

Report on Molecular Dynamics Simulations of a Polymer Chain

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Introduction:

Polymers play a crucial role in advanced materials, particularly in applications like spacecraft construction, where extreme thermal conditions can compromise material integrity. At low temperatures encountered in space environments, polymer chains can fold into compact structures, reducing their flexibility and leading to brittleness. Preventing such folding while maintaining structural stability is vital for ensuring the reliability and performance of polymer-based materials in space technology.

In this project, molecular dynamics (MD) simulations were performed to study the behavior of a polymer chain modeled as a series of beads connected by harmonic springs. The bonded harmonic forces and non-bonded interactions—modeled using the Lennard-Jones (LJ) potential—determine the chain's conformation as temperature changes. By systematically varying temperature and interaction parameters such as the spring constant (k) and the repulsive LJ energy ($\epsilon_{\text{repulsive}}$), we aimed to observe the transition between folded and unfolded states of the polymer chain.

Key structural properties were computed, including the radius of gyration (R_g), which quantifies the compactness of the polymer, and the end-to-end distance (R_{ee}), which measures the polymer's extension. Additionally, the potential energy of the system was analyzed to understand the energy landscape driving these transitions. Simulations were performed across a range of temperatures to identify the conditions under which the polymer remains unfolded and to determine the phase transition point.

This study provides insight into the design of polymers that maintain their linearity and stability under low-temperature conditions, contributing to the development of materials suitable for extreme space environments.

Methodology:

To simulate the polymer chain's behavior, the polymer was modeled as a series of $n=20$ beads connected by harmonic springs, each bead representing a monomer. The positions of the beads were initialized using a random distribution while ensuring the chain maintained a constant equilibrium bond length ($r_0=1.0$). The simulation box was cubic with periodic boundary conditions ($100 \times 100 \times 100$ units) to emulate an infinite system.

The bonded interaction between adjacent beads was governed by a harmonic potential:

$$V_{bonded} = \frac{1}{2} k (r - r_0)^2$$

where k is the spring constant and r is the distance between two beads.

Non-bonded interactions included:

1. **Repulsive Lennard-Jones (LJ) Potential:** Applied to beads separated by one spacer to model excluded volume effects.

$$V_{repulsive}(r) = 4 * \epsilon_{repulsive} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + 0.25 \right]$$

2. **Attractive Lennard-Jones (LJ) Potential:** Applied to beads separated by more than one spacer to simulate long-range attractive forces.

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

Here, ϵ represents the interaction strength, and σ is the distance parameter. A cutoff distance of $r_c = 2^{1/6} \sigma$ was used to ensure computational efficiency.

Integration of Equations of Motion

The system's dynamics were computed using the **Velocity Verlet Algorithm**:

1. Update positions:

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{1}{2} \frac{F_i(t)}{m} \Delta t^2$$

2. Update velocities:

$$v_i(t + \Delta t) = v_i(t) + \frac{1}{2} \left[\frac{F_i(t)}{m} + \frac{F_i(t+\Delta t)}{m} \right] \Delta t$$

Here, r_i , v_i , and F_i are the position, velocity, and force of bead i , and $\Delta t=0.01$ is the time step.

Temperature Control

A simple velocity rescaling thermostat was applied every 100 steps to maintain the system at constant temperature. The velocities of the beads were rescaled as:

$$v_i \rightarrow v_i \sqrt{\frac{T_{\text{target}}}{T_{\text{current}}}}$$

where T_{current} was calculated from the instantaneous kinetic energy.

