Project 2: Molecular Dynamics

Introduction

The material properties of polymer materials will vary along with their configuration. Because the temperature of the environment determines the most stable configuration of the polymer, it is important to understand the dynamics of a polymer at temperature it is likely to encounter. This can be accomplished using molecular dynamics.

In this particular scenario, the goal is to design a chain-like polymer that will remain in an unfolded configuration even at very low temperatures. When folded, the polymers being considered develop undesirable properties which render them unsuitable for an application in spacecraft. Here, molecular dynamics simulations are carried out at a wide range of temperatures to examine the phases that occur with different interactions.

Methods

All simulations carried out were for a polymer chain made up of 20 particles, using a bead-spring model. Simulations were performed using a cubic box with side lengths of 100. Positions and velocities were updated using the velocity verlet algorithm, which is carried out by looping through equations 1-4 at each step.

$$\mathrm{v}\left(t+\frac{1}{2}\Delta t\right)=\mathrm{v}(t)+\frac{1}{2}\times\frac{F(t)}{m_{particle}}\times\Delta t \tag{1}$$

$$x(t+\Delta\mathrm{t})=x(t)+\mathrm{v}\left(t+\frac{1}{2}\Delta t\right)\Delta t \tag{2}$$

$$a(t+\Delta t)=\frac{F(t+\Delta t)}{m_{particle}} \tag{3}$$

$$v(t+\Delta t)=\mathrm{v}\left(t+\frac{1}{2}\Delta t\right)+\frac{1}{2}a(t+\Delta t)\Delta t \tag{4}$$

Forces were calculated pairwise in three parts: bonded interactions, excluded volume effects, and attractive interactions. Bonded interactions were calculated between adjacent particles from a harmonic potential (equation 5). Excluded volume effects were between particles separated by one spacer using a repulsive Lennard-Jones potential (equation 6). Attractive interactions were calculated between particles separated by two or more spacers using a standard Lennard-Jones potential (equation 7). For all cases, the force is equal to the derivative of potential with respect to separation distance. The parameters used for each potential can be found in table 1.

$$U_{harmonic}(r)=\frac{1}{2}k(r-r_0)^2 \tag{5}$$

$$U_{repulsive}(r)=\begin{cases}4\epsilon_{repulsive}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], & r\le 2^{\frac{1}{6}}\sigma\\ 0, & r>2^{\frac{1}{6}}\sigma\end{cases} \tag{6}$$

$$U_{attractive}=4\epsilon_{attractive}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \tag{7}$$

Table 1. Parameters used in simulation.

Quantity	Symbol	Value
Number of particles	NA	20
Box side length	NA	100
Number of steps	NA	11,000

Timestep	Δt	0.01
mass	$m_{particle}$	1.0
Equilibrium bond length	r_0	1.0
Spring constant	k	0.25, 0.5, 1.0, 1.5
Sigma	σ	1.0
Epsilon (repulsive)	$\epsilon_{repulsive}$	1.0, 1.5, 2.0, 2.5, 3.0, 4.0
Epsilon (attractive)	$\epsilon_{attractive}$	0.5
Temperature	T	0.1 – 1.0

To analyze the results of the simulation, the end-to-end distance, potential energy, and radius of gyration were calculated. These values were calculated for 1,000 steps after an equilibration period of 10,000 steps. After 1,000 steps, the average value was taken and recorded for analysis. Potential energy was calculated as the sum of equations 5-7 for a given set of positions. End-to-end distance was calculated as the distance between the first and last particles in the chain. Radius of gyration was calculated according to equation 8 (where r_{com} is the position of the center of mass).

$$R_g = sqrt(\frac{1}{n_{particles}} \times \sum_{i=1}^{n_{particles}} (r_i - r_{com})^2 \quad (8)$$

Results

Effect of $\epsilon_{repulsive}$

Six different values of $\epsilon_{repulsive}$ were considered, ranging from 1.0 to 4.0. This value controls how strong the forces the push particles separated by one spacer are at a given distance. Higher values indicate a stronger interaction. Since stronger forces of this type will work to prevent folding, it is reasonable to expect that high values of $\epsilon_{repulsive}$ will help prevent folding at low temperatures.

