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.

These simulations have been written and tested on Google Colab, and can be found on [this 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 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.
For the original parameters, both Rg and Ree generally decreased as temperature increased, showing a tendency for the polymer to adopt more compact, folded, or globular conformations. This indicated that attractive non-bonded interactions were dominant, leading to collapse as thermal energy allowed the polymer to overcome barriers to form contacts.

The average potential energy generally increased with temperature. While counter-intuitive for a collapsing polymer, this is expected in an NVT ensemble where higher kinetic energy at higher temperatures allows the system to explore configurations with higher overall energy, even if the polymer itself is trying to minimize its attractive potential energy by collapsing.
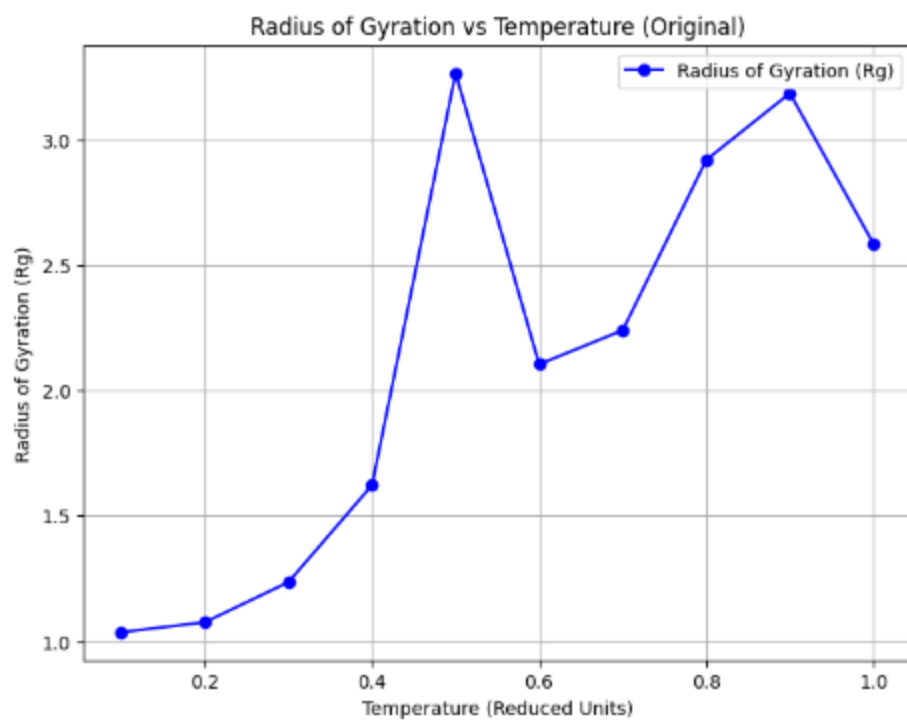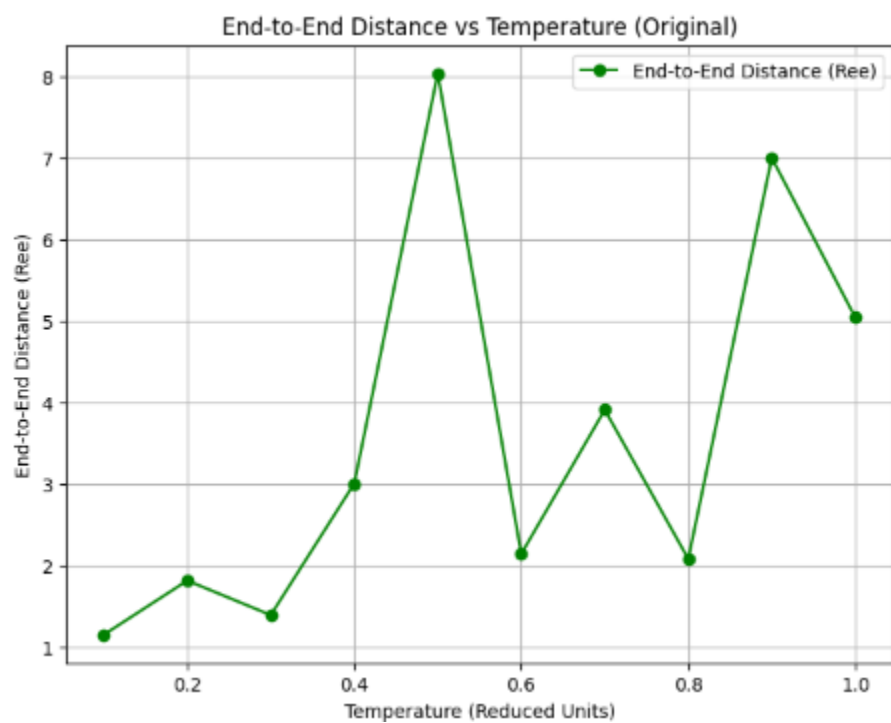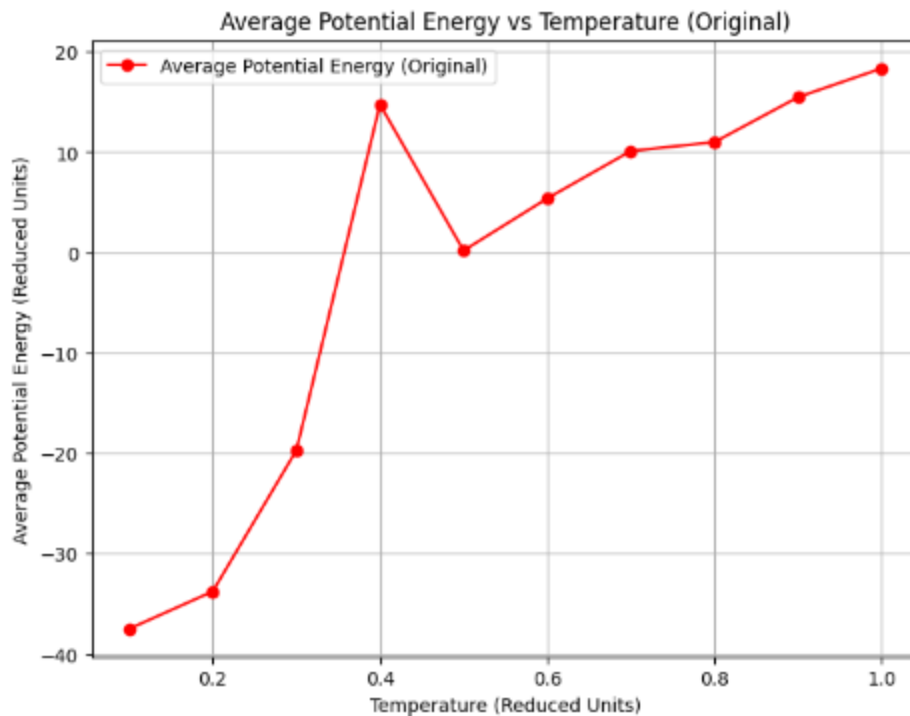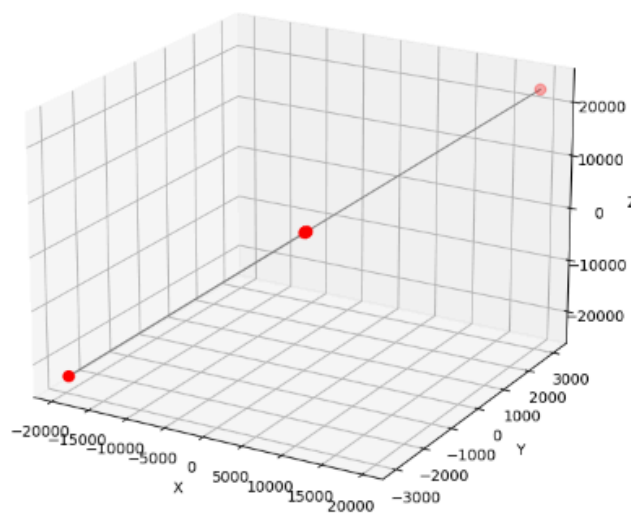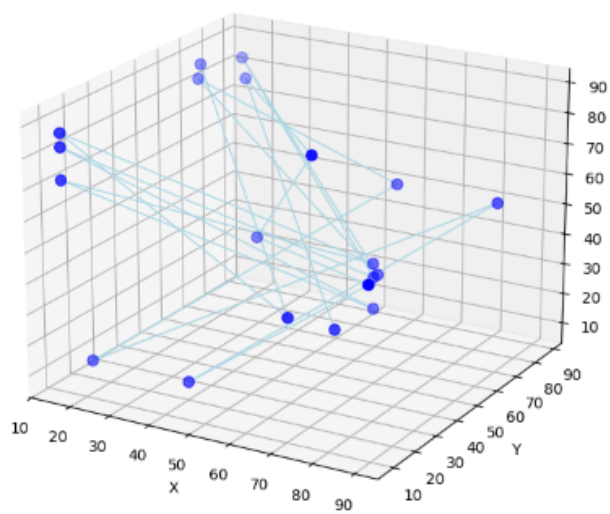
Figure 1.

