MD Simulation of Argon

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March 5, 2016

Abstract

Useful physical quantities, such as the Lennard-Jones force, temperature, pressure and heat capacity are extracted for argon using a molecular dynamics simulation written in Python. These quantities are found using the Lennard-Jones potential function and a velocity Verlet algorithm. For argon in gas, liquid and solid phase these quantities are simulated by varying the temperature and density.The results were compared to the literature values.

I. INTRODUCTION

$\mathbf{I}$N nature there are a lot of many particle systems. Each system has its own physical quantities which can be computed. To figure out these quantities a simulation technique is used, namely molecular dynamics (short: MD). MD solves the equations of Newton for each interacting atom and then calculates the forces between the particles and the potential energies. In this paper the behavior of an argon atom is simulated using molecular dynamics.

In section II we describe the different steps that need to be taken to compute the quantities of an argon atom. To calculate these quantities a MD program in Python is written. In section III we give and discuss the results for each quantity that is computed in the program. In section IV the conclusion is drawn for the MD simulation of argon.

II. METHODS

A. Interacting particles

We consider a system of $N = 108$ particles, enclosed in a cube of side L. Because we choose an argon atom we have a face-centered cubic lattice. We also choose to have periodic boundary conditions, because then the number of particles in the simulation volume will remain constant. The forces between two argon atoms can be described by the Lennard-Jones potential, $V(r)$:

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

with ϵ the strength of the potential energy , σ the value of r at which the energy is zero and r the distance between the centers of the two atoms. For argon the values are $\epsilon/k_b = 119.8K$ and $\sigma = 3.405\mathring{A}$, [1]. The intermolecular force, $F(r)$ is the gradient of the potential, which can be calculated from the Lennard-Jones potential:

$$F(r) = -\frac{dV(r)}{dr} = \frac{24\epsilon}{\sigma} \left[2(\frac{\sigma}{r})^{13} - (\frac{\sigma}{r})^7 \right] \quad (2)$$

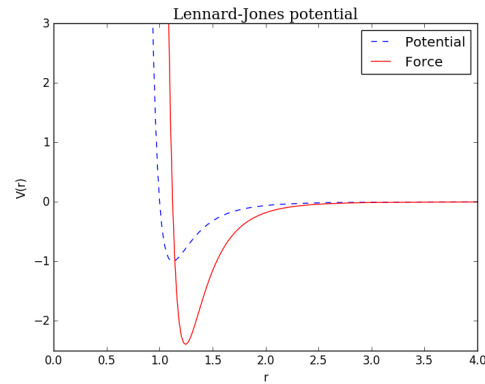**Figure 1:** *A graph of the Lennard Jones potential and force. We choose ϵ and σ to be 1.*

To compute some quantities we first have to solve Newton's equations of motions:

$$F_i = m_i \frac{d^2 r_i}{dt^2} \quad (3)$$

where m_i is the mass of the ith particle, F_i is the force acting on it and r_i is the position vector.

B. Velocit Verlet Algorithm

Solving this ODE is done with an algorithm. We use an algorithm that was invented by L. Verlet, [3], the velocity Verlet algorithm:

$$\overrightarrow{x}(t + \Delta t) = \overrightarrow{x}(t) + \overrightarrow{v}(t)\Delta t + \frac{1}{2}\overrightarrow{a}(t)\Delta t^2 \tag{4}$$

$$\overrightarrow{v}(t + \Delta t) = \overrightarrow{v}(t) + \frac{\overrightarrow{a}(t) + \overrightarrow{a}(t + \Delta t)}{2}\Delta t \tag{5}$$

with $\overrightarrow{x}$ the position vector, $\overrightarrow{v}$ the velocity vector and $\overrightarrow{a}$ the acceleration vector.

C. Energy

Because the Lennard Jones force is time independent, the total energy E is conserved. The total energy can be given by $E = E_{kin} + E_{pot}$. The potential energy, E_{pot}, is the Lennard Jones potential, (1), and the kinetic energy, E_{kin} is subscribed by:

$$K(t) = \frac{m}{2}\sum_{i=1}^{N}|v_i(t)|^2 \tag{6}$$

with m the mass of an atom and v_i the velocity of the particle. In our case the mass of an Argon atom is 6.63×10^{-26} kg.

D. Temperature

If the system is in thermal equilibrium, then Boltzmann's Equipartition Theorem relates the absolute temperature T to the kinetic energy, $K(t)$. Because Argon is a gas of monoatomic molecules it has three degrees of freedom, so its kinetic energy becomes:

$$K = \frac{3}{2}Nk_bT \tag{7}$$

with k_b the Boltzmann constant, which is 1.381×10^{-23} J K^{-1}. This equation can be rewritten to get the temperature.

