Molecular Dynamics under Lennard-Jones potential

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(Dated: February 26, 2015)

In this report we outline the results obtained using a classical molecular dynamics model for atoms interacting under the Lennard-Jones potential. The simulations were run using values compatible to the dynamics of Argon atoms as done by *Verlet* [1]. We use the simulation to calculate the pressure, the heat capacity and the correlation function of this system for different temperatures and volumes. Moreover, for the liquid phase, we reproduce the results of *Alder & Wainwright* [2] which shows that the decay of the velocity autocorrelation goes as the power $-3/2$ with time.

INTRODUCTION

Molecular dynamics has been successfully used method for studying classical many-particles systems. It has been used for the study of systems in equilibrium and also for the understanding of the behavior out of equilibrium [3]. The methodology behind the simulation is simple and consists on integrating the classical equation of motion ($\vec{F} = m\vec{a}$) through time. However, there are some subtleties used for the computation of the problem which will be explained in the next section.

In the reported simulations, both the number of particles and the system volume are kept constant. And, as a result of the fact that the forces depend only on the relative positions of the particles, both the total momentum and energy of the systems are constant, which implies that this is equivalent to a microcanonical ensemble.

The physical quantities of the system are obtained through the calculation of the ensemble averages. Therefore, we need to use a reasonable number of particles in the simulations. In our simulations we use 864 particles in line with the literature [1, 4].

In the following sections we describe the methods employed in the simulation of the molecular dynamics under the Lennard-Jones potential. Subsequently, the thermodynamic quantities and the correlation functions are presented. Finally, we discuss about the decay of the velocity autocorrelation function.

SIMULATION DESCRIPTION

The simulation approach used follows closely the description of section 8.2-4 of the book of *Thijssen* [5]. As mentioned before, we consider that the particles interact through the Lennard-Jones potential:

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

In all the simulations we follow the approach of *Verlet* [1] and use natural units, with $\epsilon = 1$, $\sigma = 1$, $m = 1$ and the Boltzmann constant $k_B = 1$. Hence, all lengths are given in units of σ, the energies are in units of ϵ and the temperature in units of ϵ/k_B. For argon, $\sigma = 3.405\text{Å}$, $\epsilon/k_B = 119.8\text{K}$ [6] and $m = 39.948\text{u}$. Using natural units we can write the force between two particles as:

$$\vec{F}_{ij} = 24 \left(\vec{r_i} - \vec{r_j} \right) \left(2 r_{ij}^{-14} - r_{ij}^{-8} \right) \tag{2}$$

where $r_{ij} = |\vec{r_i} - \vec{r_j}|$. The force over each particle is calculated as the sum over all the pairs of the force acting over it. However, we apply a cutoff distance over which we consider that the force vanishes. This is reasonable looking at the form of the force, which decays as r^{-8} for long distances. In accordance to the literature we choose $r_{\text{cutoff}} = 3.3\sigma$ [1, 5], but we do not include in our simulation a neighbour list.

With the force, to calculate the motion of the particles we need an integration method for the second order equation we need to solve ($\vec{F} = m\ddot{\vec{r}}$). This is accomplished by the use of the *Verlet Algorithm*. We outline below how the algorithm is implemented. For the details regarding the theory behind it, we recommend the reader to look at Sections 8.4 and A.7.1 of *Thijssen* book [5]. Using a time step h, the update of positions and velocities are done by:

$$\begin{aligned} &\vec{v}(h/2) = \vec{v}(0) + \vec{a}(0)\frac{h}{2} \\ &\vec{r}(h) = \vec{r}(0) + \vec{v}(h/2)h \\ &\text{Calculate } \vec{a}(h) \text{ using } \vec{r}(h) \\ &\vec{v}(h) = \vec{v}(h/2) + \vec{a}(h)\frac{h}{2} \end{aligned} \tag{3}$$

It is important to point out that the accumulated error in position after a large number of integration steps is $\mathcal{O}(h^2)$. The same holds true for the velocity. Although better precision algorithms could be implemented, the *Verlet algorithm* has the advantage of being simple and stable. Most important, the algorithm is time reversible, which warranties that the integrator will not lead to energy drift (arithmetic errors can lead to drift for long times). This is a property of the more general concept of *sympletic integrators*, which has the property of generating solutions with the same geometric properties in phase space as the continuum dynamical system. The *Verlet algorithm* is the simplest implementation of this class of integrators.

Initial conditions

Periodic boundary conditions

THERMODYNAMIC QUANTITIES

CORRELATION FUNCTION

Choice of the time step

**DECAY OF THE VELOCITY
AUTOCORRELATION FUNCTION**

CONCLUSION

In natural units, the time is given in units of $\tau = \sqrt{m\sigma^2/\epsilon}$ which, for Argon atoms, is equal to 2.156ps. Approximating the Lennard-Jones potential as an harmonic potential around the minimum, we can estimate the oscillation frequency. This is given by $\omega^2 = \frac{72\epsilon}{m2^{1/3}\sigma^2}$, which means that the period of oscillation is $T \approx 0.83\tau$. Hence, we need to choose the time step to be a small fraction os this period. In our simulations we use $h = 0.004\tau$, which is around 5% of the period and is around 10^{-14}s for argon, in line with the literature [4].

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