

Physics 905:

Simulation of Argon using Classical Molecular Dynamics

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Abstract

A classical molecular dynamics (MD) algorithm was developed using the micro-canonical ensemble and the Verlet Algorithm. The energy was maintained at roughly a constant value by implementing an Andersen Thermostat. The mean squared displacement of the atoms and the pressure of the system were calculated for $T=1-4$ at intervals of 1. Both mean squared displacement and pressure increased as the temperature of the system was increased.

1 Introduction

Molecular dynamics is a computational technique which allows the movement of atoms over time to be studied and can be used to calculate system properties such as diffusion. One application where this is interesting is in computational materials science where defects can be introduced into a system and the diffusion of atoms of a particular element can be studied. Molecular dynamics (MD) can be done using classical physics and using Newtons Equation of motion in Equation 1, classical MD, or using first-principles and solving *Schrödinger's* equation, ab-initio MD.

$$\vec{F} = m\vec{a} \tag{1}$$

In this report classical MD is used to simulate a system with a face center cubic (FCC) structure, like Argon. The results are analyzed by calculating the mean squared displacement and pressure at various temperatures.

2 Computational Details

The Molecular Dynamics algorithm reported here used the canonical ensemble, or the NVE ensemble (the number of atoms, volume and energy are kept constant), and used an Andersen thermostat. First a face center cubic (FCC) lattice was initialized and then the Box-Muller method was used to initialize the velocities. Then the system was updated at time steps, δt , of 0.0001 for 10000 time steps. At each time step the Verlet algorithm was invoked to update the positions and velocities of the atoms, and the energies (kinetic, potential and total) of the system were calculated. The results were then used to calculate the mean-squared displacement and pressure of the system at several temperatures. Below are details of the algorithm.

2.1 Initial Lattice

The initial coordinates were set up as a FCC lattice where the shortest distance between two atoms was scaled to be $2^{1/6}\sigma$. The shortest distance between two atoms was scaled as such because $2^{1/6}\sigma$ is where the Lennard-Jones potential energy is at a minimum, or where the derivative of the Lennard-Jones potential energy is zero, as seen in Figure 1. The unit cell was then replicated to make a supercell which is 3x3x3 unit cells or 108 atoms, because an FCC unit cell has four unique atom positions.

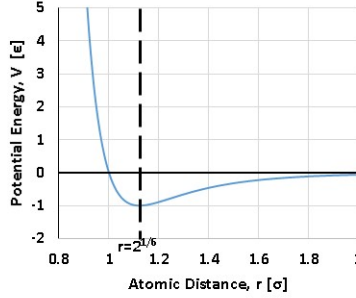


Figure 1: The Lennard-Jones potential where $r=2^{1/6}\sigma$ corresponds to the interatomic distance with the lowest energy.

2.2 Initializing Velocities using the Box-Muller Method

The initial velocities were then randomized using the Box-Muller method. Random numbers, U_1 and U_2 were chosen between 0 and 1. These random numbers were then used to calculate two random numbers on the normal distribution by using the Box-Muller method, Equations 2 and 3.

$$Z_1 = \sqrt{-2\ln U_1} \cos(2\pi U_2) \quad (2)$$

$$Z_2 = \sqrt{-2\ln U_1} \sin(2\pi U_2) \quad (3)$$

These normally distributed numbers were then used to calculate the velocities by using Equation 3. To obtain a velocity in each of the three dimensions this process was done twice and three of the calculated velocities were used for the x,y and z velocity components.

$$v_i = (k_B T / m)^{1/2} Z_i \quad (4)$$

2.3 Lennard-Jones Potential

The potential energy, $V(r)$, arising from the interaction of each pair of atoms at a distance, r , from each other was calculated using the Lennard-Jones Potential, Equation 5.

