Molecular Dynamics

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1   Introduction

We were tasked with designing a simulation modeling the interactions and dynamics of particles (modeled as Argon atoms) within an open region of space. We were able to observe the time evolution of energy, momentum, temperature, and pressure. We also found the pair correlation between the particles in our model.

2   Initial Conditions

Before letting our system evolve in time, we had to initialize the positions of particles, as well as their momenta. The particles were first arranged in a face-centered-cubic lattice. This was chosen due it being the ground state of our chosen interaction potential between the atoms: the Lennard-Jones potential:

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

Where ϵ is the depth of the attractive potential well and σ is the point at which the potential is zero. To simplify calculations, we chose a natural unit system in which

$\epsilon = \sigma = 1$. Such that equation (1) is simplified to

$$U(r) = 4(\frac{1}{r})^{12} - 4(\frac{1}{r})^6 \tag{2}$$

The minimum of this potential (at the bottom of the potential well) is the distance between diagonal atoms on the face of FCC unit cells. With natural units, this occurs when $r = 2^{\frac{1}{6}}$. From this, the length of side of one unit cells is $l = 2^{\frac{2}{3}}$. For a system with n unit c ells in each direction, the total length of our system in each directionis $L = n2^{\frac{2}{3}}$. To place the particles in our program, we placed atoms on one corner and at the center of three of the six faces of the FCC unit cell, then shifted this unit cell in about our space (n boxes in each direction) until all $N = 4n^3$ of our particles were placed.

After setting the positions of the particles, they were all given velocities according to a Guassian distribution. The momentum (equal to the velocity with $m = 1$ in our natural units) was then scaled down closer to zero by summing the total momentum (p_t) in each direction and subtracting $\frac{p_t}{N}$ from the momentum in each direction for each particle. Following this, the system was allowed to evolve in time.

3 Time Evolution

In order to study the dynamics of our system in motion, we used the force derived from the Lennard-Potential (2):

$$\mathbf{F} = - \bigtriangledown U = (\frac{48}{r^{13}} - \frac{24}{r^6})\hat{\mathbf{r}} \tag{3}$$

This was used to determine the equations of motion for the system. In order to reduce the computational cost of integrating the equations of motion through time, the Velocity Verlet Algorithm is used:

$$\mathbf{v}'(t) = \frac{\Delta t}{2}\mathbf{F}(t) \tag{4}$$

2

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \Delta t \mathbf{v}'(t) \tag{5}$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}'(t) = \frac{\Delta t}{2} \mathbf{F}(t + \Delta t) \tag{6}$$

We also chose to have periodic boundary conditions, such that when a particle crosses the walls of our region, it will reappear on the opposite side (modular division is used when updating the position in the Verlet algorithm). Furthermore, the forces are also calculated using the periodic conditions. The program uses the shorter of two distances: the actual distances between the two particles within the region or the sum of the distances of each particle to the closest edges. The second of these choices is an implementation of the periodic boundary condition. A critical radius was used, which set a limit on how far the particles could be from one another before their contributions to the force and potential were negligble.

4 Results

Using these conditions, the system was allowed to evolve in time and its properties were analyzed. We used a system of five cells in each direction, resulting in 500 total particles, at four different reservoir temperatures: .5, 1, 5, and 9 in our natural units. The system was updated for 5000 time steps of $\Delta t = .004$. Every 40 of the first 1000 time steps, the system's energy was relaxed in order to make it more stable and to ensure energy conservation. This was done by scaling the velocity as such:

$$\tilde{\mathbf{v}} = \mathbf{v}\sqrt{\frac{\mathbf{T}}{\mathbf{T_R}}} \tag{7}$$

where T is the temperature of the system (found from the kinetic energy: $K = \frac{3}{2}NT$)

and T_R is the temperature of the reservoir. Figure 1 shows the evolution of the system temperature (also kinetic energy as the two are linearly related), with the temperature staying close to the set temperature. Figure 2 shows the relaxation of the system and the conservation of energy after the stabilizing stage.

Though the system was not at zero total momentum (the randomness associated with assigning velocities to the particles limits this), conservation of the momentum to the orders of 10^{-12} and 10^-11 was observed. Figure 3 shows conservation of momentum in each direction with each point being a different step in time. The momentum increased slowly during the stabilization period before staying at a constant momentum after the relaxation stage ends (the more dense clusters of points).

Pressure was the last observable measured as the system was allowed to evolve. This was found using

$$P = \frac{1}{V}(NT - \frac{1}{D}\Sigma_{ij}r_{ij}\frac{\partial U_{ij}(r_{ij})}{\partial r}) \tag{8}$$

where D is the dimensionality of the system, and ij is over all pairs of particles (without overcounting). The second term is derived from virial relations of work and forces. Figure 4 shows the evolution of pressure with time (this time the plot is cut until after the relaxation stage is finished). A phase transition is evident in the behavior and size of the pressures in relation to temperature.

