Molecular Dynamics Simulation Using Lennard-Jones Potential

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Lennard-Jones Potential:

The Lennard-Jones Potential (Equation 1) is an approximate description of the interaction between neutral atoms [2]. The repulsive term, which scales inversely with r to the 12th power is due to the overlap of electron shell orbitals. The attractive term, which scales inversely with r to the 6th power is due to Van Der Waals interactions. The nature of this potential, as seen in Figure 1, is such that particles becomes bound together with radial distance oscillating about the potential well at $r = 2^{1/6}\sigma$. For a system of multiple particles, each one behaves as in a classical many-body problem with the forces from all the particles superposing. The force components for each particle can be calculated by equations 2 and 3.

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

$$F_x = \sum_{i\neq j} \frac{-48\epsilon}{r_{ij}^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right](x_i - x_j) \tag{2}$$

$$F_y = \sum_{i\neq j} \frac{-48\epsilon}{r_{ij}^2}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{6}\right](y_i - y_j) \tag{3}$$

Boundary Conditions:

In order to simulate an open system of moving particles, periodic boundaries efficiently capture many of the important aspects of a continuous system without having to consider an unrealistic number of particles. In two-dimensions, a particle that travels through the boundary on the right appears at the left boundary with its velocity unchanged and a particle that travels through the top boundary will appear at the bottom boundary with the same velocity. Therefore, a traveling particle moves as though unconstrained by the

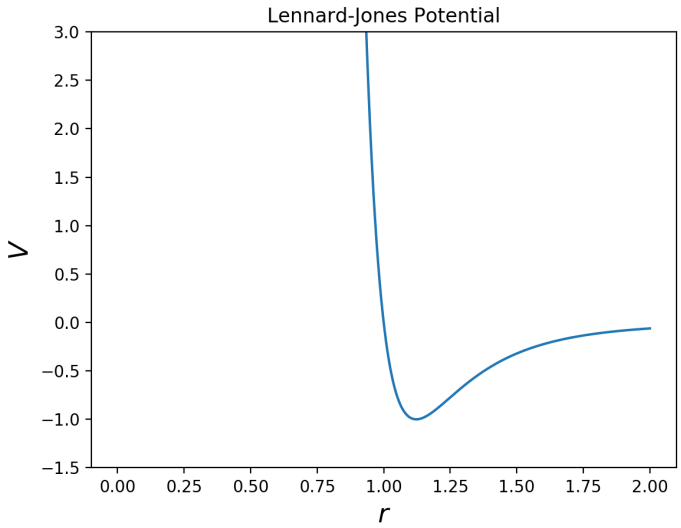

Figure 1: Lennard-Jones Potential in dimensionless units.

boundaries.

Another important feature of simulating continuous flow using periodic boundary conditions is deciding whether to use the pictured position of a particle for force calculations or to use the image of a particle as though it were on the other side of a boundary. Figure 2 depicts a situation in which the image position of a particle beyond the boundary (transparent blue particle) should be used for the force calculation (on the red particle) instead of the actual position of the particle (blue particle). Practically, this can be implemented by coding a series of if statements that say if the x-component of the distance between two particles is greater than half the boundary size, then use the image position through the left or right boundary (depending on the sign of the displacement) of the second particle instead. The same algorithm holds for the y-component (and z component in 3-dimensions).

Velocity Verlet:

I used Verlet integration to update each particle's position and velocity at each time step. This method is useful for molecular dynamics simulations because it is computationally efficient, second order accurate with time, and symplectic. Equations 4 and 5 shows the basic mathematical formulation of the method [1].