With the values considered as part of the analysis, unfolded configurations at low temperatures will be indicated by higher values of all three quantities. For end-to-end distance, this is because it measures the distance between the first and last particles, which will be longer when the chain is not folded. For radius of gyration (which is a measure of the average distance of particles from their center of mass) high values also indicate an unfolded state because they show that particles are, on average, farther from the center of mass than they would be if they were clustered. With potential energy, high values indicate an unfolded state because the particles in the chain will be outside the optimal range for the attractive interactions to lower potential energy when unfolded.

Figures 1 through 6 show these values as function of temperature for each tested value of $\epsilon_{repulsive}$ at a constant value of spring constant (k = 0.25).

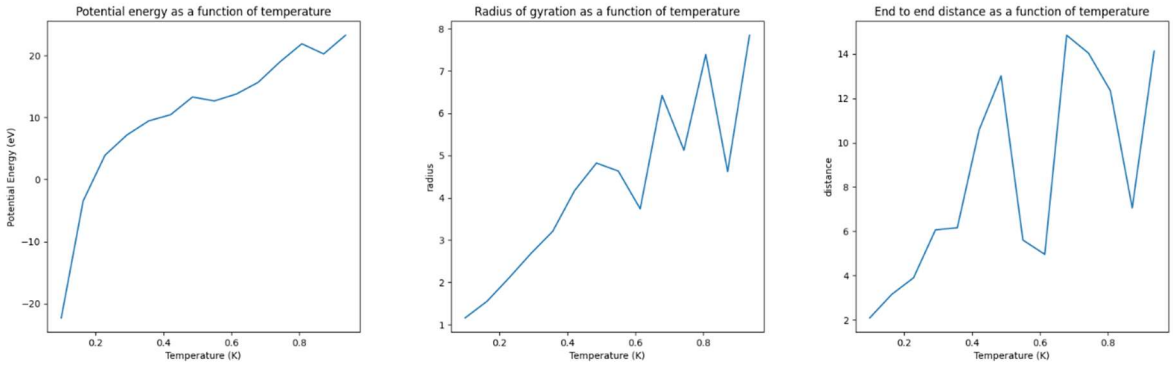

Figure 1. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 1.0$

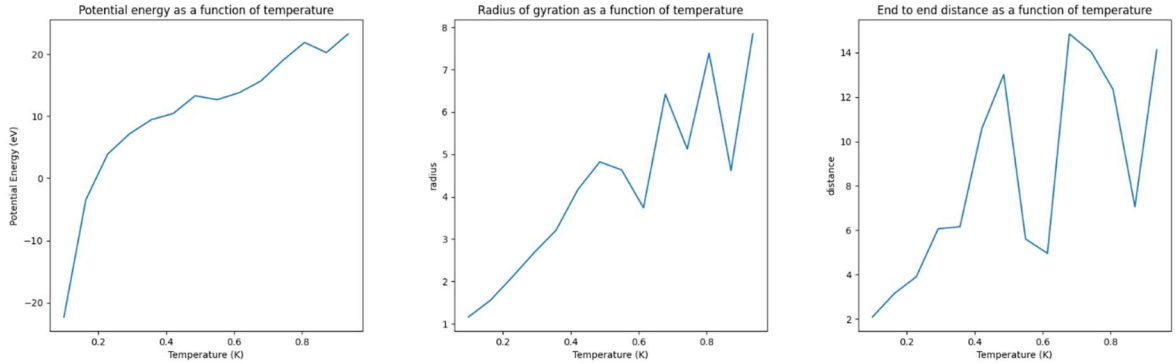

Figure 2. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 1.5$

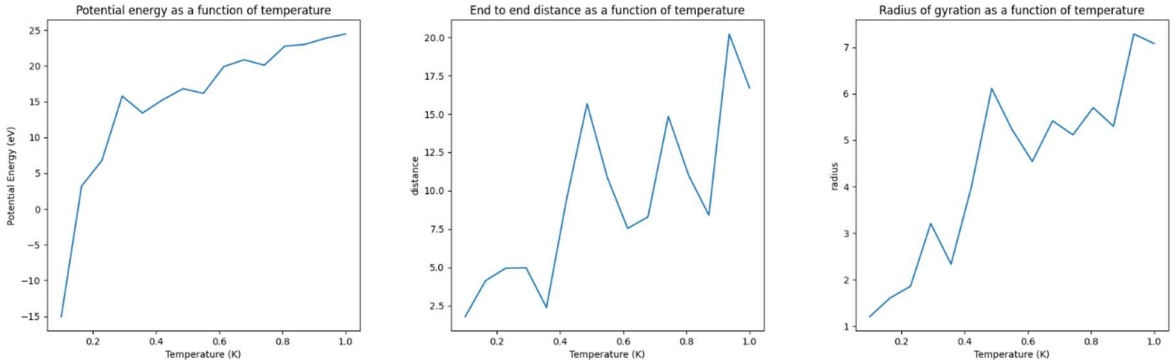

Figure 3. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 2.0$

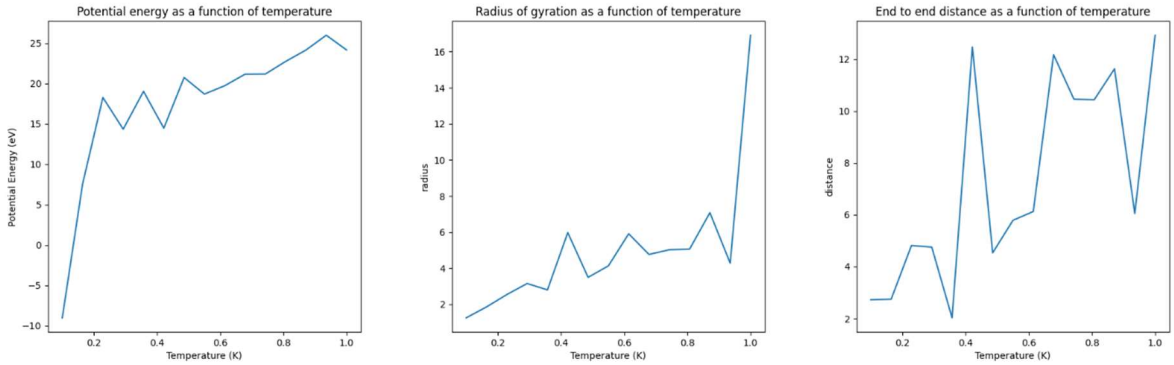

Figure 4. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 2.5$

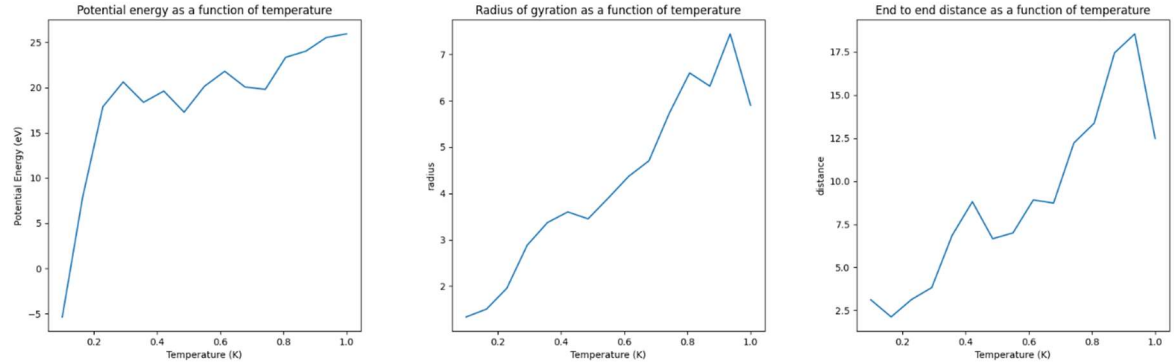

Figure 5. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 3.0$

