Introduction.

Polymer chains have many applications within multiple scientific fields, in particular within biomedical and materials science. To this end, molecular dynamics simulations can be used not only to discover various conditions under which a polymer chain may fold, but also to optimize parameters to target a phase transition. Given the wide array of applications that polymers can have both in research and industry, such simulations can be highly informative and beneficial.

Interactions within the polymer chains include bonded interactions consisting of harmonic potentials between adjacent monomers, and non-bonded interactions, which include repulsive Lennard-Jones potentials between adjacent (connected) monomers and attractive Lennard-Jones potentials between non-adjacent monomers. A key characteristic of polymer chains is their ability to undergo temperature-driven phase transitions between their folded and unfolded states. These states can be controlled and optimized by adjusting parameters such as the attractive and repulsive interactions, number of steps, equilibrium bond length, and the number and mass of the particles involved. To achieve our ideal conditions, k, the spring constant, and epsilon-repulsive, the depth of the repulsive Lennard-Jones potentials were adjusted to prevent folding at low temperatures.

The below simulations have been written and tested on Google Colab and can be found on this Chem-4050-5050 Github page under the "Project 2" folder. The code takes approximately 35 minutes to run, and will output the nine graphs and four 3-D renderings as shown in the Results section. The graphs plot the effects of temperature on the radius of gyration, end-to-end distance, and average potential energy respectively for the initial and optimized conditions. The 3-D renderings model the polymer as a bead-spring model, in which the beads represent the monomer units of the chain and the string signifies the harmonic springs that keep the polymer chain together, considering both bonded and non-bonded interactions.

Methods.

Necessary modules for simulation include NumPy and MatPlotLib, as well as the Axes3D submodule from MatPlotLib to create the 3-D graphs. Multiple functions are then defined, including periodic boundary conditions, the initial position and velocity, harmonic forces, and Lennard-Jones forces. To update the positions and velocities, a velocity Verlet algorithm is also defined. Separate lists are then created for the radius of gyration, end-to-end distance, and average potential energies to store calculated values. The following parameters were used for the initial simulation.

Time Step	Simulation Steps	Equil. Steps	Box Size	Mass	rθ
0.1	10,000	2,000	100.0	1.0	1.0

# of Particles	Sigma	Max. Iterations	Epsilon Attr.	Epsilon Rep.	k
20	1.0	50,000	0.5	1.0	1.0

To simulate the polymer chain across different temperatures, the temperature was set to reduced units from 0 to 1.0 by steps of 0.5. A steepest descent formula was used to construct a minimized polymer configuration. A graph of the radius of gyration, end-to-end distance, and average potential energy are plotted against temperature, and the initial and minimized polymer configurations are plotted in 3-D using a bead and string model (Figures 1 - 4).

From these results, optimal conditions are obtained when k is increased from 1.0 to 1.5 and epsilon_repulsive is increased from 1.0 to 3.0, while all other parameters are kept consistent. Using these optimized parameters, the radius of gyration, end-to-end distance, and average potential energy are plotted against temperature and each are combined with the initial conditions to create overlays (Figures 5 - 10). Finally, the polymer configuration at low and high temperatures are plotted in 3-D using optimized parameters (Figure 11).

Results.

Under the initial parameters, the radius of gyration, end-to-end distance, and average potential energy increase at low temperatures, followed by a sharp decrease around 0.5 reduced units, then follow slow increase until a reduced temperature of 1.0. Specifically, the radius of gyration and end-to-end distance reach a maximum at a temperature of 0.5 reduced units, while the average potential energy reaches a maximum at a temperature of 0.4 reduced units. Combined, the maximum values followed by sharp declines indicates a temperature-driven phase transition around 0.45 reduced temperature units. This signifies that attractive non-bonded interactions were dominant over bonded interactions, leading to collapse at high temperatures. In addition, the increase in average potential energy continuing to rise despite a drop in the radius of gyration and end-to-end distance at a reduced temperature of 0.9 indicates an increase in the disorder of the polymer despite attempts to reduce the potential energy through collapsing.