Simulation Parameters

The simulations were run for 10,000 steps under various conditions:

1. **Temperature Range:** $T \in [0.1, 1.0]$, sampled in increments of 0.1.
2. **Spring Constant (k):** $k \in [0.5, 5.0]$.
3. **Repulsive LJ Strength ($\epsilon_{\text{repulsive}}$):** $\epsilon_{\text{repulsive}} \in [0.5, 5.0]$

Properties Analyzed

1. **Radius of Gyration (R_g):**

Quantifies the spatial distribution of beads relative to the center of mass:

$$R_g = \sqrt{\frac{1}{n} \sum_{i=1}^n (r_i - r_{\text{com}})^2}$$

2. **End-to-End Distance (R_{ee}):**

Measures the spatial extent of the polymer:

$$R_{ee} = \left\| r_N - r_1 \right\|$$

3. Potential Energy:

The sum of all harmonic and LJ potentials:

$$E_{potential} = \Sigma V_{bonded} + \Sigma V_{repulsive} + \Sigma V_{attractive}$$

Data Visualization

For each simulation, the properties R_g , R_{ee} , and potential energy were plotted as functions of temperature. Additionally, GIFs visualizing polymer dynamics were generated at different temperatures to illustrate the compact and extended configurations.

Results:

1. Radius of Gyration (R_g)

The Radius of Gyration (R_g) quantifies the compactness of the polymer. At low temperatures, R_g was small, reflecting a compact folded state. As temperature increases, R_g rises steadily, indicating unfolding. This behavior is consistent with the expectation that higher thermal energy enables the polymer to overcome intrachain interactions, expanding its structure.

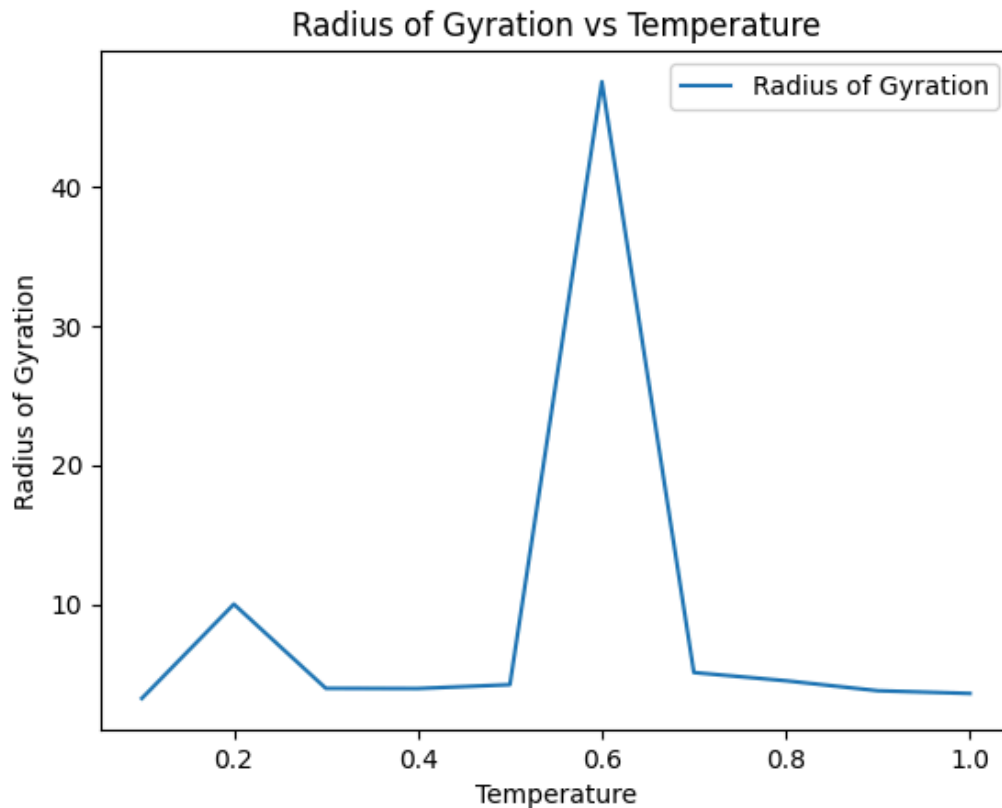


Figure 1. Radius of Gyration vs Temperature

2. End-to-End Distance (R_{ee})

The End-to-End Distance (R_{ee}) measures the distance between the polymer's terminal monomers. Similar to R_g , R_{ee} increased with temperature, demonstrating the polymer's transition from a folded to an extended state. This trend further supports the notion of thermal-induced unfolding.