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5)$$

The force on each atom from every other atom was calculated by taking the derivative of the Lennard-Jones Potential at r , Equation 6.

$$F = \frac{dV}{dr} = -24\epsilon \left[\left(\frac{\sigma^6}{r^7} \right) - \left(\frac{2\sigma^{12}}{r^{13}} \right) \right] \hat{r} \quad (6)$$

2.4 Updating Positions and Velocities using the Verlet Algorithm

The positions were updated by using the Taylor Series expansion for position, Equation 7, and the velocities were updated by using the Taylor Series expansion for velocity where the derivative of velocity with respect to time was taken as the average of the acceleration at the current time step and the next time step, Equation 8.

$$x(t + \delta t) = x(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 \quad (7)$$

$$v(t + \delta t) = v(t) + \frac{1}{2}(a(t) + a(t + \delta t))\delta t \quad (8)$$

$$a_t = \frac{F_t}{m} \quad (9)$$

Equations 7 and 8 solved by using the Verlet Algorithm. This was done by replacing the variable v with Equation 10, calculating the new positions with v using Equation 11, recalculating the forces on/accelerations of the atoms in the system and then updating the velocities using Equation 10 again with the new accelerations.

$$v = v + \frac{1}{2}a\delta t \quad (10)$$

$$x = x + v\delta t \quad (11)$$

2.5 Andersen Thermostat

The Andersen Thermostat was used five times, once every 100 time steps for the first 500 time steps, in order to maintain a constant energy value. The Andersen Thermostat scales the velocities, v , by a factor to return the temperature, T , back to the initial temperature, T_0 . The value of T was computed using Equation 12, a relationship between the Maxwell-Boltzmann distribution and the kinetic energy. The constant that the velocities needed to be scaled by, $\sqrt{\frac{T_0}{T}}$, was determined by finding the ratio of Equation 12 at the initial temperature and desired velocity to Equation 12 at the current velocities and temperature. Then Equation 13 was used to update the velocities to the correctly scaled values.

$$\frac{3}{2}(N - 1)k_B T = \frac{1}{2} \sum_i m_i |\vec{v}_i|^2 \quad (12)$$

$$v = \sqrt{\frac{T_0}{T}} v \quad (13)$$

2.6 Periodic Boundary Conditions

The periodic boundary conditions of the system are accounted for when the shortest distance between two atoms must be found for the forces and potential energies to be calculated. This is done by using Equation 14 to find the distance between the atoms and then adjusting the distance between the atoms using Equation 15, where the `boxLength` is the length of the sides of the cubic supercell.

$$dr(:) = r(j,:) - r(i,:) \quad (14)$$

$$dr(:) = dr(:) - NINT(dr(:)/boxLength) * boxLength \quad (15)$$

Equation 15 allows the shortest distance between two atoms to be found by subtracting the length of the box from the distance between the atoms if the distance between the atoms is more than half of the box length.

Additionally, the position of the atoms must be readjusted if necessary so that they lie within the supercell lattice. This is done using Equation 16.

$$r(:, :) = Modulo(r(:, :), boxLength) \quad (16)$$

2.7 Pressure

The system pressure is calculated using the ideal gas law plus a correction factor, from the virial theorem, since it is not like an ideal gas at every temperature, Equation 17.

$$p = \frac{1}{V} \left(Nk_B T + \frac{1}{3} \sum_{i < j} \vec{r}_{ij} \cdot \vec{F}_{ij} \right) \quad (17)$$

2.8 Mean Squared Displacement

The mean squared displacement (MSD) of the atoms is a way to analyze the diffusion behavior of the atoms and was calculated using Equation 18.

$$MSD = \frac{1}{N} \sum_{i=1}^N (x_i(t) - x_i(t=0))^2 \quad (18)$$

The diffusion coefficient, D , can be calculated by plotting the MSD against time, t , and dividing by 6, as seen by the relationship between MSD and D in Einstein's equation or Equation 19.

$$MSD = 6Dt \quad (19)$$

Diffusion is exponentially dependent on temperature, as seen by the Arrhenius equation in Equation 20. The values of D , D_0 and E were not calculated in this report but they can be calculated from the data reported here.

$$D = D_0 \exp(-E/k_B T) \quad (20)$$

3 Results and Discussion

The kinetic, potential and total energies were calculated for $T=1-4$ at increments of 1. When the Andersen Thermostat was not applied the kinetic energy decreased initially before equilibrating, as seen for $T=3.0$ which is plotted in Figure 2.