E. Pressure

The pressure, P, can be found by solving the virial theorem, [1, 3]:

$$\frac{P}{n\,k_b\,T} = 1 - \frac{1}{3\,N\,k_b\,T}\langle\sum_i\sum_{j>i}r_{ij}\frac{\partial V(r)}{r_{ij}}\rangle_{cut-off}$$
$$- \frac{2\,\pi\,N}{3\,k_b\,T\,V}\int_{r_{cut-off}}^{\infty}r^3\frac{\partial V(r)}{r}g(r)\,dr \tag{8}$$

where the left hand side of the equation, $\frac{P}{n\,k_b\,T}$, is the compressibility factor, $g(r)$ is the pair correlation function which we discuss further on. On the right hand side the first part of the equation is for argon as an ideal gas, the second part is the virial theorem and the third part is a correction for all particles outside a certain cut-off distance.

F. Specific heat

From Lebowitz' theorem, [1, 4], we can find the specific heat, C_v:

$$\frac{\Delta E_{kin}^2}{\langle E_{kin}\rangle^2} = \frac{2}{3\,N}(1 - \frac{3\,N}{2\,C_v}) \tag{9}$$

where $\Delta E_k in$ is the fluctuation in kinetic energy. This equations only holds when the number of particles, the volume and the total energy are constant, which is our case.

G. Correlation function

The pair correlation function is useful to find the average distance between particles. Or in other words it describes how the density varies as a function of distance between particles. The correlation function is found in terms of n(r) as [1]:

$$g(r) = \frac{2V}{N(N-1)}\left[\frac{\langle n(r)\rangle}{4\pi r^2\Delta r}\right] \tag{10}$$

where r is the distance between particles and $n(r)$ number of pairs for an interval of $[i\Delta r, (i+1)\Delta r]$.

III.   Results and discussion

The following section we will be presenting the results. The quantities that are determined are the average temperature T, the pressure $\beta P/\rho$ and the specific heat C_v. These were determined with different kind of values for the following parameters: the density ρ and the initial temperature T_0, represented in table 1.

Table 1: *Table of thermodynamical results. With $\rho = N/V$ is the density, T_0 is the desired temperature and $\beta = 1/k_b T$ is the thermodynamic beta.*

$\rho(1/\sigma^3)$	$T_0(\epsilon/k_b)$	T	$\beta P/\rho$	C_v
0.88	1.0	1.0660	1.7155	2.1633
0.3	3.0	3.2053	1.1389	1.6378
1.2	0.5	0.5135	28.8044	2.5943
0.8	1.0	1.0457	1.7155	2.1633

A.   Gas phase

The parameters for the gas phase are $\rho = 0.3$ and $T_0 = 3$. A simulation with these parameters was done for the average temperature, the pressure and the specific heat. The results are pictured in figure 2a and figure 2b and in table 1. We see a maximum in the graph for the pair correlation function in figure 2b. This maximum represents the distance at where the most particles can be found. In the gas phase this is around $r = 1.0$. The reason why the maximum value does not have a distance smaller than 1 is because of the Lennard-Jones potential. As can be seen in figure 1 the minimum is around $r = 1$. We choose a higher temperature than the liquid or solid state and because of this higher temperature we are getting a higher potential energy that the other two states.

B.   Liquid phase

The parameters for the liquid phase are $\rho = 0.8$ and $T_0 = 1$. A simulation with these parameters was done for the average temperature, the pressure and the specific heat. The results are pictured in figure 2c and figure 2d and in table 1. As already mentioned in section A a

higher temperature results in a higher energy. Because we have a lower temperature, we see a lower kinetic and potential energy in figure 2c. In the liquid state of argon the pair correlation function has maxima around $r = 1$ and $r = 2$.

C.   Solid phase

The parameters for the solid phase are $\rho = 0.5$ and $T_0 = 1$. A simulation with these parameters was done for the average temperature, the pressure and the specific heat. The results are pictured in figure 2e and figure 2f and in table 1. This state has the lowest temperature simulated, so the system of argon atoms has the lowest kinetic and potential energy. We see a lot of peaks here, what can be explained by the FCC lattice. Because the atoms of argon oscillate at their positions in the lattice, the positions can be seen as innerparticle distances. We expect a peak at $r = 1$, $r = \sqrt{2}$, $r = \sqrt{3}$, etc. This is exactly what we see in figure 2f.

IV.   Conclusion

In this paper we looked at several quantities of argon. These quantities were the temperature, the pressure and the specific heat. We used a molecular dynamics simulation to get these. We obtained results for a gas, liquid and solid state of argon. These results resemble the literature values from table 2 very close.