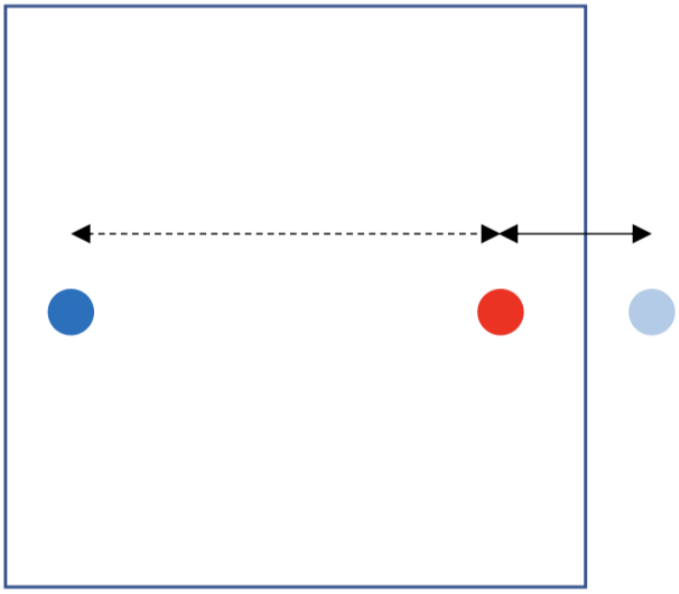

Figure 2: Example of a nearest neighbor calculation

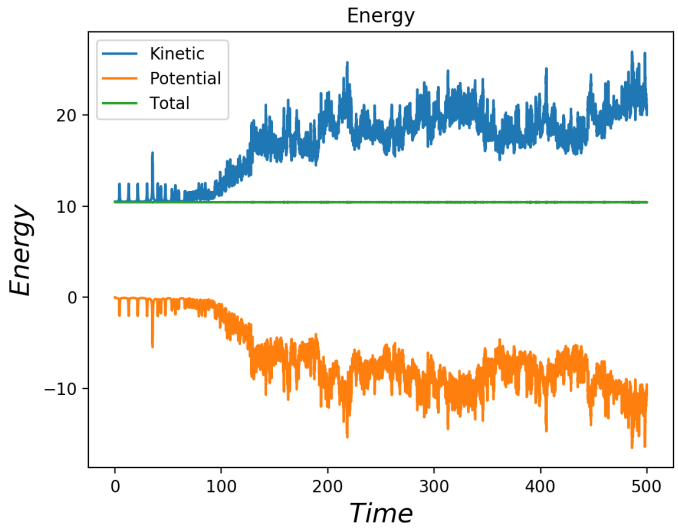

Figure 3: Energy plots for a system of 21 particles interacting via the Lennard-Jones potential.

$$\vec{x}(t+\delta t) = \vec{x}(t) + \vec{v}(t)\delta t + \frac{1}{2}\vec{a}(t+\delta t)\delta t^2 \tag{4}$$

$$\vec{v}(t+\delta t) = \vec{v}(t) + \frac{1}{2}[\vec{a}(t) + \vec{a}(t+\delta t)]\delta t \tag{5}$$

Results:

I have supplied two animation files in the Github depository that show the motion of a system of 21 particles and a system of 100 particles. Figure 3 shows the energy plots for the attached animation of 21 particles interacting via the Lennard-Jones potential. Figure 4 shows the total momentum of all the particles for the same animation. To a high degree of accuracy, both total energy and momentum are conserved. Figures 5 shows the energy plot for a system of 100 particles interacting via the Lennard-Jones potential. An interesting qualitative aspect to note is the formation of particle clusters. Figure 6 shows a time slice of the animation of 21 particles in which several particle clusters can be seen. These clusters are semi-stable, breaking apart when colliding with another particle or cluster but otherwise staying together with continuously changing shape.