While the initial polymer condition appears to have only three monomers, the 20 total monomers are overlapping across three positions, as the initial conformation allows for monomer overlap. The other 3-D plots have been adjusted to prevent this overlap through repulsive forces.
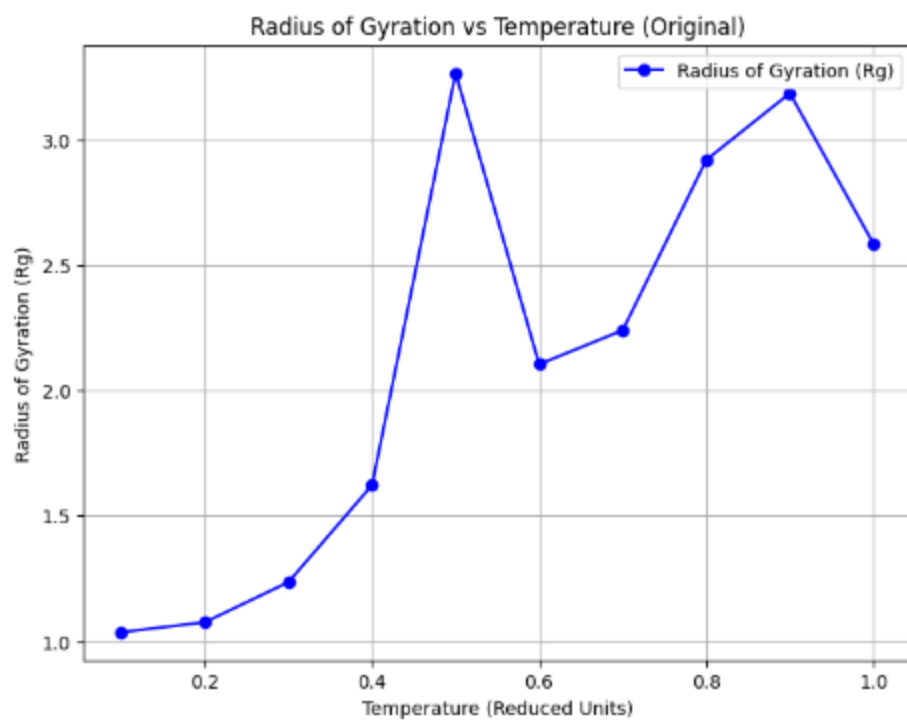
Figure 1. Radius of Gyration vs Temperature under Initial Parameters
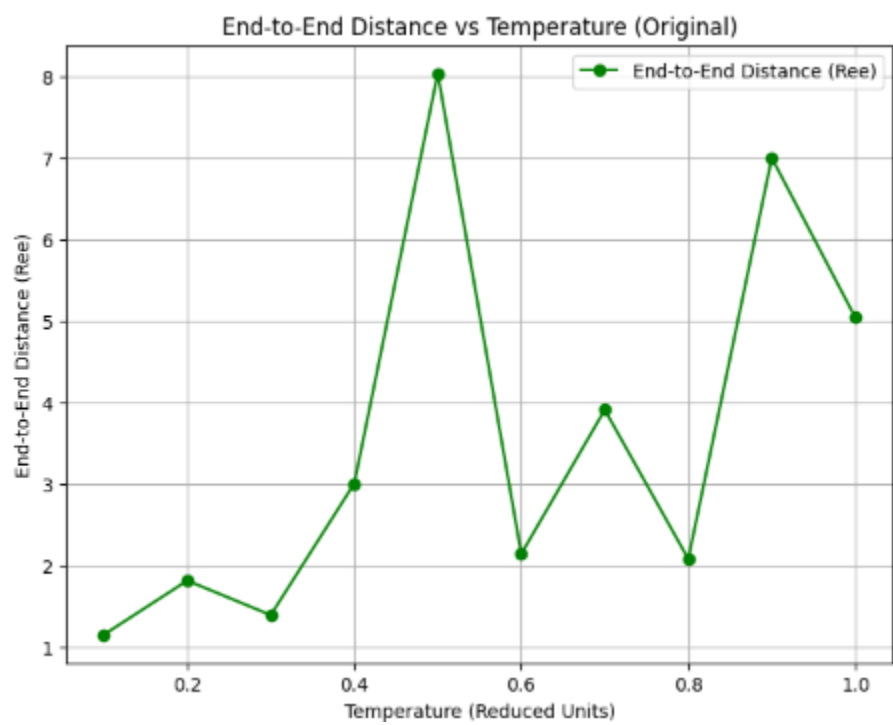

