

Molecular Dynamics Simulation of Argon

P. Hansler, D. Kuitenbrouwer, and A. Lovell

February 25, 2015

Abstract Write the abstract here - what the project is and what we are going to show.

1 Introduction

-demand for researching dynamical phenomena -MD is based on equations of motion, -i obtain static properties (pressure energy etc) but also one can obtain the location and momentum of each particle at each moment in time. -The latter is an advantage over other methods. [2] -MD is for example applied in biological physics, in the study of macromolecules [1] **Somewhere put something about the initial conditions - the whole crystal things, and pictures and whatnot for the unit cell, etc.**

Need some actual introduction about why molecular dynamics calculations are interesting or something of the sort to get the paper/report going. Can't just jump into everything. Some background or something.

This report is broken into the following sections. In Section 2, we will briefly discuss the theory behind the calculations in this report. Section ?? presents the results of our calculations, including a thermostat, correlation functions for the three states of matter, and pressure calculations. We will then give a brief conclusion in section 4. An appendix is found at the end of this report to discuss the method used for error analysis.

2 Theory

2.1 Crystalline Array

2.2 Interaction

To describe the interaction between each of the argon atoms, we use the Lennard-Jones potential, which accounts for the short-range repulsive force between the two atoms due to Coulomb repulsion and the longer-range attractive forces from dipole-dipole and dipole-induced dipole forces. The form of the potential is as

follows:

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

where r is the distance between the two atoms, ϵ gives the depth of the potential well, and $\sigma = 2R$ where R is the internuclear distance between the two atoms - σ measures the distance at which the potential between the two particles is zero.

put in a figure of the LJ potential and label everything - σ and ϵ

When the two atoms are far enough apart, they can be viewed as non-interacting. For this reason, we can introduced a cut-off radius, r_c , beyond which the potential is taken to be zero. Thus, we use the interaction **Look up how you've done this before**

From this, we immediately know the form of the force between the two atoms as well. The force is radial, acting to bring the atoms closer together if $r > r_{\min}$ and repelling them if $r < r_{\min}$. For our purposes, it is convenient to write the forces in terms of their Cartesian coordinates.

$$\begin{aligned} F_x &= 24\epsilon x \\ F_y &= 24\epsilon y \\ F_z &= 24\epsilon z \end{aligned} \quad (2)$$

From the force between each pair of particles, the momenta and positions can be calculated, leading to the dynamics of the system. This also allows calculation of thermodynamical quantities, such as pressure and correlation functions.

For these calculations, we will take $\epsilon = 1$ and $\sigma = 1$. **This is a terrible sentence: To extract dimensionally correct quantities, we can just account for this at the end of the calculations.**

2.3 Velocity Verlet Method

The paper is in *Phys. Rev.* **159**, **98** (1967). Also I have it written down in my comp phys notebook, so take the equations out of there - and make sure they match up with what is in the code. This paper is the Verlet method and not the velocity Verlet method, which seem to be different. Very similar to the **leapfrog algorithm**.

The method chosen for the position and momentum calculations is the Verlet method. While both can be calculated from introductory physics equations,

$$p_{i+1} = p_i + F\Delta t \quad (3)$$

and

$$x_{i+1} = x_i + \frac{p_i}{m} + \frac{1}{2} \frac{F(\Delta t)^2}{m} \quad (4)$$

this can lead to numerical inaccuracies in the position calculation because of the dependence on the square of the time step and both the previous force and momentum. **Now talk about the Verlet Method and how it works, which was actually used in the original paper during a molecular dynamics simulation of argon.**

The method still uses (3) for the updated momentum calculation, but instead of (4) for updating the position, one has

$$\text{position} \quad (5)$$

Maybe put in the derivation, and again why this is beneficial.

Along with taking $\epsilon = 1$ and $\sigma = 1$ in the Lennard-Jones potential, we will also take $m = 1$, with the same motivation. At the end of the calculations, we can always put the proper values back in to extract dimensionally correct quantities.

2.4 Thermodynamics

Along with updating the position and momentum of each particle to see how the system equilibrates, there are also several thermodynamical quantities that we can calculate in order to learn more about the system we have created. Before calculating any quantities, we want to model our system as being in contact with a thermostat to keep it at a constant temperature. We do this by renormalizing the velocity.

Through the Virial Theorem, the average velocity and temperature of a system are related by

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T \quad (6)$$

where m is the mass of the system, $\langle v^2 \rangle$ is the time average of the square of the velocity, k_B is Boltzmann's constant (equal to one in a system where we take temperature and energy to have the same unit), and T is the temperature of the system. Therefore, to enforce a target temperature, T_o in our system, the system must have a certain average velocity, $\langle v^2 \rangle_o$ given by

$$\frac{1}{2}m\langle v^2 \rangle_o = \frac{3}{2}k_B T_o \quad (7)$$

Dividing (6) by (7) and taking the square root of each side, we have

$$\sqrt{\frac{\langle v^2 \rangle}{\langle v^2 \rangle_o}} = \left(\frac{T}{T_o} \right)^{3/2} \quad (8)$$

Thus we can renormalize each velocity with

$$v = \lambda v_o \quad (9)$$

where $\lambda = (T/T_o)^{3/2}$ to ensure a constant temperature.

Once the system is at a constant temperature, we can calculate the correlation function. The correlation function measures the amount of disorder in a system, and therefore gives a distinct shape based on the state of matter - solid, liquid or gas. To calculate the correlation function, $g(r)$, we count the number of particles inside a spherical shell of $r + \delta r$ and normalize by the volume of that shell. Taking δr to be much smaller than r , we can approximate the volume of each shell by

$$\begin{aligned} \Delta V &= \frac{4}{3}\pi(r + \delta r)^3 - \frac{4}{3}\pi r^3 \\ &= \frac{4}{3}\pi \left[r^3 \left(1 + \frac{\delta r}{r} \right)^3 - r^3 \right] \\ &= \frac{4}{3}\pi \left[r^3 \left(1 + 3\frac{\delta r}{r} + \mathcal{O}(\delta r^2) \right) - r^3 \right] \\ &= 4\pi r^2 \delta r \end{aligned} \quad (10)$$

where the third line uses the Taylor approximation of $(1 + z)^n = 1 + nz + \dots$. Thus the correlation function is

$$g(r) = \frac{N_r}{4\pi r^2 \delta r} \quad (11)$$

There are many
of method - or
 nts and calculate
 put error bars on
 ous one is to run
 rocess is lengthy
 ng positions and

f time. In each
 ome mean value
y or something
each time step
 ber of time steps
 blocks, say 1500
 ivalent to having
 we can calculate
 ed as

(13)

(14)

ne quantity value

t for a decreasing

References

- [1] B. de Groot, Computational Biomolecular Dynamics Group, Max Planck Institute for Biophysical Chemistry. Retrieved from http://www3.mpibpc.mpg.de/groups/de_groot/
- [2] Thijssen, J.M.(2007). Computational Physics. Cambridge, Cambridge University Press.