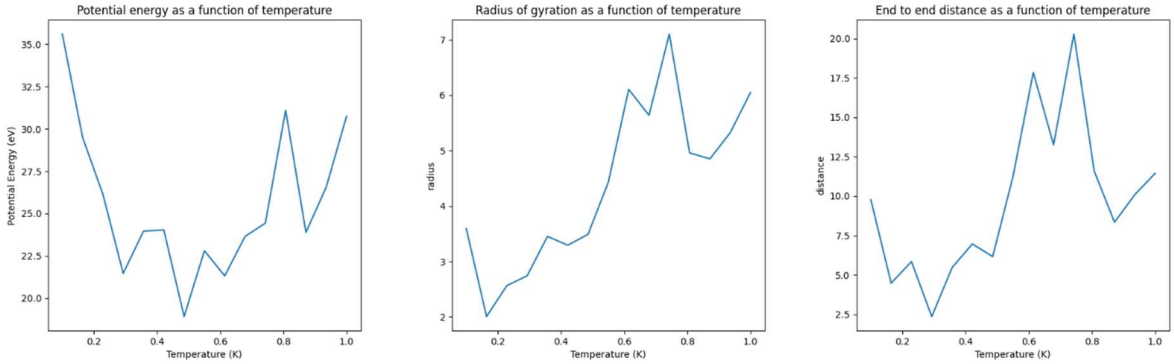

Figure 6. Potential energy, radius of gyration, and end-to-end distance for $k = 0.25$ and $\epsilon_{repulsive} = 4.0$

From the results shown in figures 1-6, it can be seen that only the set with $\epsilon_{repulsive} = 4.0$ have the high values at low temperature. This suggests that the minimum value of $\epsilon_{repulsive}$ that allows for the polymer to remain unfolded is ≥4.0. this can be confirmed by comparing the configurations at T = 0.1 for each set (see Figure 7).

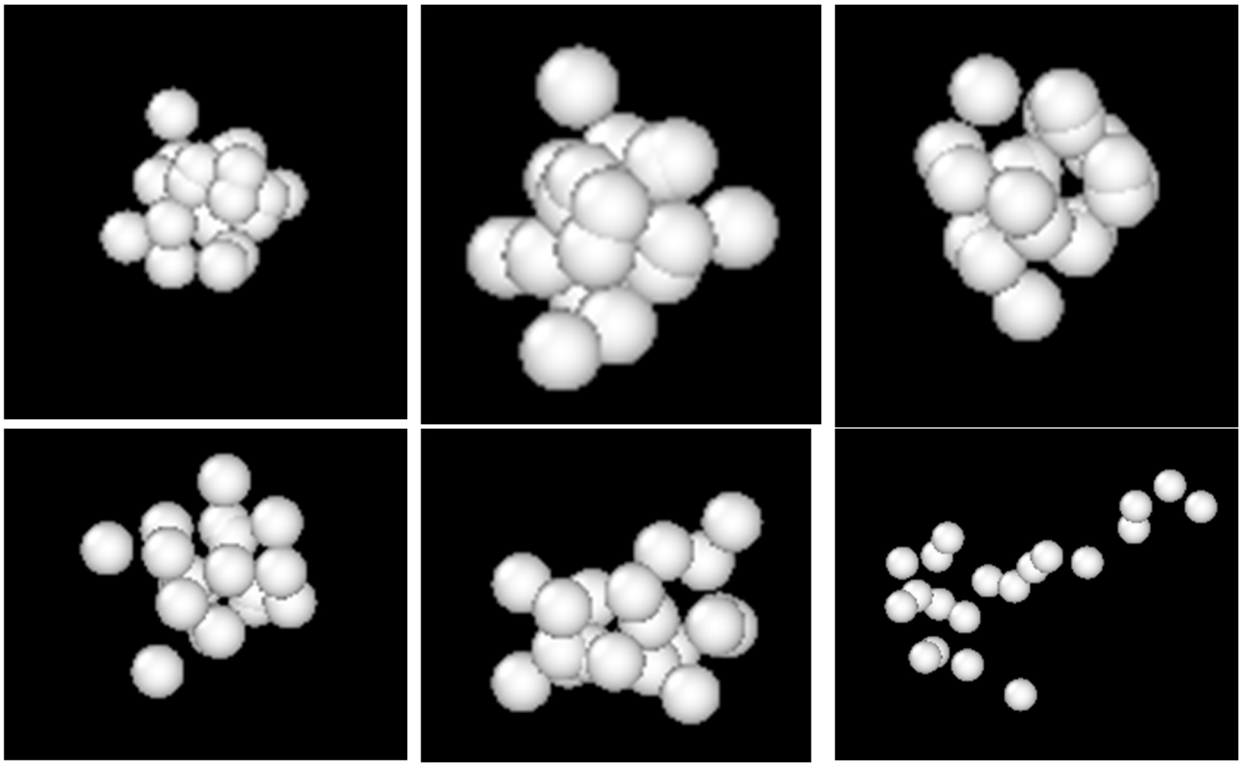

Figure 7. Structures of polymer chains at T = 0.1 for $k = 0.25$ and $\epsilon_{repulsive}$ = 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 going from left to right in rows