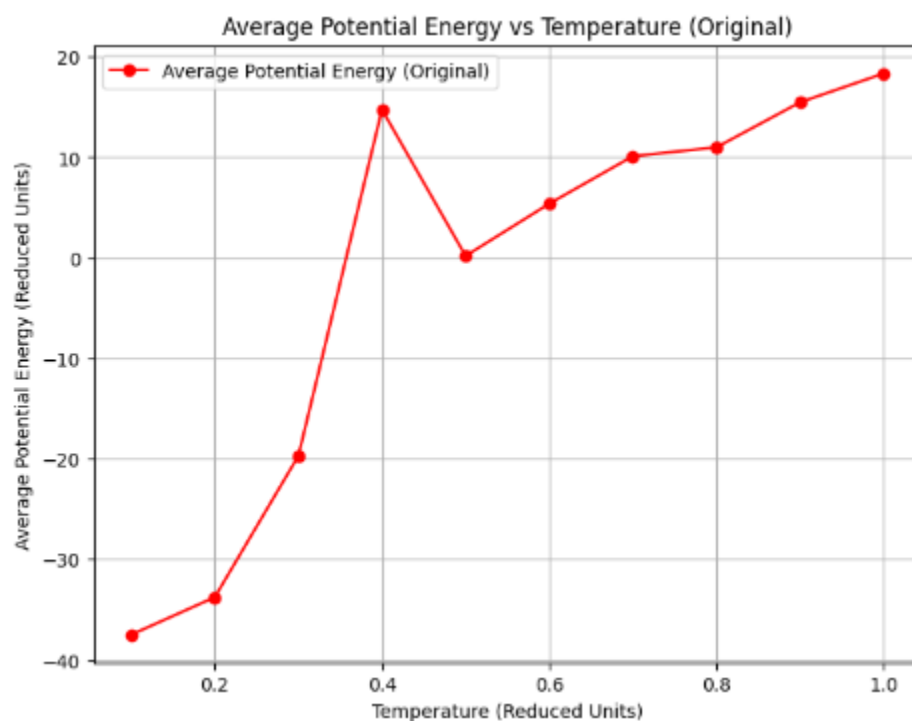Figure 2. End-to-End Distance vs Temperature under Initial Parameters

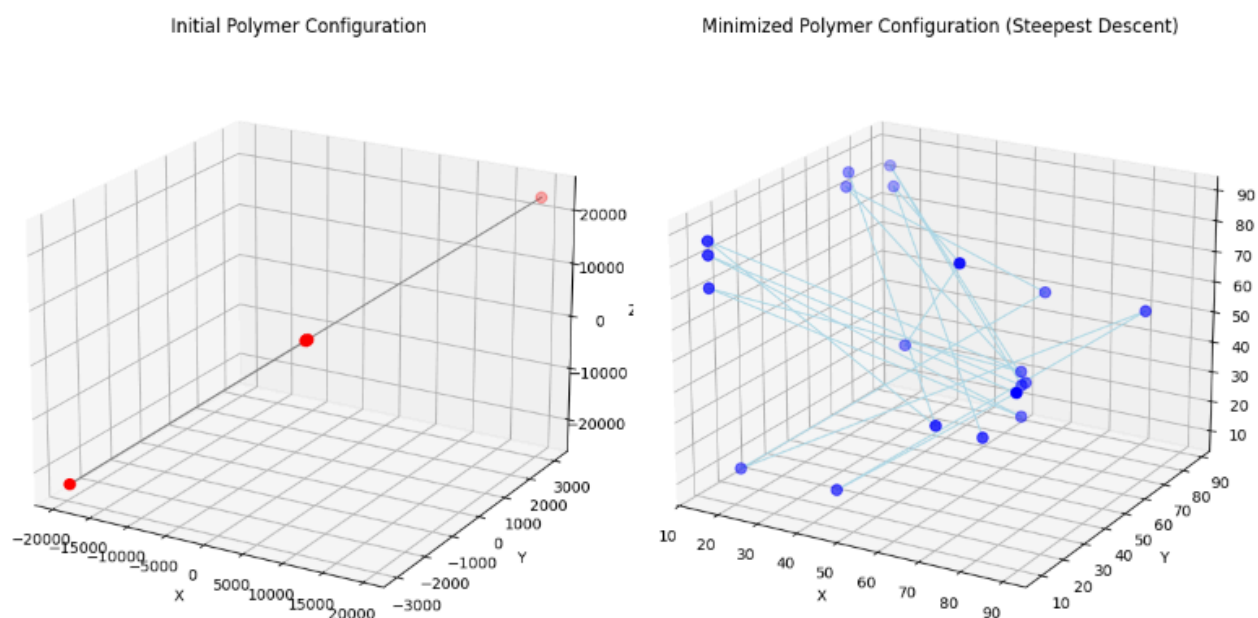Figure 3. Average Potential Energy vs Temperature under Initial Parameters