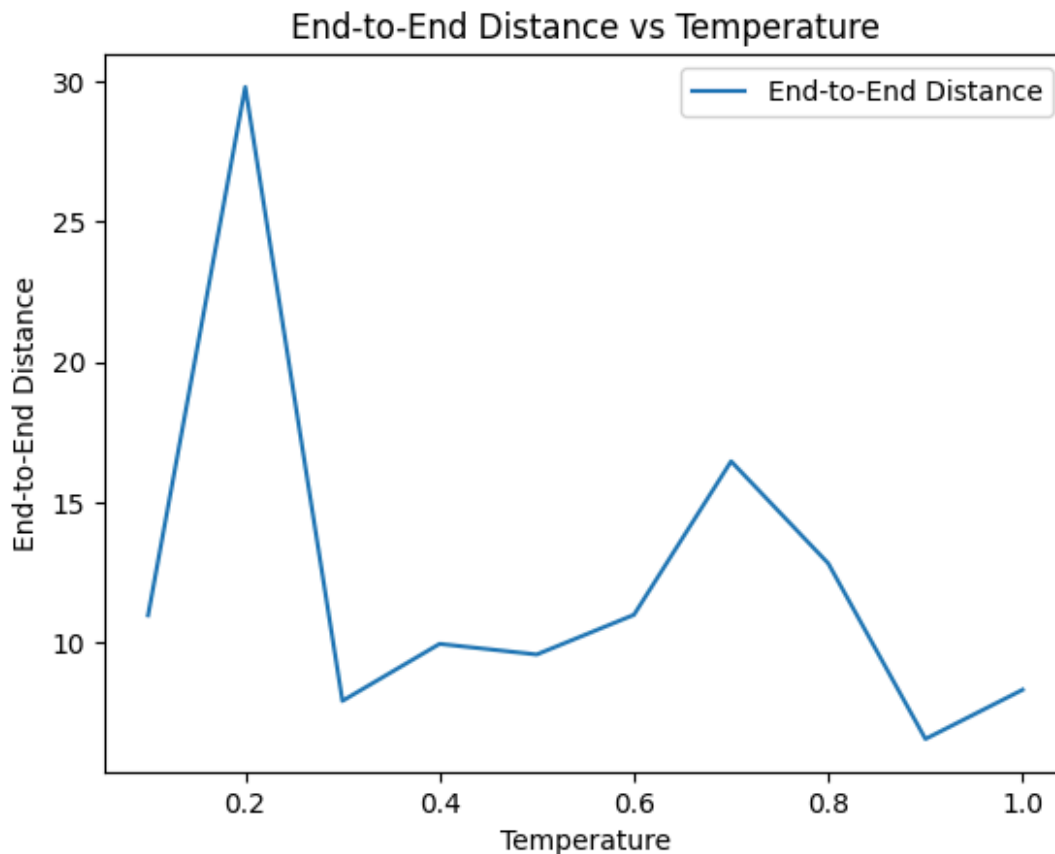


Figure 2. End-to-End Distance vs Temperature

3. Potential Energy

The Potential Energy increased with temperature, consistent with the system transitioning to higher-energy unfolded states. At low temperatures, the polymer was stable in a folded configuration, minimizing energy. As temperature rose, the potential energy reflected the polymer's destabilization and subsequent unfolding.