Table 2: *Literature values for pressure and potential energy from J. Thijssen, [1]. With $\rho = N/V$ is the density, T_0 is the desired temperature and $\beta = 1/k_b T$ is the thermodynamic beta.*

| $\rho(1/\sigma^3)$	$T_0(\epsilon/k_b)$	T	$\beta P/\rho$	$U(\epsilon)$
0.88	1.0	0.990	2.98	−5.704
0.80	1.0	1.010	1.31	−5.271
0.70	1.0	1.014	1.06	−4.662

References

[1] J.M. Thijssen, *Computational Physics*, Cambridge University Press, 2007.

[2] A. Rahman, *Correlations in the Motion of Atoms in Liquid Argon*, Phys. Rev. 136(A405–A411), Oct. 1964.

[3] L. Verlet, *Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules*, Phys. Rev. 159(98) , July 1967.

[4] J.L. Lebowitz, L. K. Percus, L. Verlet, *Ensemble Dependence of Fluctuations with Application to Machine Computations*, Phys. Rev. 153(250) , January 1967.
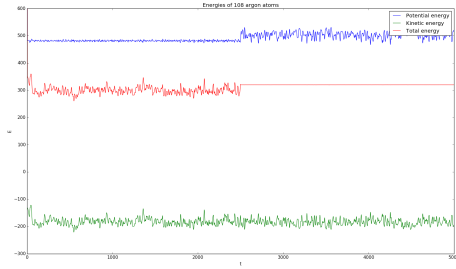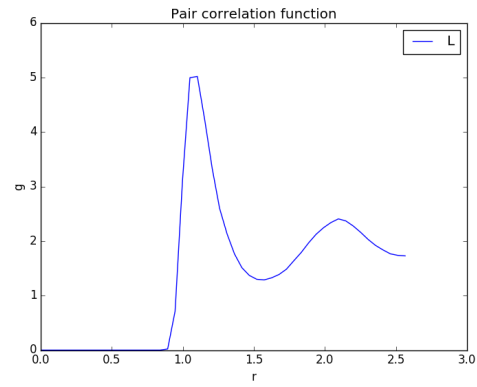
(a) *The kinetic, E_{kin}, potential, E_{pot}, and total energy, E, plotted as function of time, t. Argon is in the gas phase.*
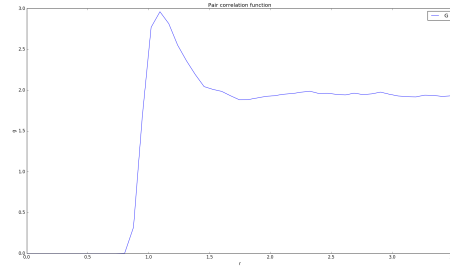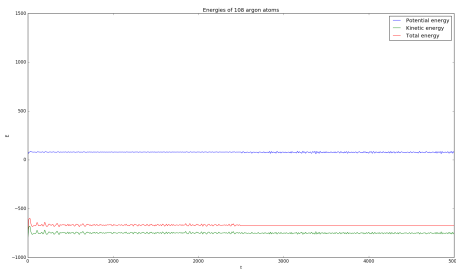

(b) *The pair correlation function, g, plotted as function of the distance, r.*
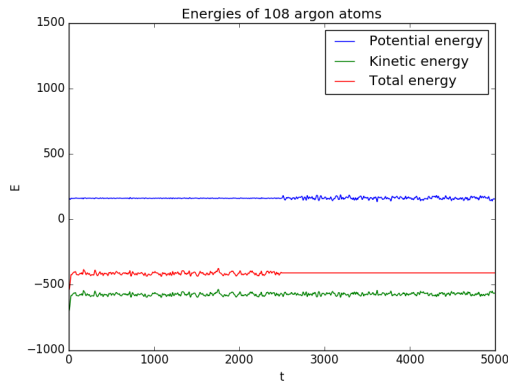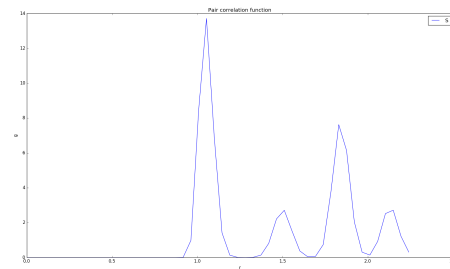

(c) *The kinetic, E_{kin}, potential, E_{pot}, and total energy, E, plotted as function of time, t. Argon is in the liquid phase.*

(d) *The pair correlation function, g, plotted as function of the distance, r.*

(e) *The kinetic, E_{kin}, potential, E_{pot}, and total energy, E, plotted as function of time, t. Argon is in the solid phase.*

(f) *The pair correlation function, g, plotted as function of the distance, r.*

Figure 2: *The energies and pair correlation functions of argon in gas, liquid and solid phase.*