

# Molecular Dynamics Simulation of a Lenard-Jones Interacting Molecule for Obtaining Macroscopic Static Physical Properties

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## Abstract

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## I. INTRODUCTION

**I**N this paper we intend to derive experimental macroscopic properties of a material from a microscopic description of the molecular interactions. In statistical physics many macroscopic quantities of many-particle systems can be found as an ensemble average over the possible microscopic states. Any practical macroscopic system consists of so many possible microscopic states that it is infeasible to average over all of the possible states computationally. But given a large subset of the possible states, we may assume that physical quantities averaged over the subset are close to the ensemble average. In molecular dynamics (MD) we initialize a specific state determined by some system parameters and let it evolve in time, traversing along its physical trajectory in the phase space as determined by the equations of motion. We therefore generate a large subset of possible states which are correlated in time. Using appropriate averaging over time we can obtain estimates of the ensemble average and therefore the relevant physical quantities.

We restrict ourselves to studying static physical properties of the system at equilibrium, although MD could also be used to study dynamical properties of a system. We carry out simulations for Argon, which is studied extensively in the literature and is modeled easily using the Lenard-Jones interaction potential. First we compute the heat capacity and compare it to theoretical results in the case of a hot and dilute gas or a cold and dense solid to verify the result. Next we compute the pressure as a function of the density at different temperatures and compare this with experimental results. Finally we compute the pair correlation function and comment on its qualitative behavior.

## II. METHODS

### II.I. Molecular Dynamics and the interaction potential for Argon

For the simulation a box of fixed dimensions  $L \times L \times L$  is considered containing  $N$  particles obeying periodic boundary conditions. During the simulation we keep track of the particle positions  $\mathbf{r}_i$  and particle velocities  $\mathbf{v}_i$ . At each time step we calculate the total force on each particle  $i$  due to the interaction potential  $U(\mathbf{r}_i, \mathbf{r}_j)$  with all other particles  $j$ . We assume only pairwise interaction between the particles and that this interaction only depends on the distance between particles  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . An interaction potential that works particularly well for argon is the Lennard-Jones potential which is given by

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

The total force  $\mathbf{F}_i$  on a single particle  $i$  is then given by

$$\mathbf{F}_i = - \sum_{j \neq i}^N \frac{\partial u_{LJ}}{\partial r} \bigg|_{r=|\mathbf{r}_{ij}|} \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|} \quad (2)$$

We neglect any external forces, resulting in the following equations of motion of the  $N$  particles

$$\frac{\partial^2 \mathbf{r}_i}{\partial t^2} = \frac{\mathbf{F}_i}{m_i} \quad i \in [1, N] \quad (3)$$

#### Discretisation: Verlet Algorithm

The simulation is performed using time steps of size  $\Delta t$ , the equations of motion are then discretised using the Verlet algorithm [1]. For the position vectors we get

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{F}_i}{m}(\Delta t)^2, \quad i \in [1, N], \quad (4)$$

and for the velocity at  $T + \Delta t$  we get

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \Delta t \frac{\mathbf{F}_i(t + \Delta t) + \mathbf{F}_i(t)}{2m}, \quad i \in [1, N]. \quad (5)$$

#### Periodic Boundary Conditions

After each coordinate update, we need to check if the particles still reside within the boundaries of the box. If this is not the case we use periodic boundary conditions to translate the particles by the box length  $L$  back in the box. These periodic boundary conditions can be applied separately in each dimension, so for a single dimension  $x$  we get the following update rule for the position of a single particle

$$r_x \rightarrow r_x \mod L \quad (6)$$

And the same holds for the  $y$  and  $z$  coordinates of the particle. These boundary conditions are also applied in the force calculation by the sum of (2), where the closest image of the particle  $j$  with respect to particle  $i$  is chosen to be used, since that gives the largest contribution to the force. Indeed, if  $L > 5\sigma$  then all other images of particle  $j$  are further away from particle  $i$  than the typical cutoff distance of  $2.5\sigma$  for the Lenard-Jones potential and therefore their contributions to  $\mathbf{F}_i$  can be neglected.

