Project 2 Report

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1 Introduction

Polymer folding is a critical phenomenon that impacts material properties and biological functions, such as protein folding and the behavior of synthetic polymers. Understanding the factors that influence polymer folding, such as temperature and interactions, can provide a theoretical treatment for applications ranging from drug delivery to material design. This study simulates a polymer chain in a periodic cubic box to investigate a few properties that provide insight to phase transitions, which can allow differentiation between folded and unfolded states.

2 Methods

A molecular dynamics simulation was implemented to model a polymer chain of 20 particles in a periodic cubic box. The methods used to run the simulation are outlined as follows.

2.1 Equations of Motion

The velocity Verlet algorithm was used to integrate the equations of motion, updating the particle positions, velocities and effective forces with each step. The following calculations were performed for each step:

$$\mathbf{v}_{i+1/2} = \mathbf{v}_i + \frac{\mathbf{F}_i}{m}\frac{\Delta t}{2}, \tag{1}$$

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \mathbf{v}_{i+1/2}\Delta t, \tag{2}$$

$$\mathbf{v}_{i+1} = \mathbf{v}_{i+1/2} + \frac{\mathbf{F}_{i+1}}{m}\frac{\Delta t}{2}, \tag{3}$$

where $\mathbf{v}_i, \mathbf{v}_{i+1/2}$, and $\mathbf{v}_{i+1}$ are the initial, midpoint, and final velocities respectively; $\mathbf{r}_i$ and $\mathbf{r}_{i+1}$ are the initial and final positions; $\mathbf{F}_i$ and $\mathbf{F}_{i+1}$ are the initial and final forces; m is the mass of the particles; and Δt is the time step for the Verlet algorithm.

2.2 Forces

Forces on the particles were calculated using a combination of harmonic and Lennard-Jones potentials. The harmonic forces account for bonded interactions, and the Lennard-Jones forces account for non-bonding interactions.

Harmonic Potential:

The following equation was used to compute forces between neighboring particles:

$$\mathbf{F}_{\text{bond}} = -k(r - r_0)\hat{\mathbf{r}}, \tag{4}$$

where r is the distance between consecutive particles, r_0 is the equilibrium bond length, k is the spring constant, and $\hat{\mathbf{r}}$ is the unit vector along the bond direction.

Lennard-Jones Potential:

A repulsive Lennard-Jones potential was used to model the repulsive interaction between particles separated by a single spacer.

$$\mathbf{U}_{\text{LJ,rep}}(r) = \begin{cases} 4\epsilon_{\text{rep}}\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \frac{1}{4}\right], & r < 2^{1/6}\sigma \\ 0, & r \geq 2^{1/6}\sigma, \end{cases} \tag{5}$$

where σ is the characteristic length scale, ϵ_{rep} is the repulsive interaction strength, and r is the distance between particles.

An attractive potential was used between beads separated by more than one spacer.

$$\mathbf{U}_{\text{LJ,att}}(r) = 4\epsilon_{\text{att}}\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{6}$$

where again, σ is the characteristic length scale, ϵ_{att} is the attractive interaction strength, and r is the distance between particles.

2.3 Thermostat

To maintain the target temperature, velocities were periodically rescaled based the square root of the ratio between the target and instantaneous temperatures.

$$T_{\text{inst}} = \frac{2K}{3Nk_B}, \qquad \mathbf{v}_i \leftarrow \mathbf{v}_i\sqrt{\frac{T_{\text{target}}}{T_{\text{inst}}}}, \tag{7}$$

where K is the kinetic energy, T is the temperature, and k_B is Boltzmann's constant.

3 Results

3.1 Phase Transitions

Figure 1 shows the radius of gyration, R_g, as a function of temperature. R_g is perhaps the most important measure used to determine the phase of a polymer since it indicates how coiled it is; the larger R_g is, the more extended the polymer. At low temperatures, R_g is small, indicating a folded state. As temperature increases, R_g generally decreases, but a sharp jump in R_g at $T = 0.7$ is evidence of a phase transition from a folded conformation to an unfolded conformation.
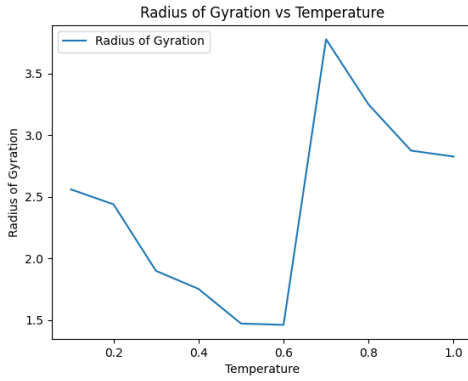
Figure 1: Radius of gyration as a function of temperature.

End-to-end distance is another useful metric for determining the phase of the polymer. When the polymer is folded, the end-to-end distance tends to be smaller than when the polymer is unfolded. Similarly, the end-to-end distance (R_{ee}) in Figure 2 supports this trend observed for R_g as a function of T, with a general decrease in R_{ee} with respect to T, and evidence of a phase transition near $T = 0.7$.
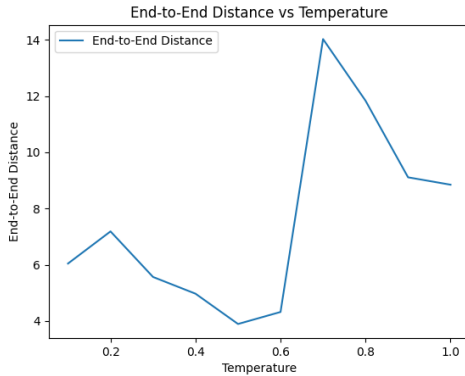

Figure 2: End-to-end distance as a function of temperature.

