

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	$r\theta$
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.

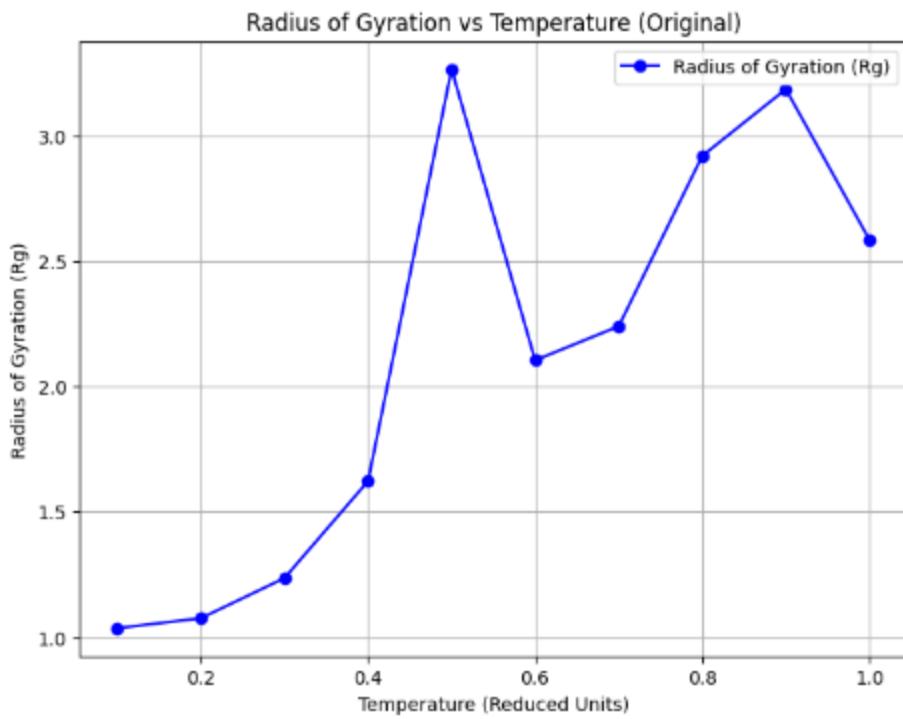


Figure 1.

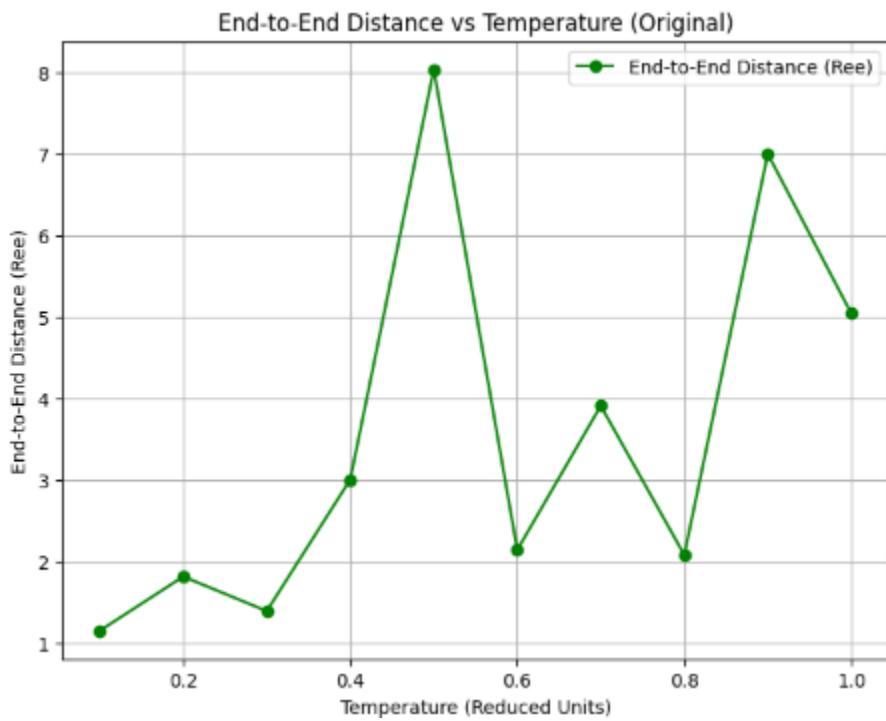


Figure 2.