Effect of k

Four different values of spring constant (k) were tested to determine which values allow for the polymer to remain unfolded at low temperatures. This value determines how easily the individual particles can move relative to their neighbors. The results for potential energy, radius of gyration, and end-to-end distance are provided for all values of k with $\epsilon_{repulsive} = 4.0$ in figures 6 and 8 through 10.

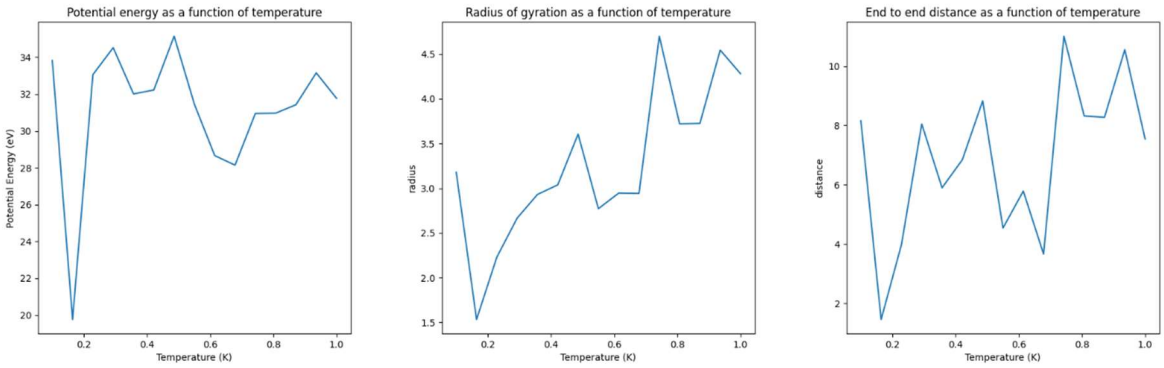

Figure 8. Potential energy, radius of gyration, and end-to-end distance for $k = 0.5$ and $\epsilon_{repulsive} = 4.0$

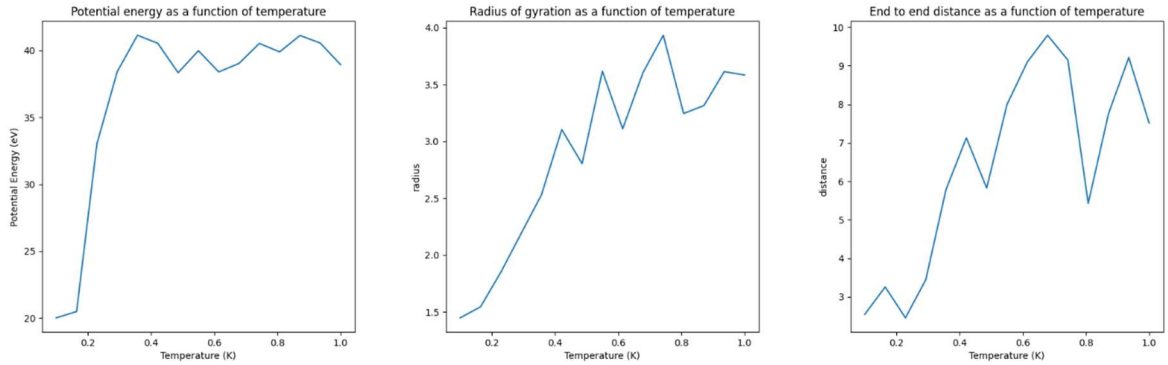

Figure 9. Potential energy, radius of gyration, and end-to-end distance for $k = 1.0$ and $\epsilon_{repulsive} = 4.0$