Figure 4. Initial and Minimized Polymer Configuration under Initial Parameters

Under optimized conditions, the radius of gyration and end-to-end distance were significantly higher for each reduced temperature, indicating that a less compact conformation was maintained even at high temperatures. Increasing the spring constant and repulsive Lennard-Jones interactions results in more compact conformations being energetically unfavorable as the repulsive interactions between adjacent monomers result in a more significant contribution to the polymer chain than interactions between attractive forces between non-adjacent monomers. This also contributes to the higher average potential energy as these repulsive forces require more energy to be overcome at higher temperatures.

Similar to the initial parameters, the radius of gyration and end-to-end distance both showed a maximum followed by a sharp decrease, indicating a temperature-driven phase transition at 0.3 reduced temperature units. The average potential energy also showed a spike at this temperature, though its maximum was reached at 0.6 reduced temperature units, which was likely due to the polymer chain exploring more energetically unfavorable conformations at increased temperatures that would not be possible at low temperatures.
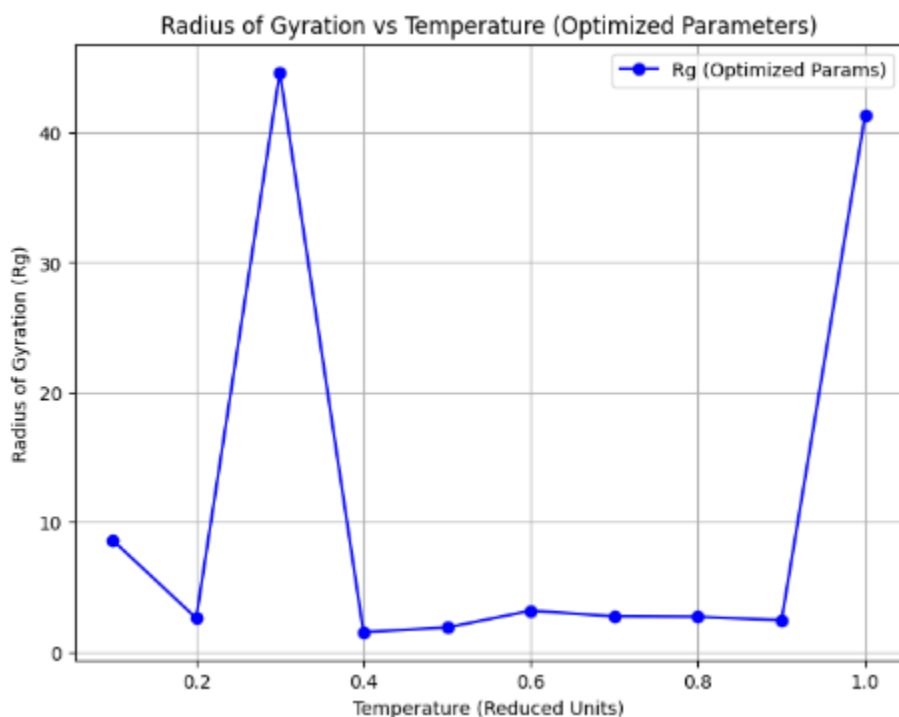