Pair correlation was also measured.

$$g(r) = \frac{2V}{N(N-1)} \frac{<n(r)>}{4\pi r^2 \Delta r} \tag{9}$$

For a certain distance r, $n(r)$ particles are found within a range Δr about r as measured from the center of one particle. Pair correlation represents the relative probability of finding a particle within small shells (centered at one particle) of thickness Δr. Within

the function, the time-averaged value $< n(r) >$ is used. In the simulation, calculating this number following the final time step suffices for this average, as the system has been allowed to move towards equilibrium. Figure 5 displays this for four different temperatures. It is shown that there are sharper peaks for lower temperatures and these peaks smooth out for higher temperatures. This is related to the system transitioning between phases and becoming more diffuse.

5   Conclusions

The results of this project provide evidence in the usefulness of approximation methods (such as the Verlet algorithm) and easing the computing cost of programs within small scale simulations. The program written to simulate this collection of Argon atoms provided accurate data (disregarding the choice of units) and physical trends. Conservation laws were satisfied (seen from the energy and momentum outputs) and phase transitions were observed (from pair correlation and pressure).
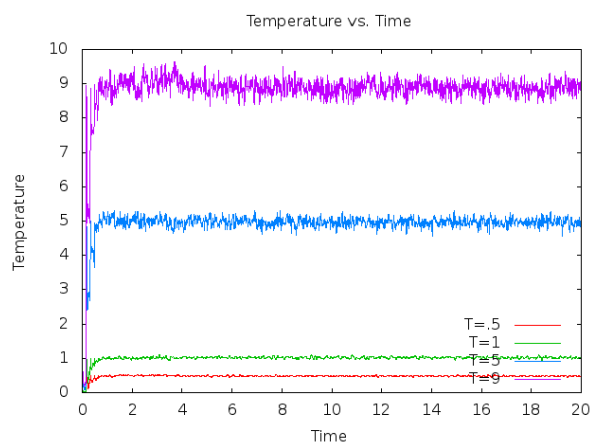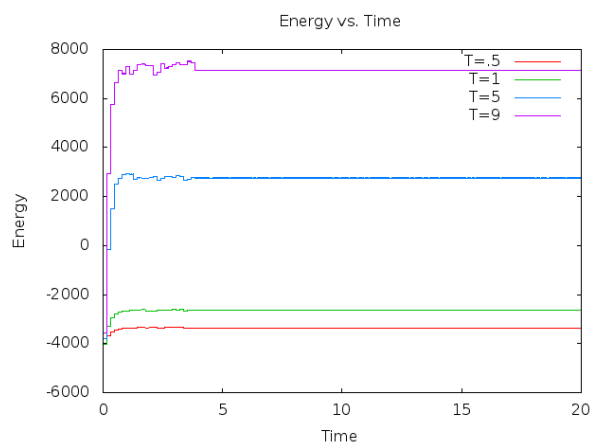
Figure 1: Evolution of system temperature

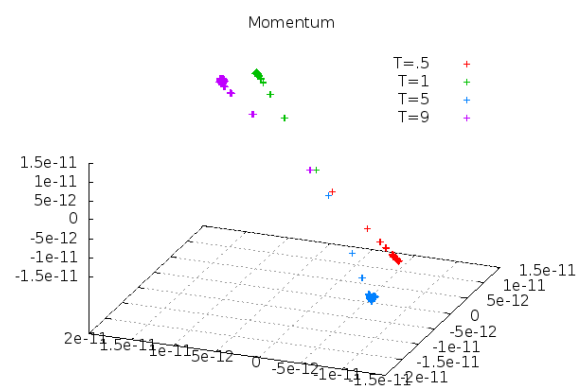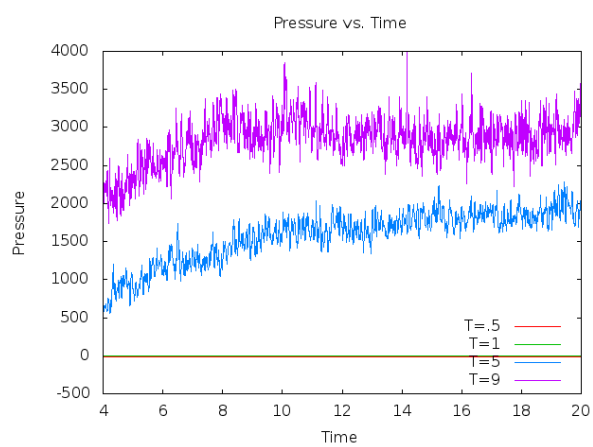Figure 2: Evolution of total energy (Kinetic + Potential)
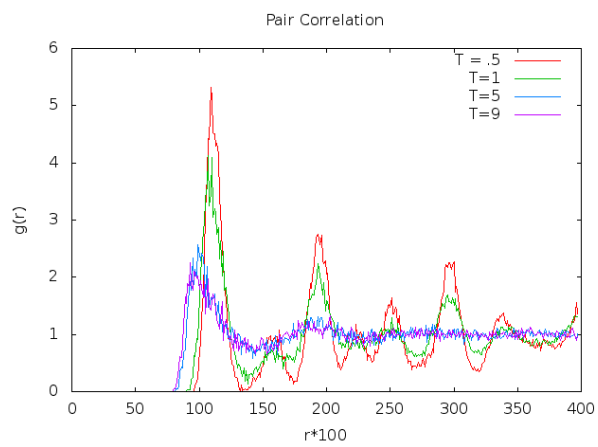
Figure 3: Conservation of Momentum

Figure 4: Pair correlation

Figure 5: Pair correlation