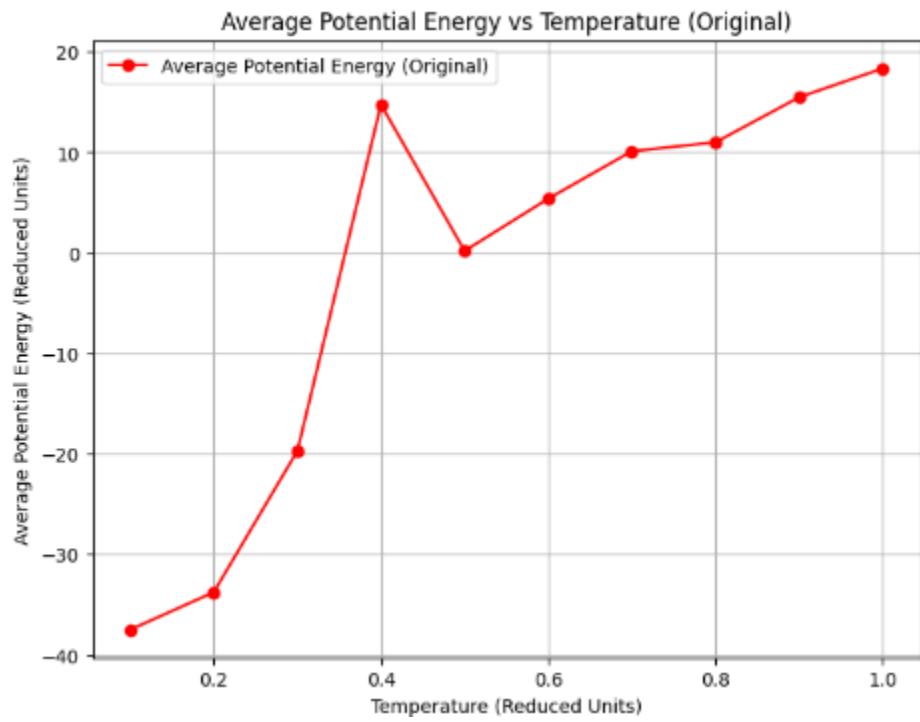
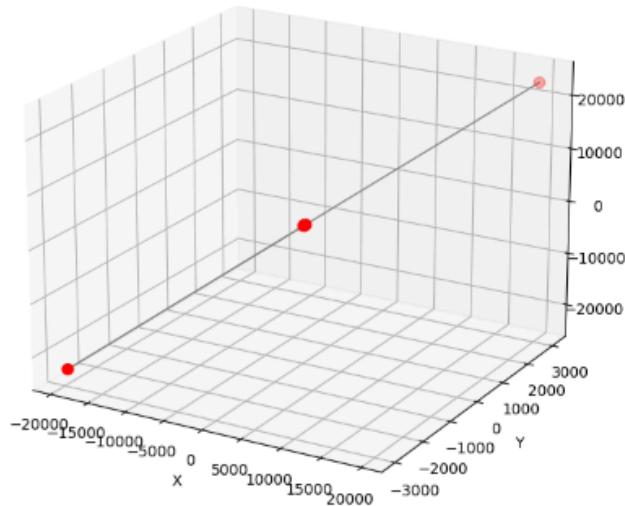


Figure 3.

Initial Polymer Configuration



Minimized Polymer Configuration (Steepest Descent)

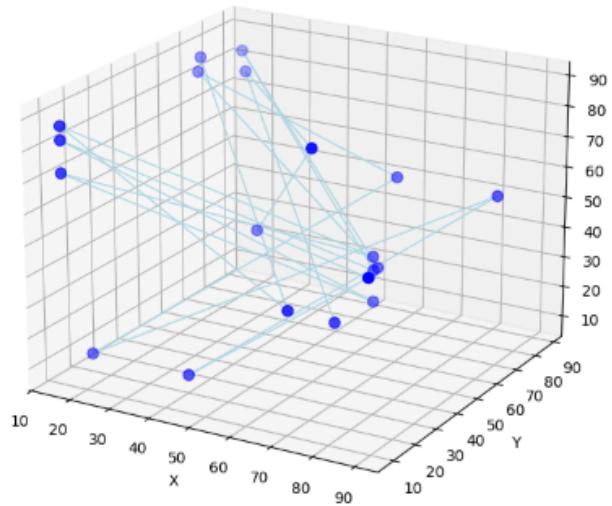


Figure 4.