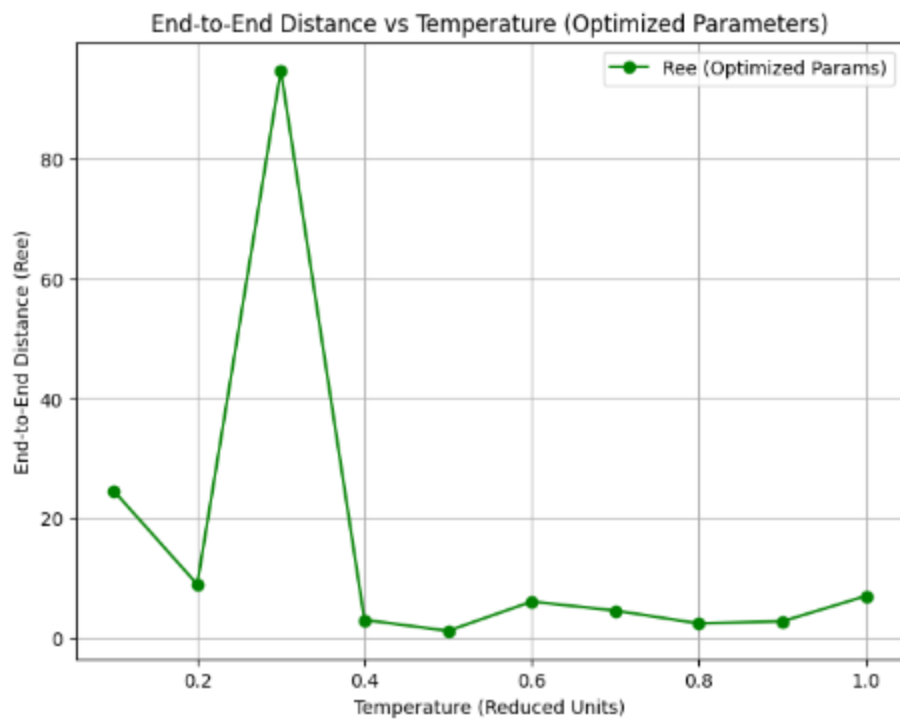Figure 5. Radius of Gyration vs Temperature under Optimized Parameters

Figure 6. End-to-End Distance vs Temperature under Optimized Parameters
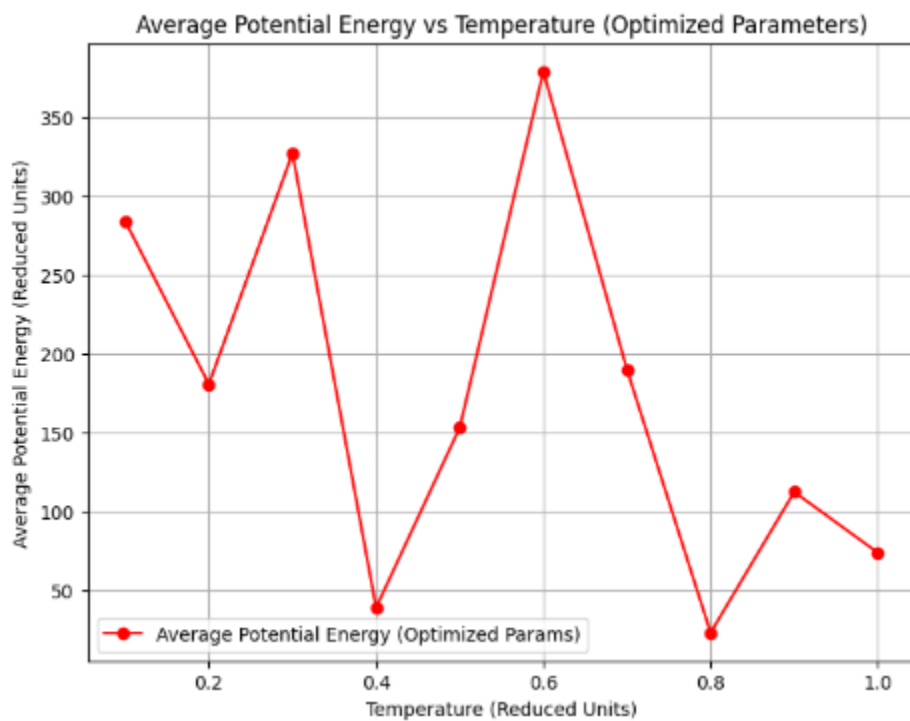