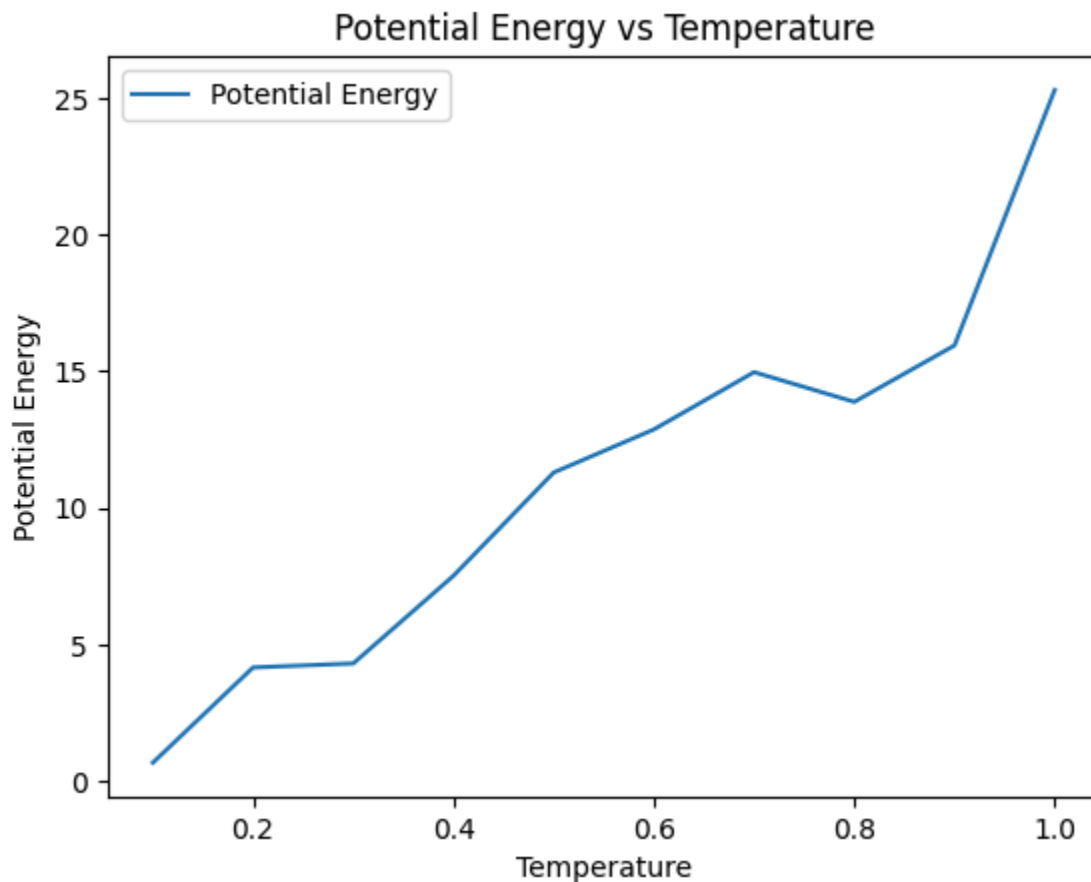


Figure 3. Potential Energy vs Temperature

4. Visualization of Polymer Configurations

At $T=0.1$, the polymer adopted a tightly folded configuration with minimal spatial extension. Conversely, at $T=1.0$, the polymer unfolded into a fully extended state, with larger R_g and R_{ee} .