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.

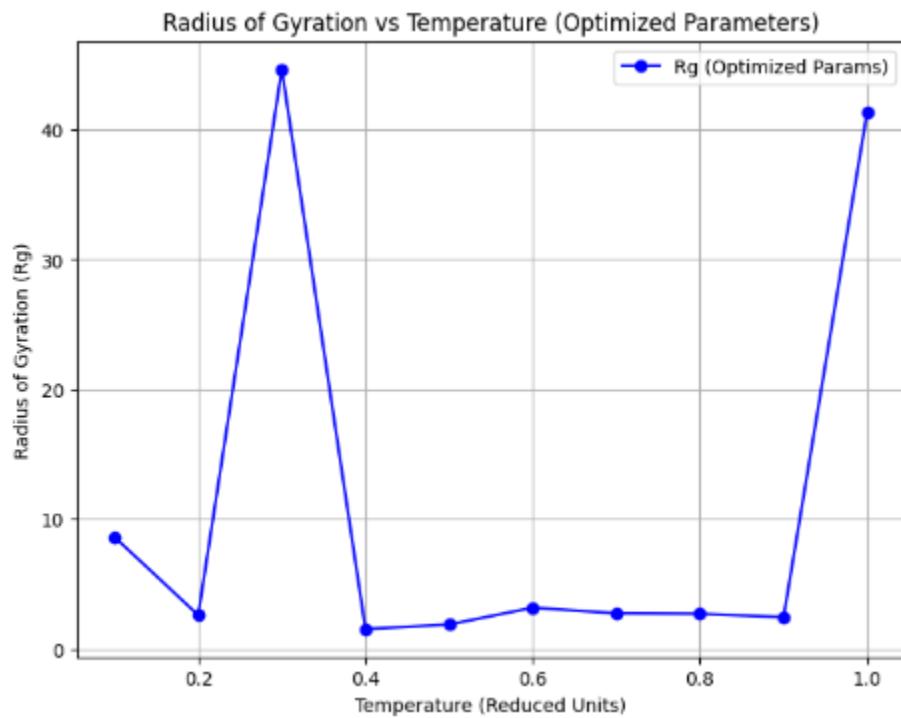


Figure 5.

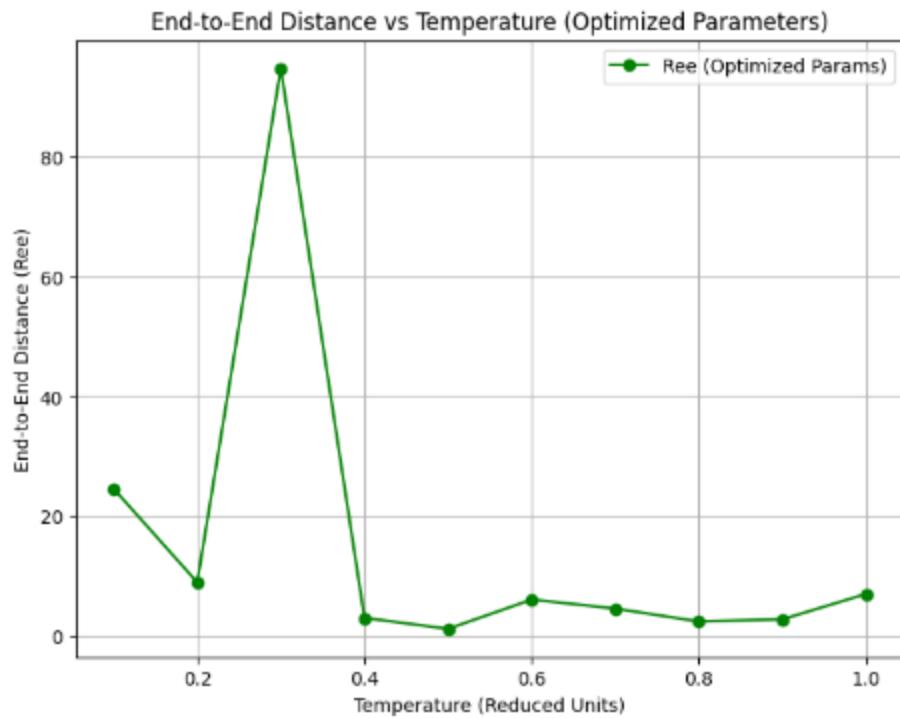


Figure 6.