### Initial conditions

Solid argon at low temperatures and high density is experimentally seen to form an FCC lattice. The FCC is an orthorhombic lattice containing four particles per unit cell. If we assume the first particle to be located at position  $(0,0,0)$  the others are located at  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)$  if the unit cell has length 1. We use these positions as initial positions for the particles.

For the initial velocity we use the fact that the probability of a particle having a certain kinetic energy  $K$  is given by the boltzmann weight

$$P(K_i) \sim e^{-\frac{|\mathbf{v}_i|^2}{2T}} \quad (7)$$

From this we can see that each component of  $\mathbf{v}_i$  is normally distributed with mean zero and standard deviation equal to  $\sqrt{T}$ , where we used the natural units described in the next section. Due to the finite amount of particles, sampling from the normal distribution with mean zero will in general not result in a zero mean velocity. To compensate for this we subtract the residual mean velocity after sampling ensuring that there is no net momentum.

### Natural Units of Computation

Since the Lennard-Jones potential((1)) is based on two parameters  $\sigma[m]$  and  $\epsilon[J]$ , we define our distance in units of  $\sigma$  and energy in units of  $\epsilon$ . For the total SI system to be written in these natural units we need a third unit, so let's take the mass  $m$  equal to one (the unit of mass is thus the argon atomic mass). The temperature will then be expressed as  $T = \epsilon/k_B$ . These choices will also defines the unit of time as  $\tau = \sqrt{m\sigma^2/\epsilon}$ . This generalizes our model to any molecule obeying the LJ potential and forms a FCC lattice structure. If the units have to be transformed back to SI units one can simply fill in the literature values of  $\epsilon$ ,  $\sigma$  and  $m$  for the specific material. For argon these values are  $\epsilon_{Ar} = 120 \text{ k}_B$ ,  $\sigma_{Ar} = 0.34 \text{ nm}$  and  $m_{Ar} = 39.95 \frac{\text{g}}{\text{mol}}$  where  $k_B$  is Boltzmann's constant. So a temperature  $T = 1$  in our simulation for argon would then correspond to  $T = 120 \text{ K}$  in SI units. For argon, we also find  $\tau \approx 2.15 \cdot 10^{-15} \text{ s}$ .

### The (N, V, E) and (N, V, T) ensemble

Since we allow for a random initial kinetic energy  $K$  and then conserve the total energy, we effectively simulate the micro-canonical ensemble (N, V, E). It is also possible to simulate the canonical ensemble (N, V, T). This amounts to our system being surrounded by a large heat bath of constant temperature. In this ensemble we therefore need the kinetic energy to remain constant. This can be achieved by rescaling the velocity at each time step as to remain at a constant kinetic energy corresponding to the temperature  $T$

$$\mathbf{v}_i \rightarrow \sqrt{\frac{3T}{\frac{1}{N} \sum_{j=1}^N |\mathbf{v}_j|^2}} \mathbf{v}_i \quad (8)$$

## II.II. Computation of physical quantities

### Computation of the heat capacity

Computing the heat capacity at constant volume can be done in the canonical ensemble using the partition function, which can ultimately be related to the rms-fluctuations of the total energy.

However in this paper, we wish to compute the heat capacity at constant volume in the microcanonical ensemble. In the microcanonical ensemble, the heat capacity at constant volume can be computed from the rms fluctuations in the kinetic energy using a formula derived by Lebowitz[2]

$$\frac{\langle K^2 \rangle - \langle K \rangle^2}{\langle K \rangle^2} = \frac{2}{3N} \left( 1 - \frac{3N}{2C_V} \right), \quad (9)$$

where  $K$  denotes the kinetic energy, and  $N$  the total number of particles.