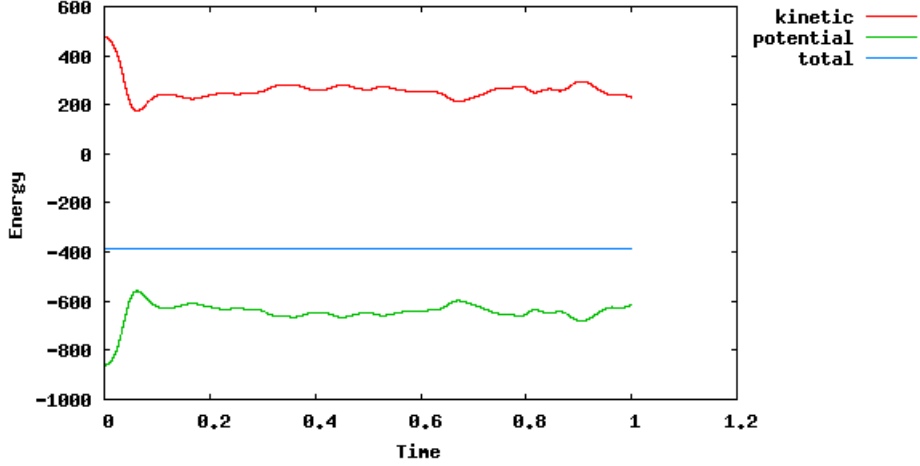


Figure 2: Calculated values of total, kinetic and potential energy for $T=3.0$ without applying the Andersen Thermostat.

Applying the thermostat corrected this initial decrease and made the equilibrated temperature at the end of the simulation closer to the initial temperature, as seen for $T=3.0$ in Figure 3.

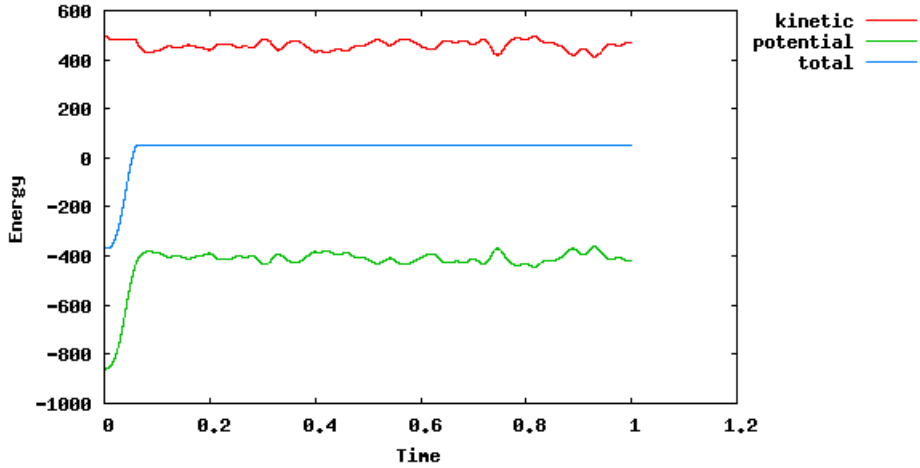


Figure 3: Calculated values of total, kinetic and potential energy for $T=3.0$ with applying the Andersen Thermostat.

The total energies at each calculated temperature were each compared, Figure 4. The

observed trend was that total energy increases as temperature increases, which is intuitive because the atoms move more at higher temperatures. Additionally, at $T=1.0$ the energy appears to be largely potential and at higher temperatures the energy seems to largely come from kinetic energy. This also is intuitive because the atoms should move faster at higher temperatures.

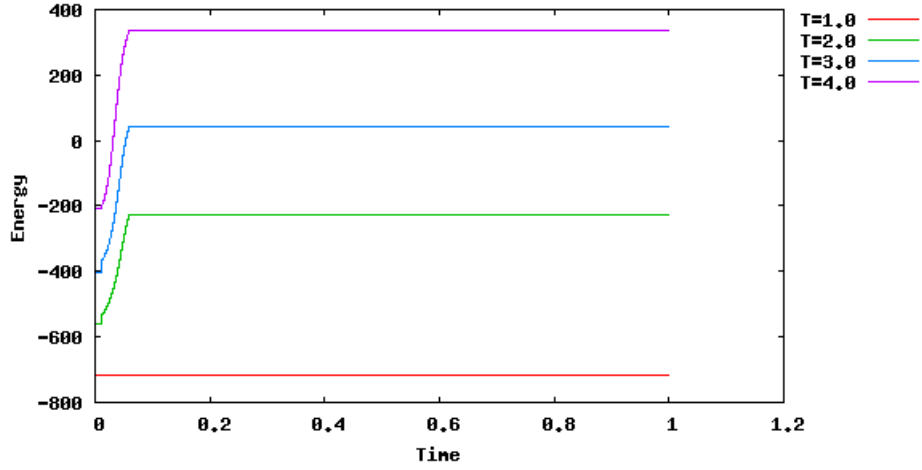


Figure 4: Calculated values of total energy for $T=1.0-4.0$, with the Andersen Thermostat applied.