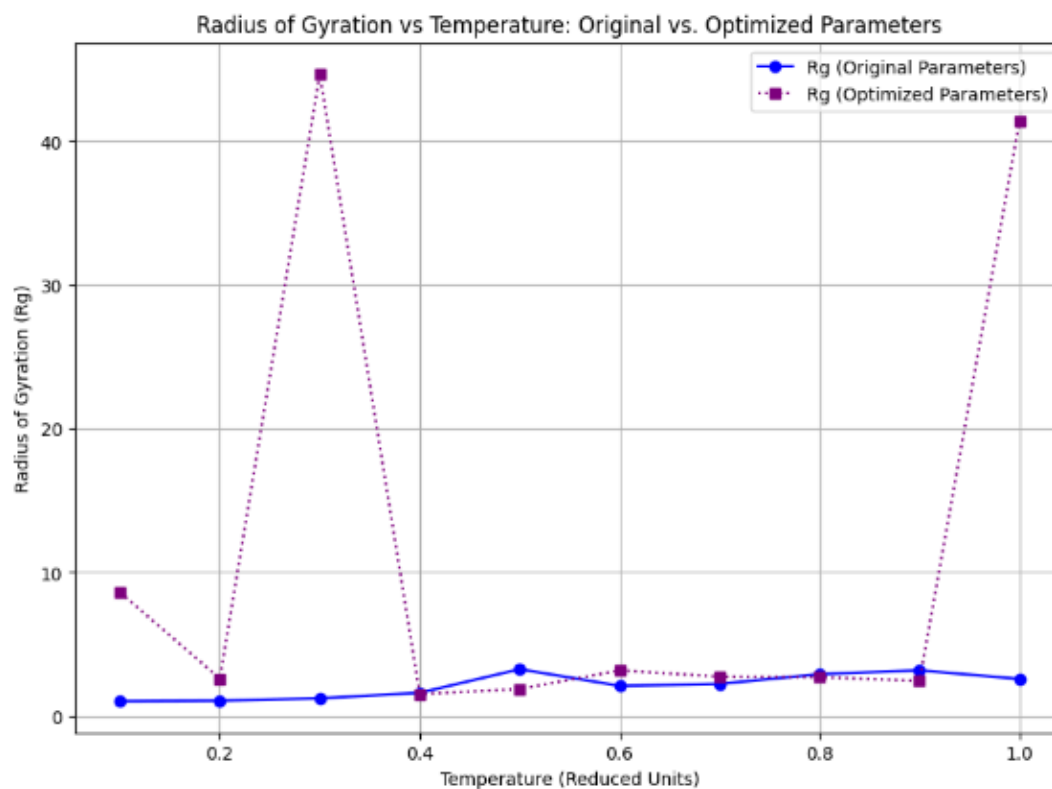Figure 7. Average Potential Energy vs Temperature under Optimized Parameters

