim 1, \quad (7)$$

since $\frac{\epsilon}{K_B} \sim 100$. From that, we can conclude that the time step h should be smaller than 1, of the order of $10^{-2} - 10^{-3}$. For our simulation, we choose a value of $h = 0.005$.

C. Verlet algorithm

The Verlet algorithm (see [1]) is the most simple and reliable numerical algorithm to integrate the equations of motion. It makes use of the fact that we are integrating a second order ODE (in dimensionless units):

$$\frac{d^2 \vec{r}}{dt^2} = \vec{F}(\vec{r}(t)). \quad (8)$$

If we do the Taylor expansion of $\vec{r}(t \pm h)$:

$$\vec{r}(t+h) = \vec{r}(t) + h\dot{\vec{r}}(t) + \frac{h^2}{2}\ddot{\vec{r}}(t) + \frac{h^3}{6}\frac{d^3\vec{r}(t)}{dt^3} + \mathcal{O}(h^4), \quad (9)$$

$$\vec{r}(t-h) = \vec{r}(t) - h\dot{\vec{r}}(t) + \frac{h^2}{2}\ddot{\vec{r}}(t) - \frac{h^3}{6}\frac{d^3\vec{r}(t)}{dt^3} + \mathcal{O}(h^4) \quad (10)$$

When we add this two equations, we find the standard form of the Verlet algorithm:

$$\vec{r}(t+h) = 2\vec{r}(t) - \vec{r}(t-h) + h^2\ddot{\vec{r}}(t). \quad (11)$$

The estimated error of each time step is, in the worst case, of the order of h^2 . This corresponds to the first iteration, for which we will use the following definition of the previous step:

$$\vec{r}(t-h) = \vec{r}(t) - h\vec{v}(t) + \mathcal{O}(h^2). \quad (12)$$

Otherwise, the error in the positions will be of the order of h^4 .

The velocities will be estimated from:

$$\vec{v}(t) = \frac{\vec{r}(t+h) - \vec{r}(t-h)}{2h} + \mathcal{O}(h^2). \quad (13)$$

In our program we make use a form of the algorithm which avoids the need for two force arrays, since this calculation takes a large amount of time:

$$\vec{v}' = \vec{v}(t) + h\vec{F}(t)/2, \quad (14)$$

$$\vec{r}(t+h) = \vec{r}(t) + h\vec{v}'(t), \quad (15)$$

$$\vec{v}(t+h) = \vec{v}' + h\vec{F}(t+h)/2, \quad (16)$$

where the new force $\vec{F}(t+h)$ is calculated between the second and third step.

D. Initial conditions

In our model there is a strong repulsive force for ranges typically smaller than σ . If we want the simulation to work properly it is essential that the atoms do not start very close to each other, otherwise the forces would be extremely large. This becomes simple if the initial positions are organised in a lattice structure. In the case of Argon molecules we chose face-centered cubic (fcc) lattice, which is one possible stable configuration of solid Argon [5]. We will also use this configuration for the liquid and gas states, but in this case it will change during the thermalization of the system.

In principle, we would not have to take special care of the initial velocities. When the system thermalizes by exchanging potential and kinetic energy the distribution of velocities will become Gaussian.

Nevertheless, we need to take into account the temperature of the system, since it is determined by the velocity

distribution of particles. Since we want to fix the temperature for our simulations, we will need to re-scale the velocities in order to reach the regime in which we want to work. We will first start with a Maxwell distribution for a temperature T , which is just a Gaussian distribution centered at the origin and with $\sigma = \sqrt{T}$ (in dimensionless units). By starting with this initial conditions, our system will equilibrate faster. Then, we will need approximately 300 iterations of the Verlet algorithm to thermalize the system, meaning 10 rescalings of the velocity of 30 iterations each, by a factor λ :

$$\lambda = \sqrt{\frac{(N-1)3k_B T}{\sum_i m v_i^2}}. \quad (17)$$

We know we have reached the thermalization of the system when λ is close to 1. During this thermalization kinetic and potential energy are exchanged up to a point where both, kinetic and potential, remain approximately constant. Since one of the outputs of our program is the plot of the energies (they can be seen in the Appendix) we can check both terms of the energy are constant.

E. Estimating errors

Most of the physical observables that we are computing involve the time average of a given quantity. Since the time of our system is not infinite, we can only estimate this expectation value using a finite amount of values. Therefore we need to take into account the error (or standard deviation):

$$\sigma_A = \sqrt{\frac{1}{N-1}(\langle A^2 \rangle - \langle A \rangle^2)}, \quad (18)$$

for an average of A , taking into account N values.

The data that we are dealing with is not statistically independent because each new configuration is generated from the previous one. This makes difficult the task of computing the standard deviation. A numerical way of doing this is to use the Bootstrap method.