The MSD was also calculated for $T=1-4$, Figure 5. The slope of the MSD line increased as T increased which implies that the diffusion coefficient increased as T increased. This is logical because from the Arrhenius equation, Equation 20, it is known that D is exponentially dependent on T .

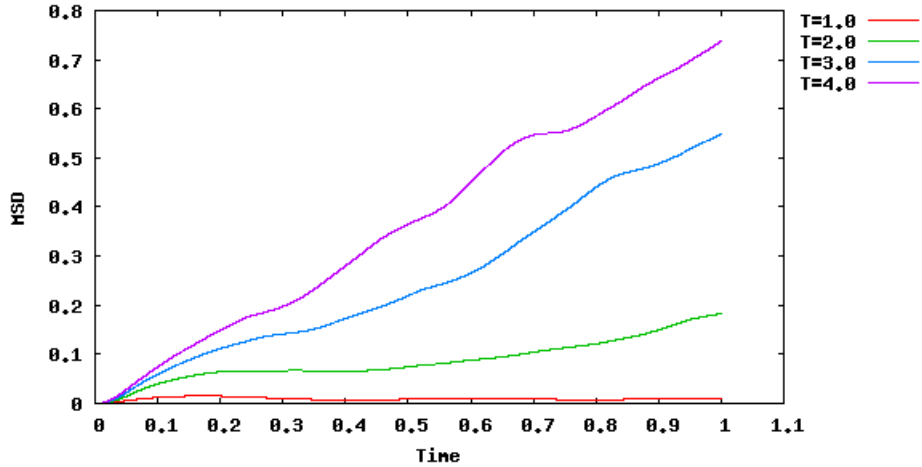


Figure 5: Calculated values of MSD for $T=1.0-4.0$, with the Andersen Thermostat applied.

The value of pressure was calculated at $T=1-4$ and plotted in Figure 6. From Figure 6 it is evident that the magnitude of pressure increased as T increased. This is logically because as the system is heated the atoms should be moving faster.

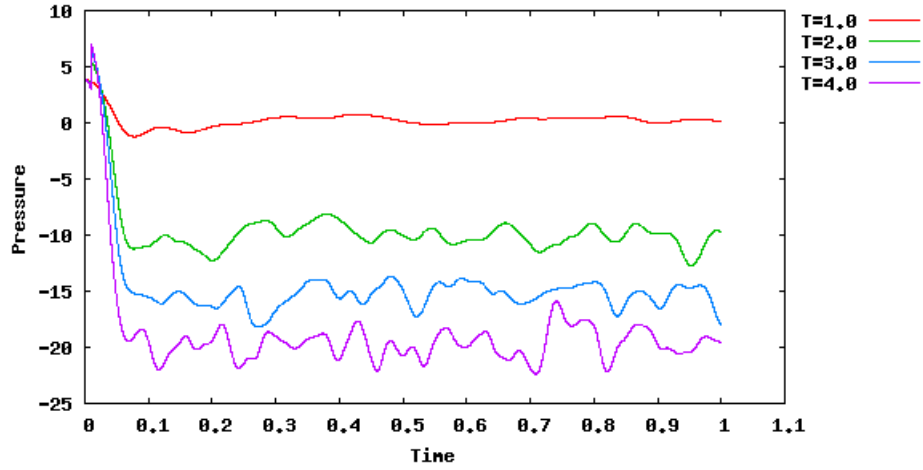


Figure 6: Calculated values of pressure for $T=1.0-4.0$, with the Andersen Thermostat applied.

4 Conclusion

From the results in this report it is evident that the Andersen Thermostat is able to control the temperature of the system and thus keep the energy total energy roughly constant. Additionally, the diffusion coefficient magnitude of pressure increased with increasing temperature.