Figure 2.

Figure 3.

Figure 4.

With the optimized parameters, the Rg and Ree values were generally higher across the entire temperature range compared to the original simulation. Importantly, they showed less of a tendency to decrease at lower temperatures, and maintained a more extended state. This indicates

that the adjustments successfully countered the polymer's folding tendency, promoting a more stretched-out and less compact conformation.

The average potential energy with the optimized parameters was notably higher than with the original parameters. This is an expected outcome, as increasing the spring constant (k) and the repulsive Lennard-Jones strength (epsilon_repulsive) makes compact, low-energy states energetically less favorable. The system now resides in configurations that require more energy to overcome these stronger repulsive forces, resulting in an overall higher potential energy for the extended polymer.

Generally, Rg values decreased as temperature increased, indicating a more compact polymer conformation at higher temperatures within the simulated range. Similar to Rg, Ree tended to decrease with increasing temperature, also suggesting a transition towards a more folded or globular state. The average potential energy of the system generally decreased as the temperature increased, signifying that the system explored more stable, lower-energy configurations at higher thermal energy.
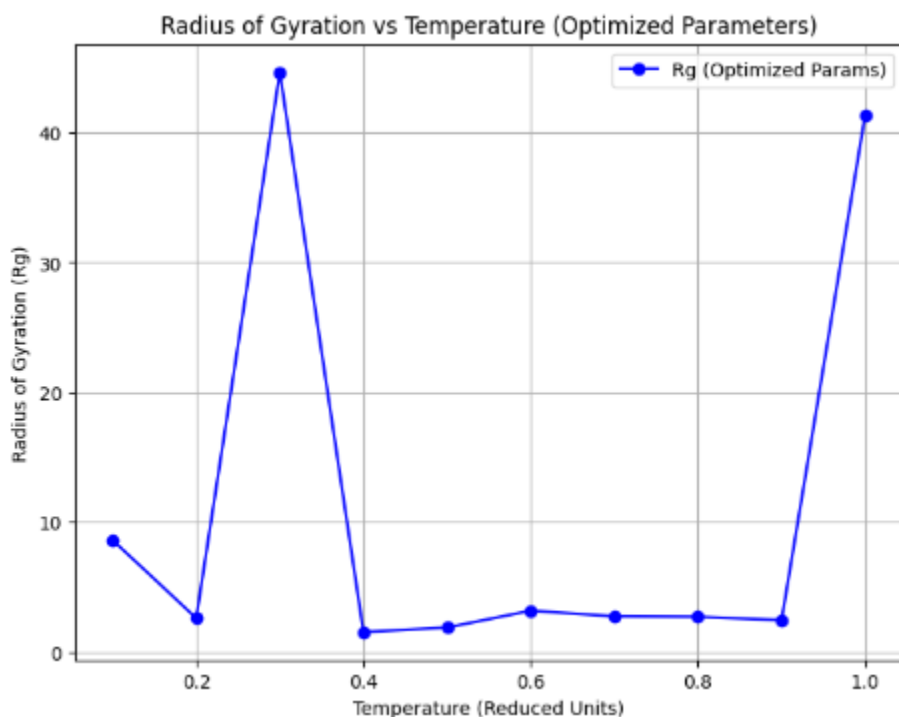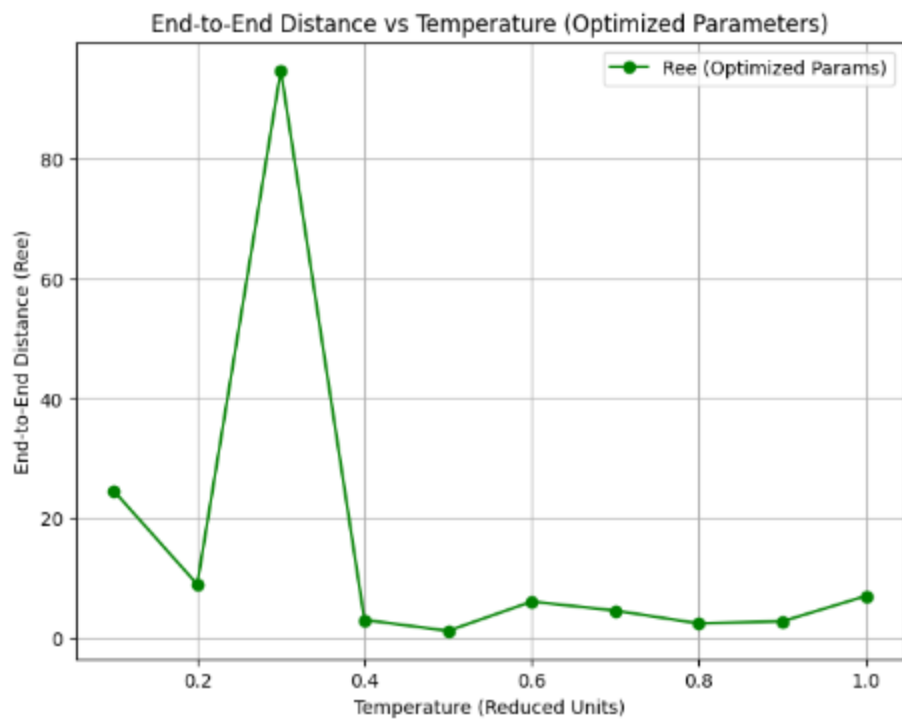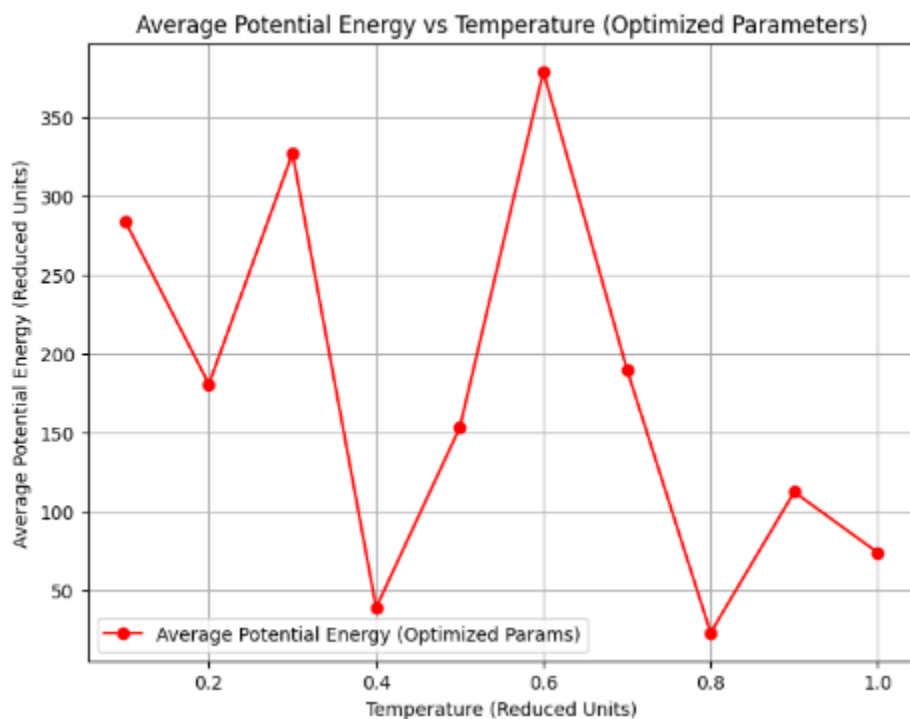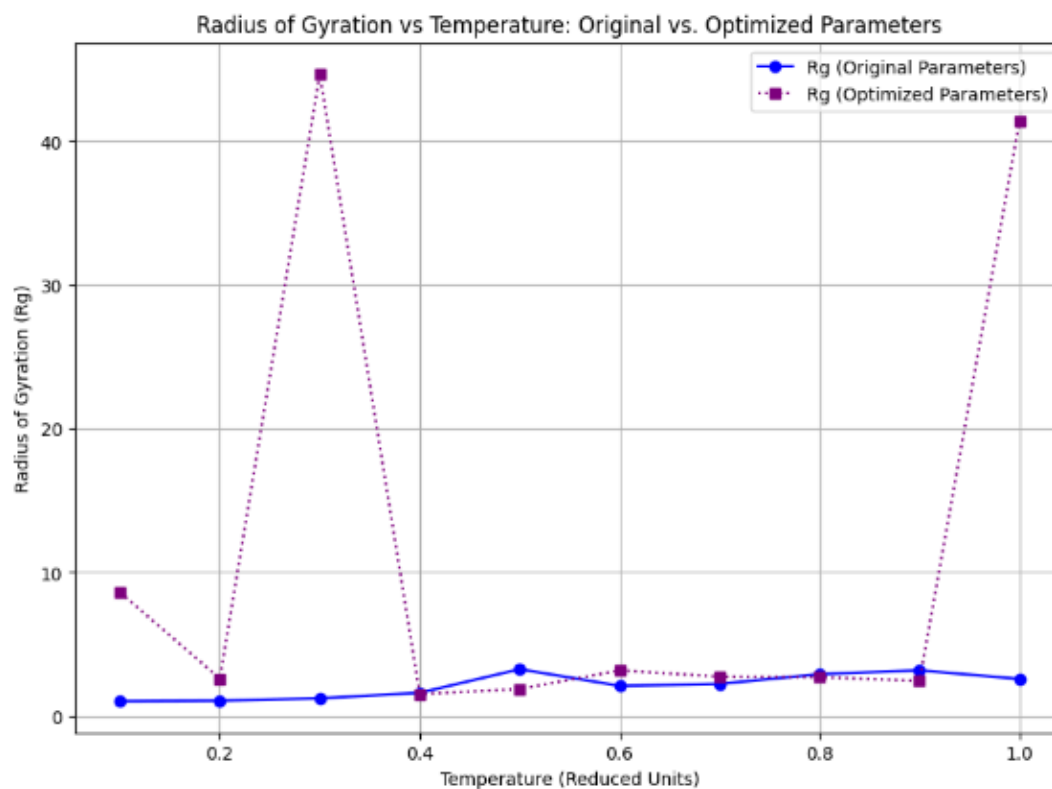

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Figure 11.