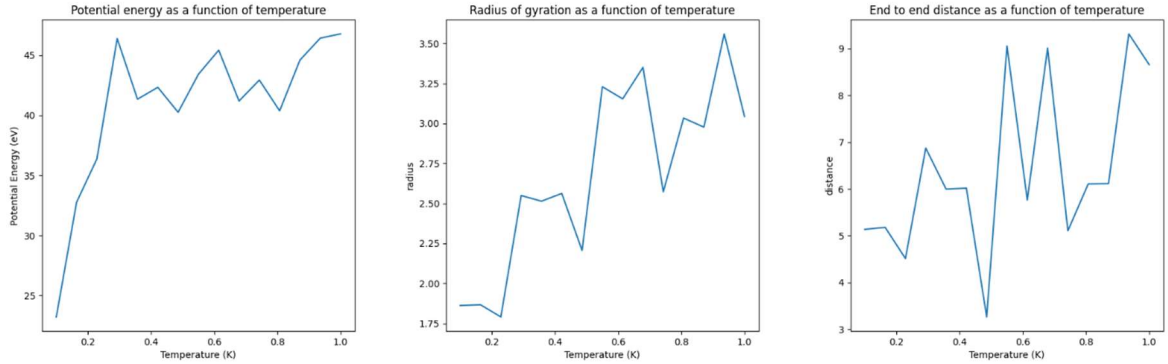

Figure 10. Potential energy, radius of gyration, and end-to-end distance for $k = 1.5$ and $\epsilon_{repulsive} = 4.0$

From these plots, it appears that the sought after behavior at low temperature occurs when $k \leq 0.5$. This is supported by examining the structures of the polymer at T = 0.1 for all values of k. the reason for this is that lower k values allow the particles to move far enough apart that the attractive interactions are sufficiently weakened that they cannot cause complete folding. This suggests that the needed values of spring constant are ≤ 0.5.