Figure 8. Radius of Gyration vs Temperature under Initial and Optimized Parameters
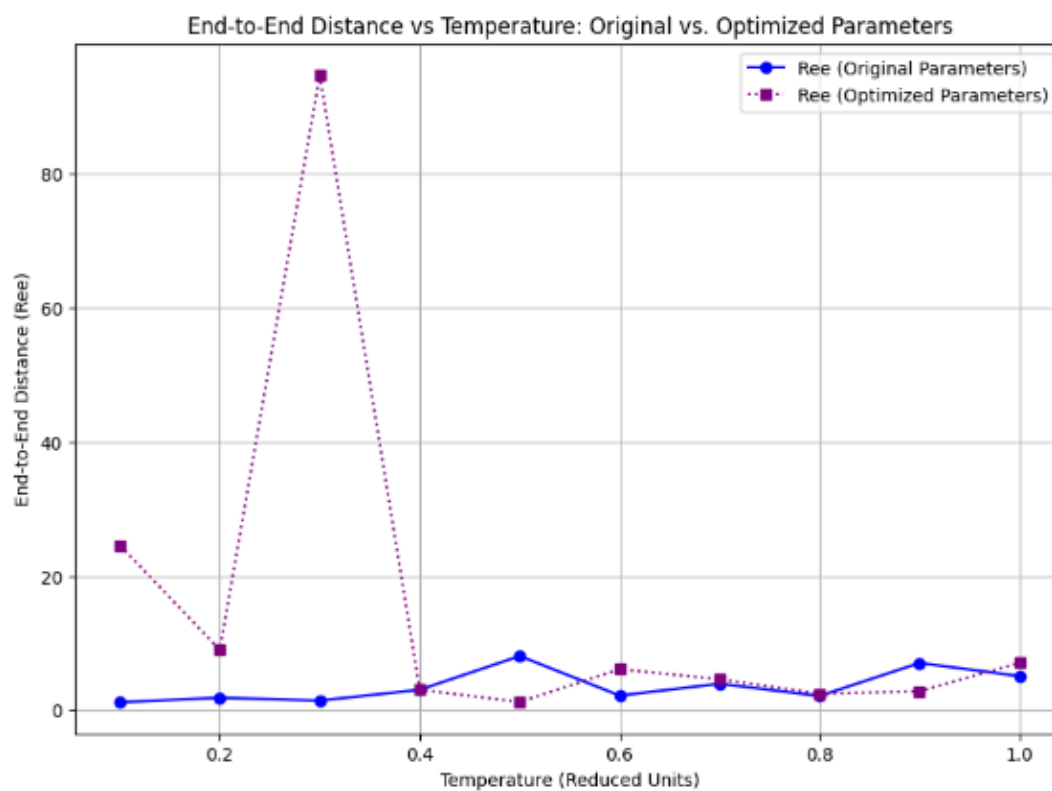

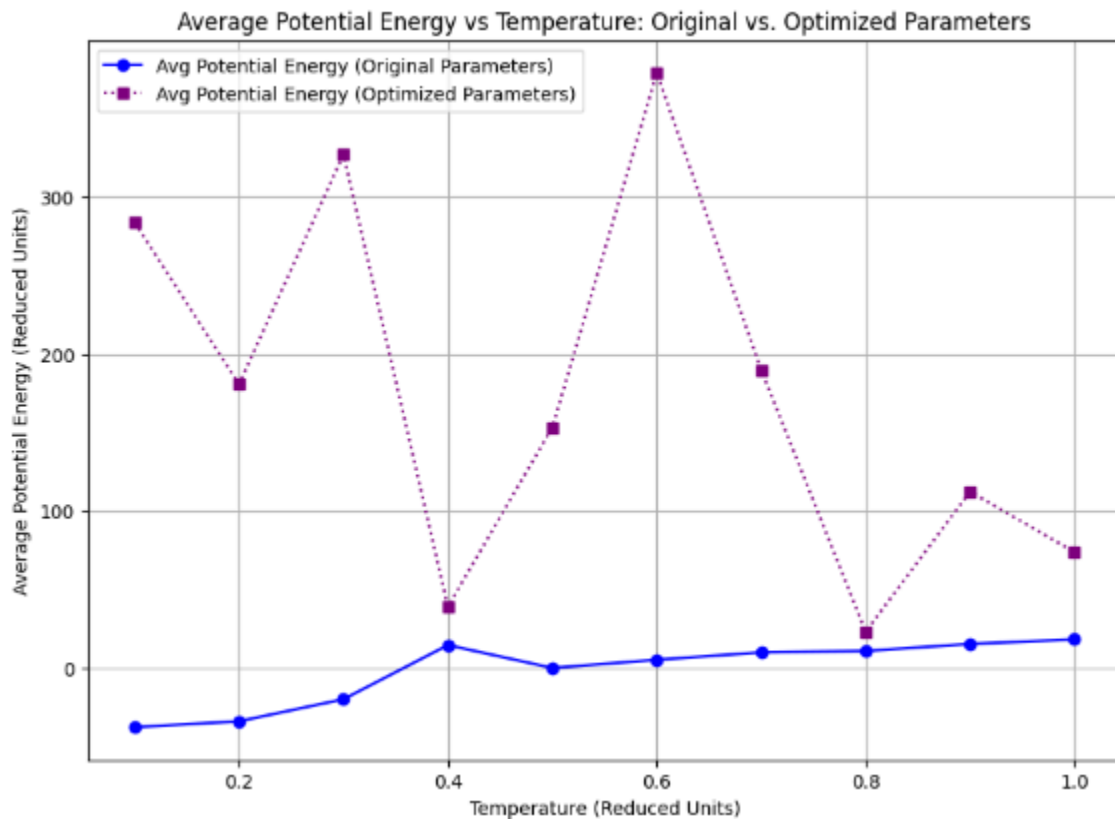Figure 9. End-to-End Distance vs Temperature under Initial and Optimized Parameters