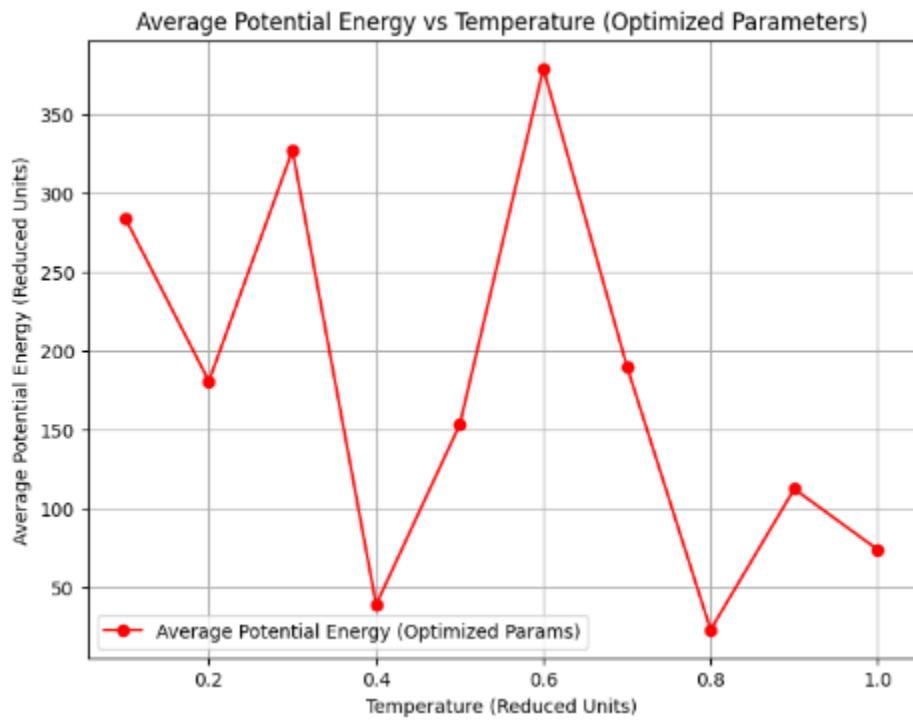


Figure 7.