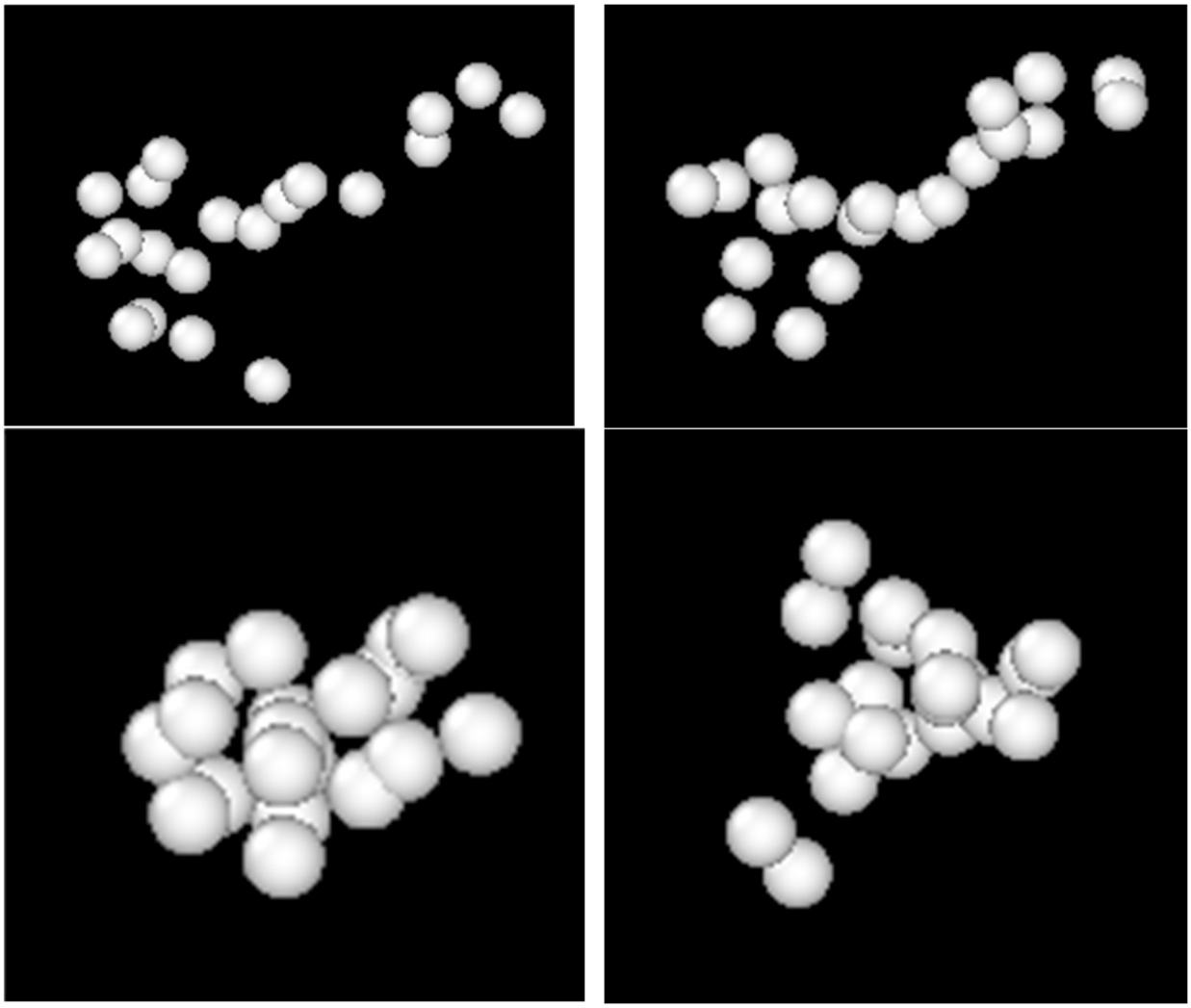

Figure 11. Structures of polymer chains at T = 0.1 for $\epsilon_{repulsive}$ = 4.0 and $k = 0.25, 0.5, 1.0, 1.5$ going from left to right in rows.

Discussion

As previously mentioned, the polymer should not fold at low temperatures when $k < 0.5$ and $\epsilon_{repulsive} > 4.0$. Determining these values was the primary goal of this work, but it is still helpful to consider the dynamics of a polymer under conditions that do allow folding to better understand how the structure of a polymer is affected by temperature. To examine these dynamics, the case where $k = 1.5$ and $\epsilon_{repulsive} = 1.0$ is considered. Figure 12 has the data for potential energy, radius of gyration, and end-to-end distance, and figure 13 contains images of the polymer chain at different temperatures.

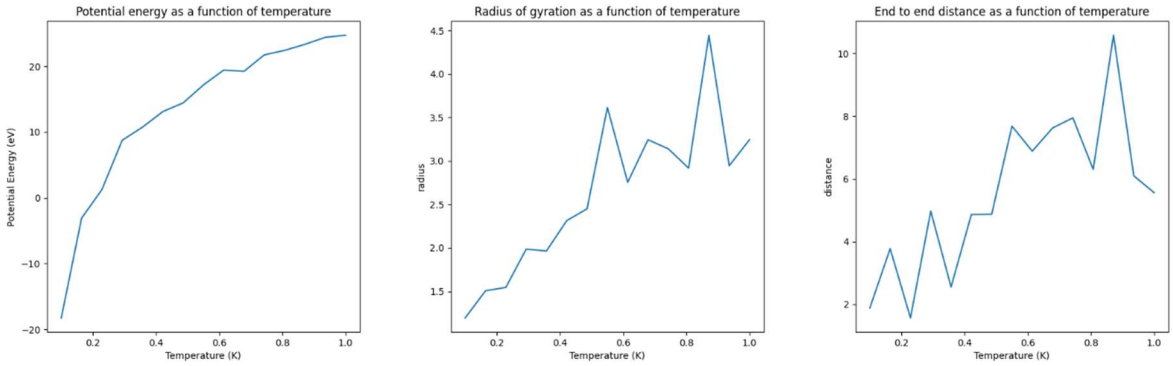

Figure 12. Potential energy, radius of gyration, and end-to-end distance for $k = 1.5$ and $\epsilon_{repulsive} = 1.0$