### Computation of the pressure

From eq. 7.36 Thijssen, using  $n\beta = \frac{2K}{3L^3}$

$$P = \frac{1}{3L^3} \left\langle 2K - \sum_{i<j}^N r_{ij} \frac{\partial V}{\partial r} \right\rangle \quad (10)$$

### Computation of the pair correlation function

The pair correlation function  $g(r)$  gives information on how the density  $n(r)$  varies as function of distance from a given reference particle compared tot the ideal gas. This is given by[3]

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \quad (11)$$

where  $\langle n(r) \rangle$  is numerically approximated by a histogram of the amount of particles in an inter-particle separation range of  $\Delta r$ .

## III. RESULTS AND DISCUSSION

In all of our simulation, we evolve in time using a time step  $\Delta t = 0.004$  in units of the natural time  $\tau$ . Unless otherwise specified, we simulate  $N = 864$  particles, which is 6 unit cells of the lattice in each dimension. Other free parameters are the density  $\rho$  and temperature  $T$  both in our natural units system. From the density and the number of particles, the volume of computations follows.

### III.I. Heat Capacity at Constant Volume

Using the parameters  $N = 864$ ,  $\rho = 0.01$  and  $T = 2.0$  simulating a hot and dilute gas, we compute the heat capacity at constant volume using (9). We find  $\frac{C_V}{N} = 1.509 \pm 0.002$  in units of  $k_B$ . We see that this is very close to the ideal gas value of  $C_V = \frac{3}{2}Nk_B$  for an ideal gas. The reason that it deviates slightly from the ideal gas case is because even though we simulate a hot and dilute gas, there is still a little bit of interaction between the argon particles, whereas the ideal gas model assumes no interaction at all.

In a second simulation we used  $N = 864$ ,  $\rho = 0.99$  and  $T = 0.1$  simulating a cold, dense solid. Computing the heat capacity using these parameters results in  $\frac{C_V}{N} = 2.99 \pm 0.12$ . This is close to the theoretical result of  $C_V = 3Nk_B$  for a system of  $N$  independent particles with 3 degrees of freedom in velocity and 3 degrees of freedom in a harmonic potential.

It is worth noting that in the first simulation only 40.000 time steps were taken, providing a formidable computational uncertainty, whereas the second simulation ran for 600.000 time steps and yields a much larger uncertainty. The reason for this is that in de dilute gas case the

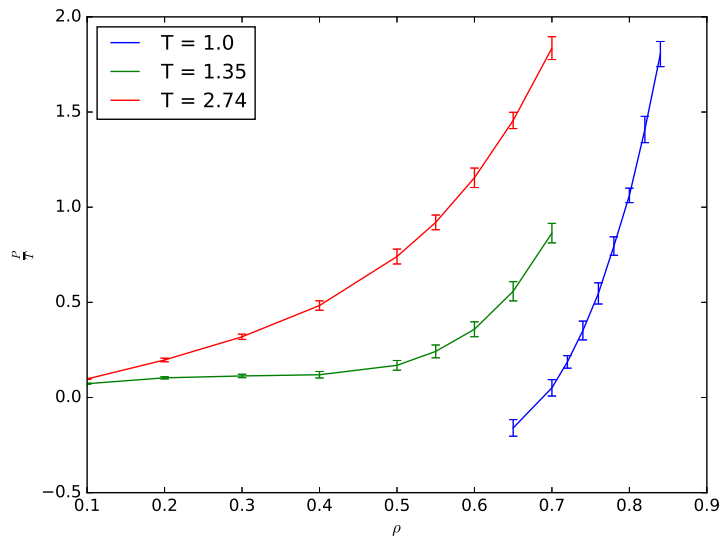


Figure 1

fluctuations in kinetic energy are negligible and computational fluctuations are averaged out fast enough. This effectively puts to left hand side of (9) to zero, yielding the result. However, in the dense solid case, the fluctuations in kinetic energy are due to physical reasons too, namely the particles being in independent harmonic potentials, constantly exchanging potential and kinetic energy as they vibrate in their lattice. It takes much more time averaging to accurately capture these fluctuations, while filtering out any computational errors.