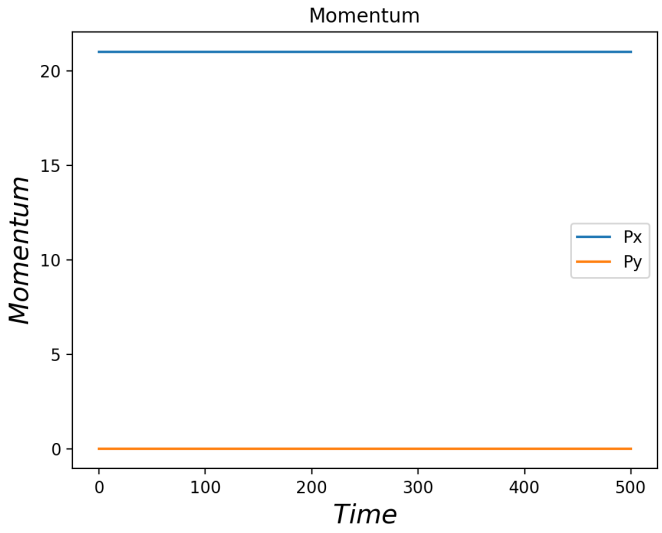

Figure 4: Momentum plots for a system of 21 particles interacting via the Lennard-Jones potential.

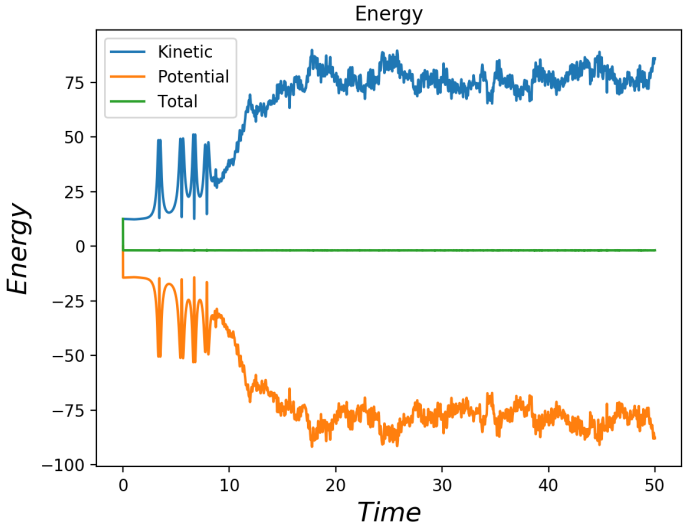

Figure 5: Energy plots for a system of 100 particles interacting via the Lennard-Jones potential.

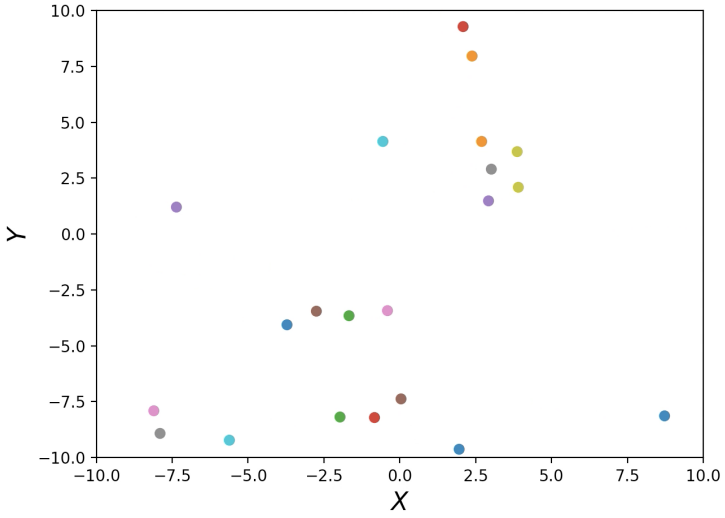

Figure 6: Time slice of a system of 21 particles interacting via the Lennard-Jones potential. Clusters of particles continuously form, change shape, and break apart.

Conclusion:

By using the Lennard-Jones potential as a computationally efficient approximation to neutral molecular interaction, I have successfully created an easily scalable program to simulate complex dynamics of a many-body system. The techniques used in this program can also be extended to 3-dimensions.

References:

[1] Swope, W. C., Andersen, H. C., Berens, P. H., and Wilson, K. R. (1982). A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. The Journal of Chemical Physics, 76(1), 637-649.

[2] Verlet, L. (1967). Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules. Physical review, 159(1), 98.