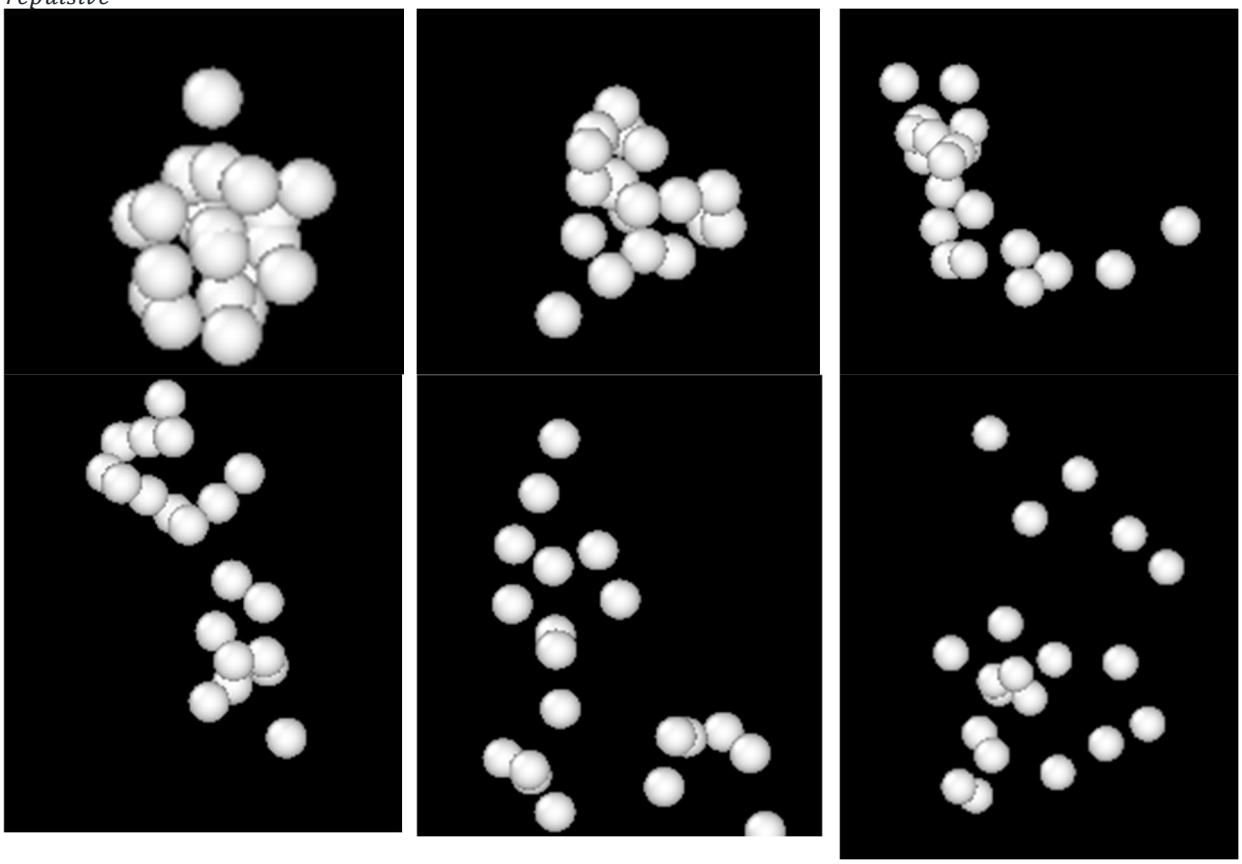

Figure 13. Structures of polymer chains at T = 0.1, 0.23, 0.42, 0.55, 0.81, 1.0 for $\epsilon_{repulsive}$ = 1.0 and $k = 1.5$ going from left to right in rows.

From these figures, it can be seen that as temperature increases, the chain becomes more dispersed, which show as an increase in potential energy, radius of gyration and end-to-end radius. From the structures of the chain shown in figure 13, the chain begins to unfold around a temperature of 0.42. This can be seen most clearly in the plots as a sharp increase in potential

energy. There are also sharper increases in both end-to-end distance and radius of gyration; however, since these values have more variation, it is harder to see.

Conclusion

Based on trends in the dynamics, the ideal conditions for a polymer that remains unfolded at low temperature are $k \leq 0.5$ and $\epsilon_{repulsive} \geq 4.0$. Knowing these values requires knowledge of the interactions of the actual compound used, but these parameters can serve as guidelines. It may also help to consider polymers at different lengths to see if these parameters are still valid if chains longer than 20 particles are used. It could also be interesting to simulate polymers of different shapes besides chains.