The Bootstrap method is based on the random resampling of the N data points (with repetition) a given number of times (n). By doing this, we will obtain new samples, and for each new sample we will compute a new value for the average. From this data, the standard deviation is calculated again using:

$$\sigma_A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}. \quad (19)$$

Note that here there is no factor $\frac{1}{n-1}$ because the error does not become smaller when we do more resamplings. In our program we choose to do 50 resamplings and we compute the error for the pressure and the specific heat.

IV. RESULTS

In this section we present and comment on the results obtained for our simulation.

A. Energy conservation

The first and most obvious result is the energy conservation. This is a feature that allows us to easily check if the program is not working properly. As we find conservation of energy for all the simulations we just show the one for gas state.

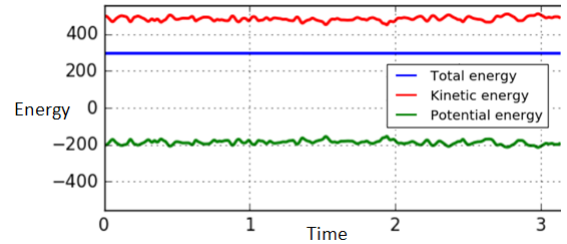


FIG. 1: Energy conservation for a gas of Argon atoms. Both time and energy are expressed in reduced units.

Note that there are no large fluctuations in the kinetic and potential energy. That indicates that when the simulation starts the system is already thermalized.

B. Pair correlation function

Figure 2 shows the pair correlation function for the three different matter states.

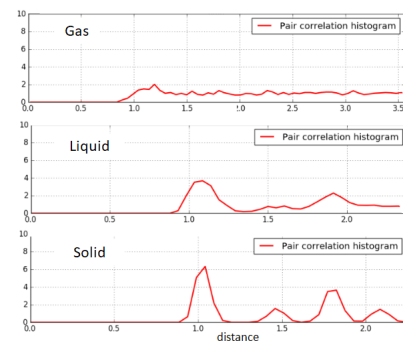


FIG. 2: Pair correlation function $g(r)$ for the three phases; gas, liquid and solid Argon. The x-axis represents a discrete array of distances at which we compute $g(r)$. For each case, the maximum distance taking into account the periodic boundary condition is half of the size of the box $L/2$. This is because at larger distances we would be over counting particles.

As we expected, in the solid state we see a higher prob-

ability of finding particles at certain distances from each other. That is reasonable since our solid keeps the fcc lattice structure. We can easily check this feature by comparing the correlation function of the solid after its thermalization and evolution with the fcc lattice one (corresponding to the initial condition), shown in figure 3.

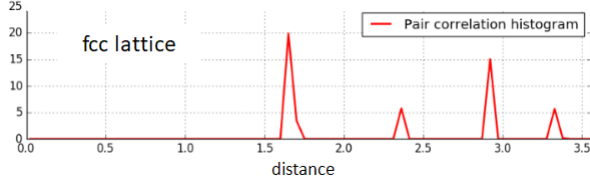


FIG. 3: Pair correlation function $g(r)$ for the fcc lattice corresponding to a size of 7 units. The structure looks very similar than the one for the solid phase in FIG. 2. The difference is due to the fact that we set up non zero initial velocities for the solid.

On the other hand, for the liquid phase we can see that the correlation is more uniform. This is even more obvious for the gas phase where there is no correlation at all. This feature was expected and is useful to check that we are working with the desired phase.

C. Pressure

The compressibility factor (i.e. pressure per unit density per unit temperature) obtained are shown in table I.

Gas	1.0923 ± 0.0064
Liquid	2.118 ± 0.012
Solid	14.4051 ± 0.0081

TABLE I: Compressibility obtained for the different phases in reduced units.

These results are within the same order of magnitude found in other references such as Verlet, 1967 [1] (see Section II).

D. Specific heat

The values obtained for specific heat are shown in Table II.

Gas	1.7540 ± 0.0019
Liquid	1.9285 ± 0.074
Solid	4.783 ± 0.0060

TABLE II: Values for the specific heat obtained for the different phases in dimensionless units.

Specific heat is inherent to every substance but it can be seen that there is a dependence of the specific heat with temperature. As we see in our results, the value for the specific heat is a bit higher for smaller temperatures, which would correspond to the solid state.

If we convert these values to the physical units again, we find the specific heat for Argon in the gas state to be $0.3666 \pm 0.0013 \frac{J}{gK}$. We can compare this value with the experimental one which is $0.54 \frac{J}{gK}$, obtaining relative error of the 30%.

It is worth noticeable that the behaviour of the specific heat for the solid phase is rather unstable in the beginning (see Figure 6). This is due to the fact that we calculate specific heat from deviations of kinetic energy and these are large in the beginning of the program. When the program starts running the fluctuation measured are big since we have very small data so the average value is not very accurate yet. After some time we see that it stabilises for a given value.