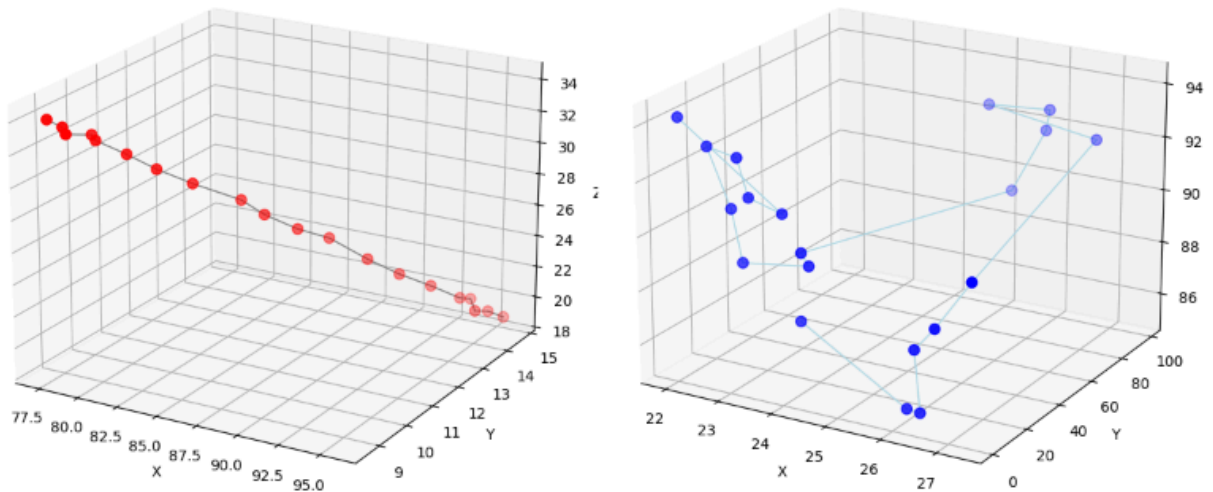Figure 10. Average Potential Energy vs Temperature under Initial and Optimized Parameters

Figure 11. Polymer Configuration at Low and High Temperature under Optimized Parameters

Discussion.

Under the initial conditions, the polymer showed a transition from a less compact to more compact state as temperature increased, with a temperature-driven phase transition occurring around 0.45 reduced units. Under optimized conditions, the polymer showed significantly higher average potential energy for all temperatures and a temperature-driven phase transition occurring around 0.3 reduced units. This is ideal, as the optimization of parameters was targeted to prevent folding of the polymer at low temperatures. Similarly, while the minimized polymer configuration showed very sparsely connected monomers with high bond lengths, the polymer configurations for the optimized parameters showed considerably more closely packed monomers with shorter bond lengths, indicating more spatially and energetically favorable configurations. Overall, the optimized parameters allowed for considerably easier identification of the temperature-drive phase transition given the sharper increases in the radius of gyration, end-to-end distance, and average potential energy. Furthermore, the polymer configuration at a low temperature appears considerably more relaxed and linear compared to the more compact polymer configuration under high temperatures, indicating proper optimization parameters.

Conclusion.

By changing various parameters involved in the interactions between monomers in a chain, molecular dynamics simulations can greatly aid in studies of temperature-dependent polymer folding. In addition, temperature-based graphs that monitor for phase transitions can help determine optimal parameters to prevent or induce folding under various conditions. Further work on this specific project could include altering the chain length of the polymer and performing energy minimization before the molecular dynamic simulations to see the effects and potential optimization of the folding behavior. Further work beyond this project could include the utilization of more advanced thermostats like Nosé-Hoover dynamics, changing parameters such as the number of particles or time step, and creating a chain of monomers with different properties to gain insights into their interactions and folding conditions.