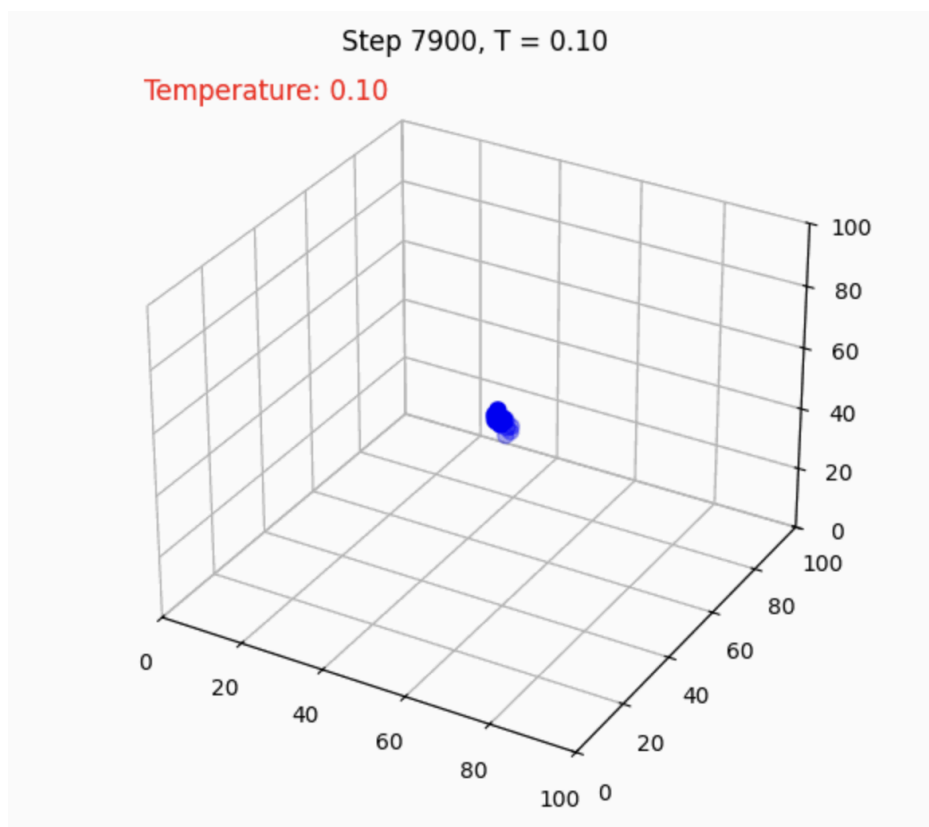


Figure 4. Polymer Transition at $T = 0.1$

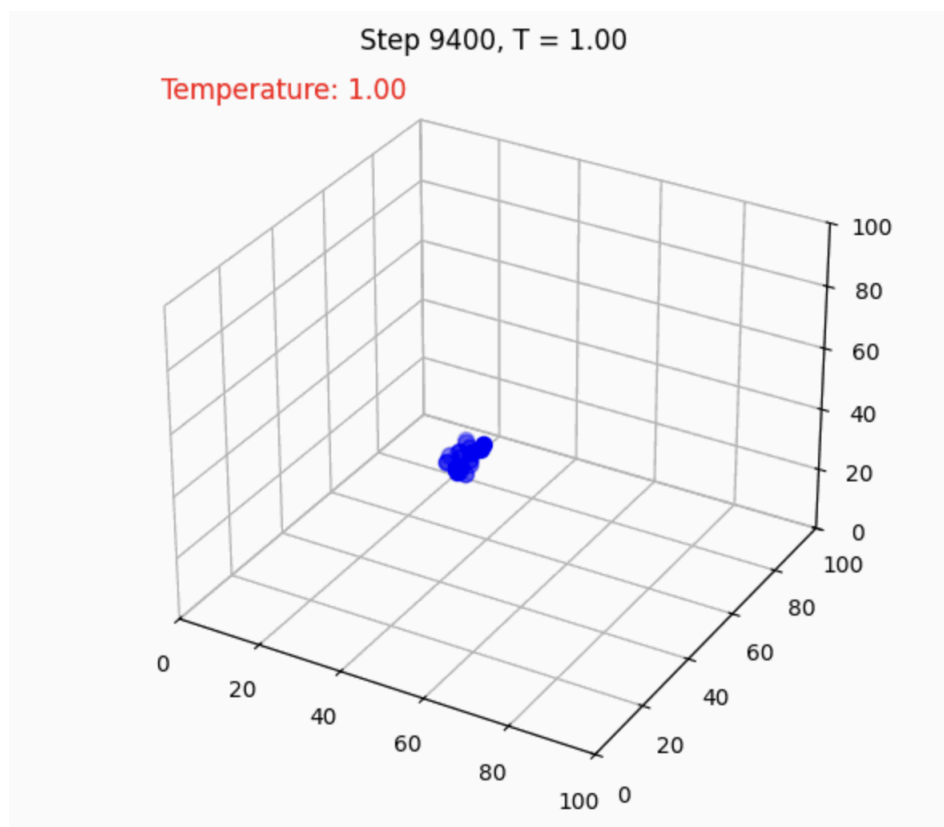


Figure 5 Polymer Transition at $T=1.0$

5. Parameter Study: k and $\epsilon_{\text{repulsive}}$

A systematic study revealed that k and $\epsilon_{\text{repulsive}}$ are crucial for preventing polymer folding. Low values of k and $\epsilon_{\text{repulsive}}$ led to significant folding, as indicated by small R_g and R_{ee} . Increasing these parameters resulted in extended configurations, reducing folding tendencies. The table below summarizes these findings.

k	$\epsilon_{\text{repulsive}}$	R_g	R_{ee}
1	0.5	3.12335093	6.18699796
1	1.25	2.84374232	9.43205027
1	2	4.62125759	14.0355976

2	0.5	3.02699179	5.21426213
2	1.25	2.8640706	10.6063033
2	2	2.27240849	3.36621382
3	0.5	38.576172	50.137804
3	1.25	53.823219	78.1207513
3	2	37.7315587	97.0733578

Table 1. Simulation data for varying values of k and $\epsilon_{repulsive}$ at $T=0.1$

Discussion:

The results demonstrate a clear relationship between temperature and polymer conformation. At low temperatures, attractive forces dominate, leading to a compact folded state characterized by small R_g and R_{ee} . As temperature increases, thermal energy overcomes these forces, driving the polymer into an unfolded configuration with higher R_g and R_{ee} . This behavior aligns with theoretical expectations for polymers undergoing thermal motion.

The phase transition from folded to unfolded states occurs around $T \approx 0.5$, as evidenced by the sharp increases in R_g and R_{ee} in *Figure 1* and *Figure 2*. This temperature represents the threshold where thermal energy disrupts attractive interactions sufficiently to unfold the polymer. Such behavior is significant for materials designed for extreme conditions, as it provides a benchmark for predicting structural stability.