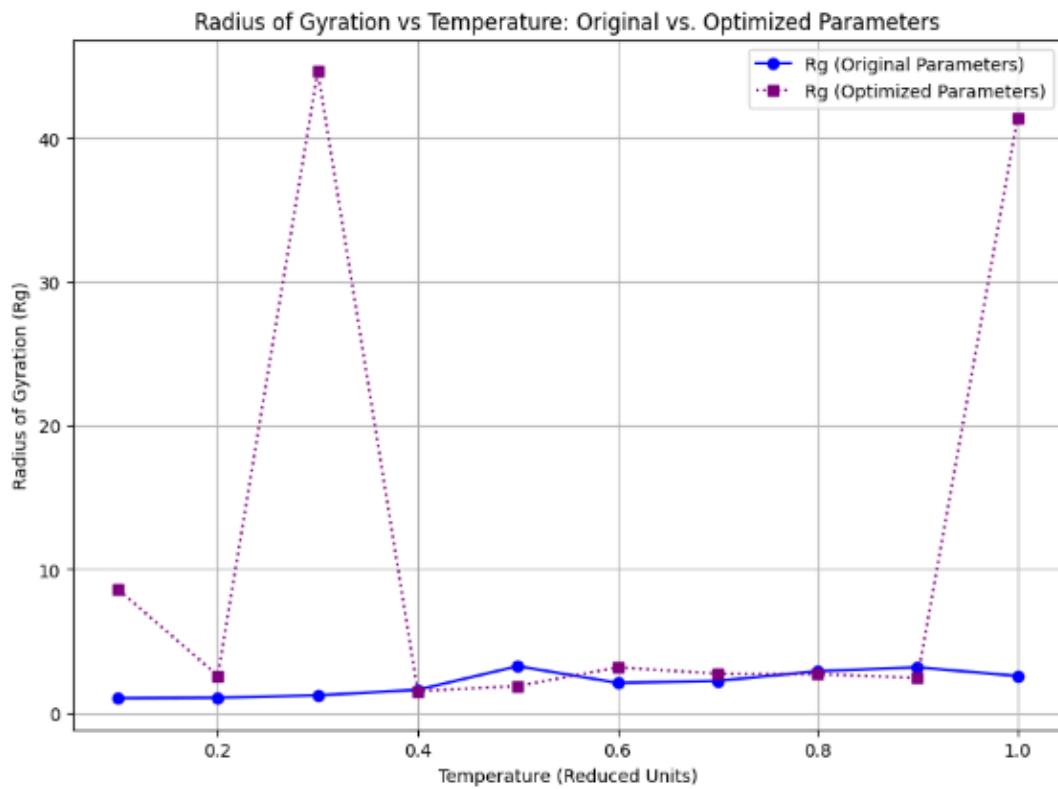


Figure 8.

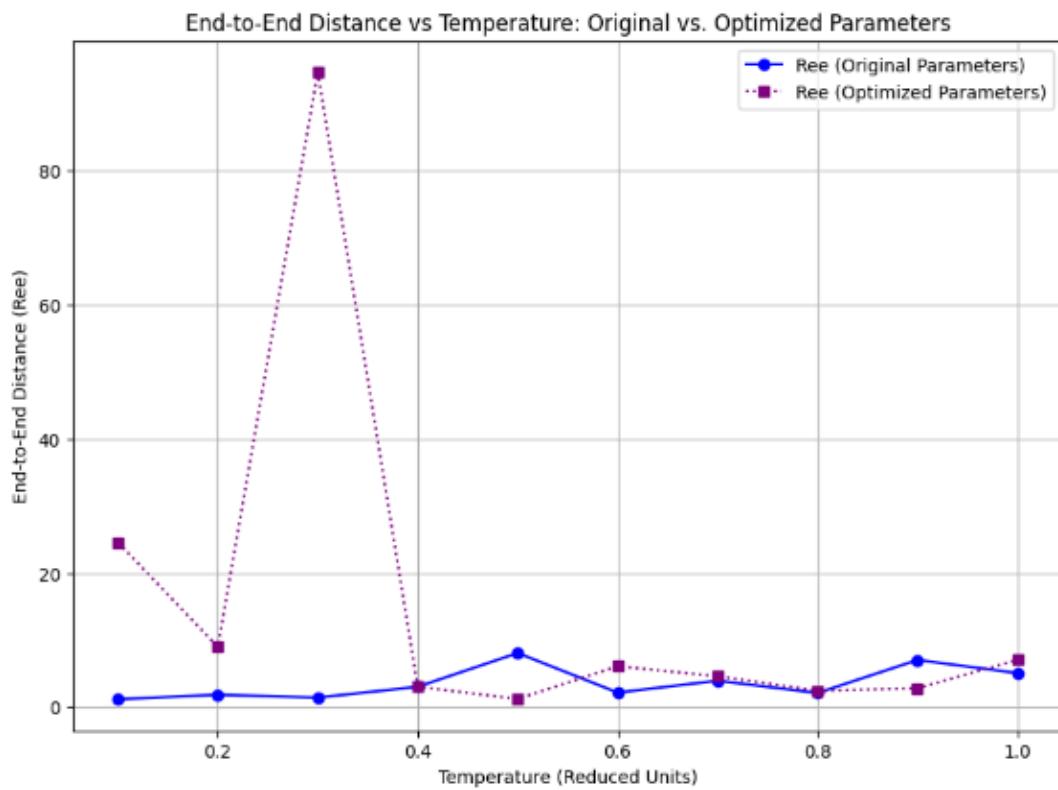


Figure 9.