### III.II. Pressure as a function of density at various temperatures

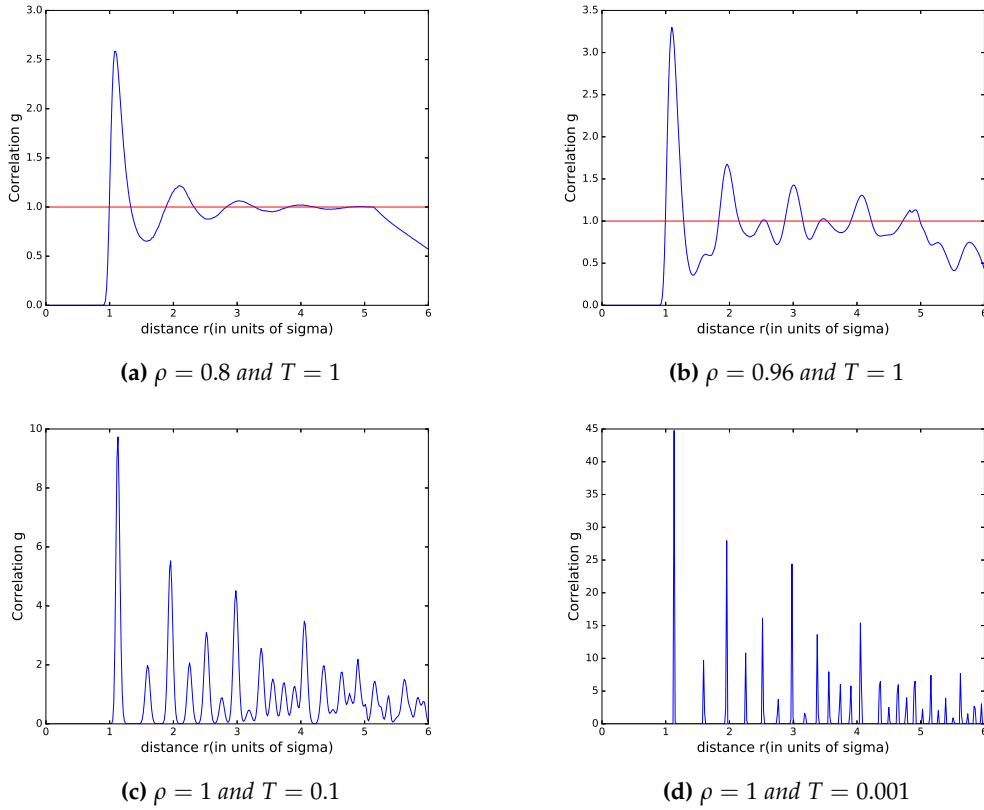
Bla bla results pressure.....

### III.III. Correlation function

For the correlation function we use the (N, V, T) ensemble, so the velocity is scaled at each timestep as to keep a constant kinetic energy. The correlation function is then calculated using (11). In figure 2 the results are shown for the gas, solid and liquid phase. The fall off at large distances is due to the finite amount of unit cells taken(6). In the solid phase, 2c and 2d, the effect of temperature is clearly visible in the increase of peak height and decrease of peak width at lower temperature, since the molecules have less oscillation amplitude, giving less spread in  $g$ .

## IV. CONCLUSIONS

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**Figure 2:** Shows four evaluations of the correlation function at different densities and Temperature. The gas phase is shown in a, where we clearly see the convergence to 1 for large distances. In b the density a liquid phase is seen. In c and d one clearly sees the discrete peaks corresponding to the FCC structure seen in a solid.

## REFERENCES

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