3.2 Potential Energy

Shown in Figure 3, with increasing temperature, the potential energy fo the polymer tends to increase. This aligns with expectation.
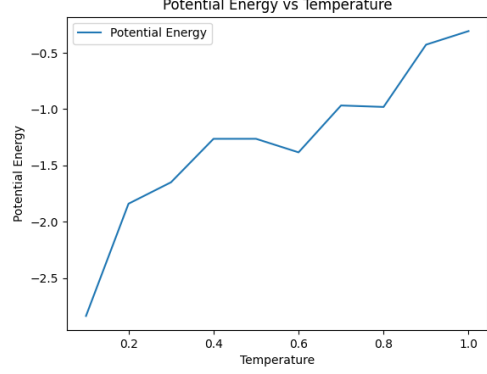

Figure 3: End-to-end distance as a function of temperature.

At lower temperatures, the chain adopts configurations that minimize potential energy, due to the low thermal energy available to it. As temperature increases, the polymer can sustain a broader range of conformational states, leading to higher average potential energy. The somewhat linear relationship observed suggests a direct relationship between thermal energy and the polymer chain's configurational freedom.

3.3 Parameter Optimization

A small range of spring constants and $\epsilon_{\text{repulsive}}$ ($\in$ [0.1, 2]) were explored to minimize polymer folding at low temperatures. This minimization was quantified by evaluating how R_g and R_{ee} varied with respect to each of these parameters. At $T = 0.1$, both R_g and R_{ee} peaked when $k = 0.7$ as shown in Figures 4 and 5.
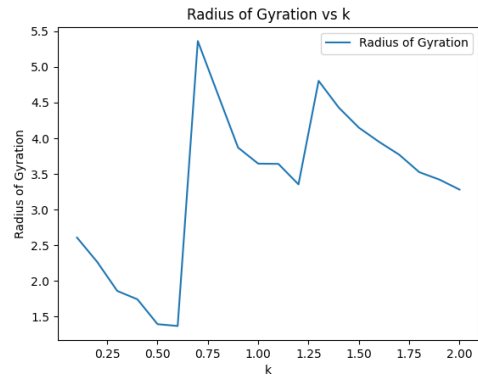

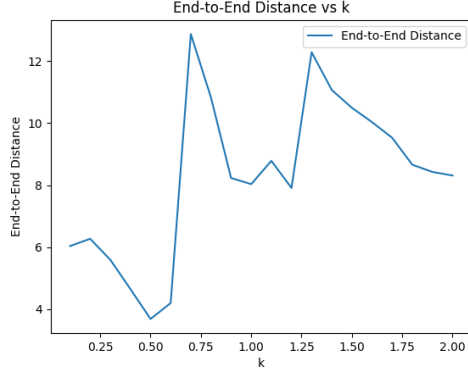Figure 4: End-to-end distance as a function of temperature.

Figure 5: End-to-end distance as a function of temperature.

At $T = 0.1$, $\epsilon_{\text{repulsive}}$ also exhibited peaks in R_g and R_{ee} at $\epsilon_{\text{repulsive}} = 0.7$, as shown in Figures 6 and 7. However, these plots show a maximal preference for extended conformations at the minimum values of $\epsilon_{\text{repulsive}}$ sampled.
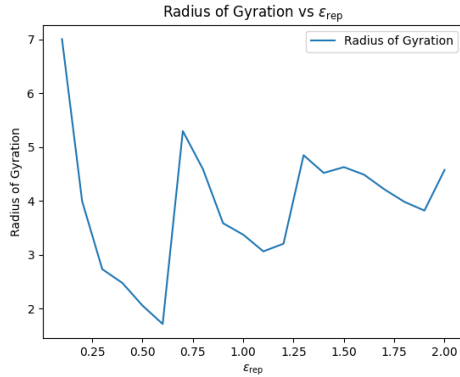

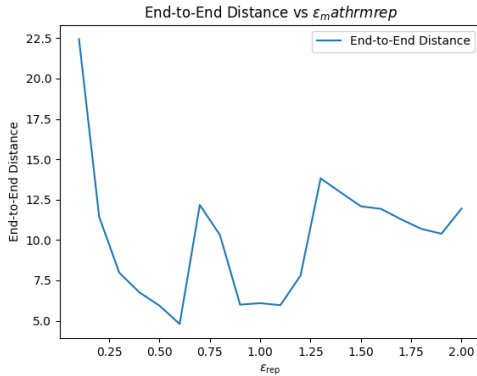Figure 6: End-to-end distance as a function of temperature.

Figure 7: End-to-end distance as a function of temperature.

4   Discussion

The aforementioned results provide clear evidence of a phase transition in the polymer chain as a function of temperature, as indicated by abrupt changes in both R_g and R_{ee}. At low temperatures, the polymer remains in a compact, folded state, minimizing its potential energy due to restricted thermal motion. However, as the temperature increases, the polymer transitions to an extended, unfolded state, characterized by larger R_g and R_{ee} values. The sharp changes near $T = 0.7$ suggest a critical temperature where the polymer undergoes a significant conformational shift.

The consistency in results demonstrates that the methods employed provide a means to sample polymer dynamics and gain valuable insights into its configurational behavior across a range of parameters.

5   Conclusion

This study investigated the temperature-dependent behavior of a polymer chain, demonstrating a phase transition from a folded to an unfolded state at a critical temperature of $T = 0.7$. The radius of gyration, end-to-end distance, and potential energy all provided consistent evidence of this transition, revealing fundamental insights into the dependency of polymer conformation upon physical parameters.

Future work could explore a broader range of interaction parameters, investigating the effect of increasing chain length or introducing branches. Additionally, incorporating more sophisticated thermostats or sampling techniques could be used to improve the accuracy of these results.