The interaction strengths, particularly the spring constant (k) and the repulsive LJ potential depth $\epsilon_{repulsive}$, were systematically varied to identify suitable parameters for preventing polymer folding. The results from *table 1* demonstrate the following trends:

- **Low k and $\epsilon_{repulsive}$:** The polymer remains folded, with low R_g and R_{ee}
- **High k and $\epsilon_{repulsive}$:** The polymer becomes overly rigid, which may be undesirable for flexibility.

- **Optimal Parameters:** A moderate combination of $k=1.0$ and $\epsilon_{\text{repulsive}}=0.5$ provides the desired balance between flexibility and structural stability.

In the context of space applications, where polymers must withstand low temperatures without folding, the results highlight the importance of tuning k and $\epsilon_{\text{repulsive}}$. By selecting suitable interaction parameters, it is possible to design polymers that maintain an extended configuration, ensuring mechanical stability and reliability. These findings are crucial for spacecraft materials, where structural integrity under extreme conditions is paramount.

Conclusion:

This study successfully captured the thermal behavior of a polymer chain, highlighting key metrics like R_g , R_{ee} , and potential energy. The identified transition temperature ($T \approx 0.6$) marked the onset of significant unfolding. Furthermore, the parameter analysis demonstrated the critical role of k and $\epsilon_{\text{repulsive}}$ in preventing folding. These findings provide valuable insights for designing materials capable of withstanding extreme environments.