V. CONCLUSIONS

In this project we have simulated a computational model for Argon molecules where the atoms interact through the Lennard-Jones potential and we have successfully obtained values for macroscopic physical quantities. The value for specific heat obtained for Argon atoms in our simulation for the gas state is in the order of magnitude of the experimental result. The values obtained for the pressure and the pair correlation function agree with the theoretical perspective. We can conclude from here that Lennard-Jones potential is a good description of the interaction between Argon atoms. Other references [1] have explored other elements with less successful results.

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VI. APPENDIX

In this appendix we show all the results obtained with our code. Please, note that the error bars are not shown in the images since their value is small and not appreciable in the images. On the left it is shown a representation of each phase. We can see how for the solid state the lattice configuration remains during more than 1000 time steps of computation. On the right we present four different graphics. The first one shows the conservation of energy. Notice that we start the plotting after the thermalization. The second one is compressibility, followed by specific heat. Finally, we show the correlation function.

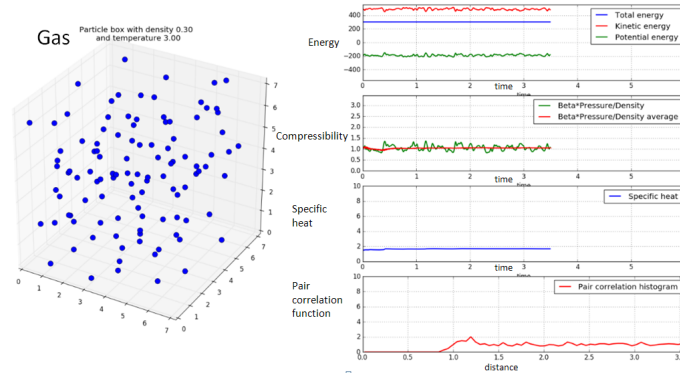


FIG. 4: Simulation for density 0.30 and temperature 3.0, which corresponds to the gas state of the system after a time of approximately 700 time steps of simulation.

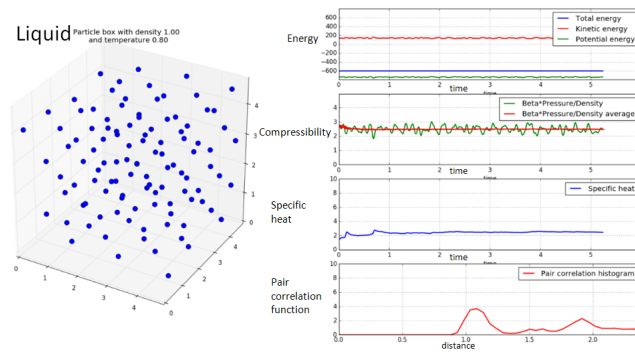


FIG. 5: Simulation for density 0.80 and temperature 1.0, which corresponds to the liquid state of the system after a time of approximately 1060 time steps of simulation.

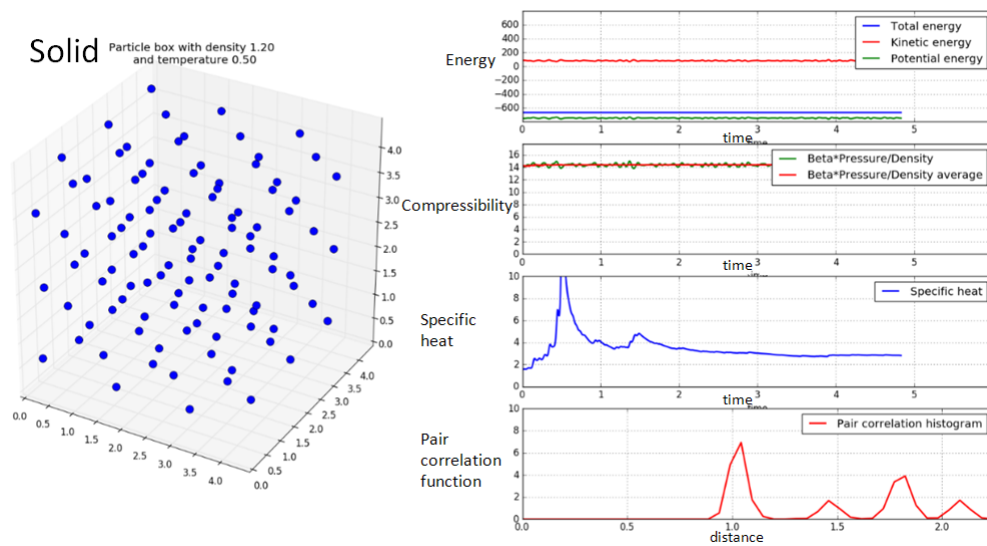


FIG. 6: Simulation for density 1.20 and temperature 0.5, which corresponds to the solid state of the system after a time of approximately 980 time steps of the simulation.