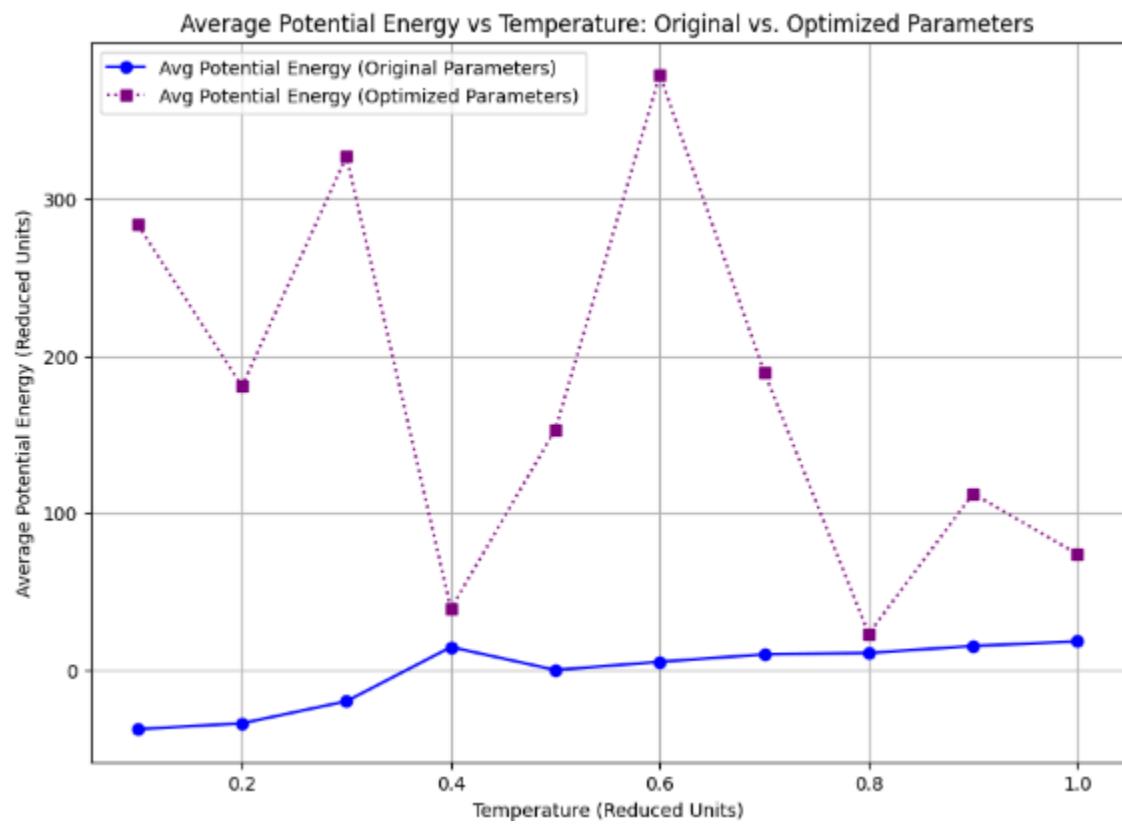


Figure 10.

Polymer Configuration at Lowest Temperature (Optimized Parameters) Polymer Configuration at Highest Temperature (Optimized Parameters)

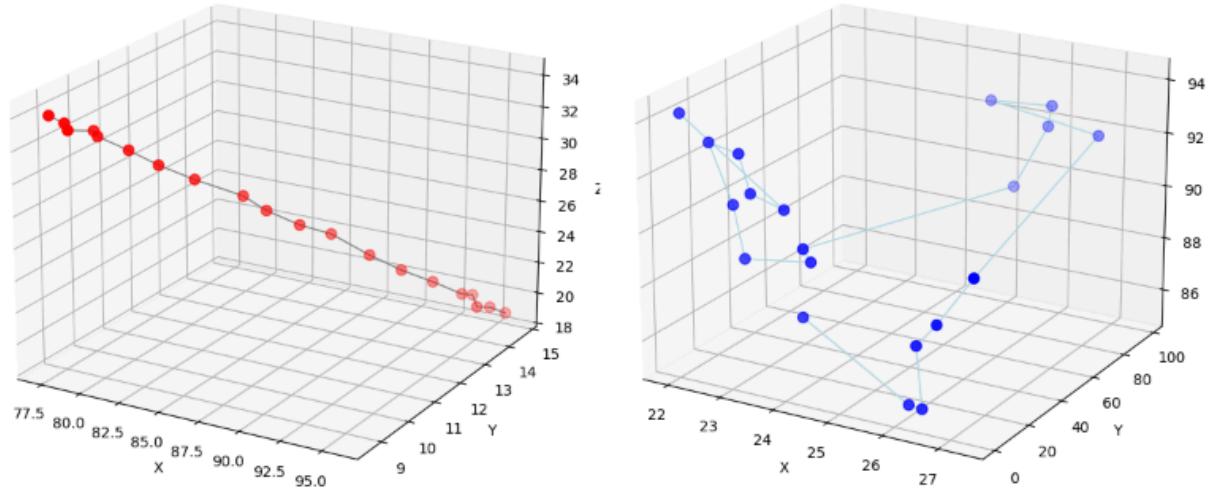


Figure 11.