

Controlling Polymer Folding Through Temperature, Spring Constant, and Repulsive Interaction Parameters: A Molecular Dynamics Study

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1. Introduction

Polymer folding is an important phenomenon that significantly influences the mechanical and thermal properties of polymer materials. Understanding how polymers behave under different conditions, such as varying temperatures and interaction strengths, is necessary for designing advanced materials with tailored properties. In particular, polymer folding plays a major role in determining the stability, durability, and functionality of materials, which is especially important in applications like aerospace, drug delivery, and smart materials.

The purpose of this simulation study is to investigate the conformational behavior of a polymer chain under different interaction parameters, specifically focusing on the effect of repulsive, attractive forces, and temperature. By using molecular dynamics simulations with a bead-spring model, we aim to analyze the impact of varying interaction strengths on key structural properties of the polymer, such as the radius of gyration and end-to-end distance. This understanding will provide insights into how to optimize polymer design to prevent undesirable folding, which can lead to brittleness and reduced mechanical performance.

2. Methodology

The polymer chain was modeled using a bead-spring approach, where each bead represents a monomer unit in the chain. The interactions between adjacent beads were modeled using harmonic spring potentials, which are characterized by a spring constant (k) and an equilibrium bond length (r_0). These bonded interactions ensured that the chain structure adhered to realistic bond constraints. For non-bonded interactions between beads, the Lennard-Jones potential was used to capture both repulsive and attractive forces, providing a framework to model the folding and unfolding behavior of the polymer. The repulsive component of the Lennard-Jones potential

prevented overlap between beads, while the attractive component accounted for non-bonded monomer interactions.

The simulations were conducted in a cubic simulation box with periodic boundary conditions to mimic an infinite system and eliminate edge effects. The equations of motion were integrated using the velocity Verlet algorithm, chosen for its efficiency and ability to conserve energy in molecular dynamics simulations. A velocity rescaling thermostat was employed to maintain the target temperature during the simulation, ensuring that the polymer chain reached thermal equilibrium. This approach allowed for stable control over temperature-dependent polymer behavior.

The simulation process was divided into two main phases: equilibration and sampling. Two equilibration phases were considered as 20,000 and 140,000 steps, allowing the system to stabilize and reach equilibrium. During this phase, potential energy was monitored to confirm that the system had reached a steady state without significant fluctuations. Following equilibration, a sampling phase of 1,000 steps was conducted for the 20,000 steps equilibration, and 10,000 steps for the 140,000 steps equilibration, to collect data for analysis under equilibrium conditions.

The bead-spring polymer model was parameterized to study the effects of varying interaction strengths, specifically focusing on the spring constant (k) and the repulsive interaction strength ($\epsilon_{\text{repulsive}}$). Simulations covered a range of temperatures ($T=0.1$ to 1.0) to investigate the critical transition point between folded and unfolded states, as well as low-temperature conditions ($T=0.1$) to optimize k and $\epsilon_{\text{repulsive}}$. In addition, to investigate the effect of polymer chain length on folding and conformational behavior, simulations were conducted with chain lengths of 5, 20, and 100 particles. This range allowed for a comparative analysis of short, intermediate, and long chains, shedding light on how chain length influences structural properties such as radius of gyration, end-to-end distance, and potential energy.

After obtaining the configuration of polymer at each step, key structural properties including the radius of gyration, end-to-end distance, and potential energy, were calculated during the sampling phase to evaluate the conformation behavior of polymer. These properties provided

insights into how the interaction parameters influenced polymer folding and unfolding, helping to identify optimal conditions for preventing undesirable folding.

3. Results and discussion

3.1. Polymer behavior at different temperature

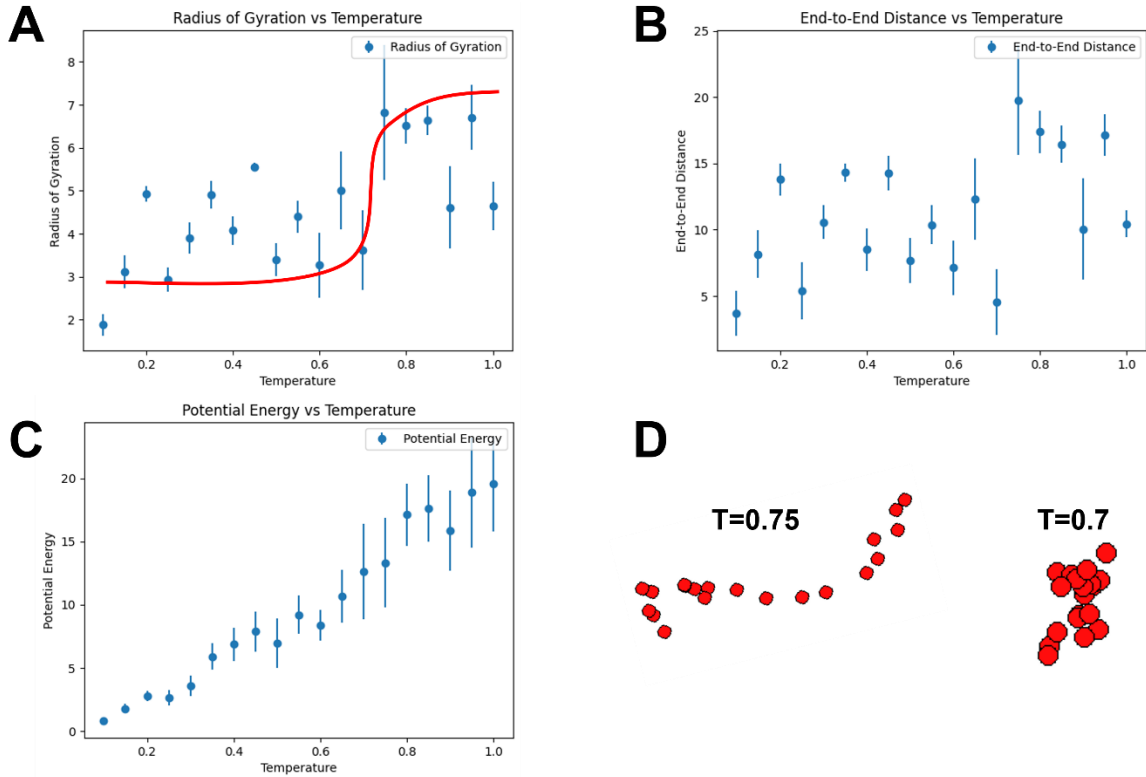


Figure 1. (A) Radius of Gyration, (B) End-to-End Distance, (C) Potential Energy, and (D) Polymer configurations before and after transition state.

The polymer's behavior was analyzed across a temperature range of 0.1 to 1.0. As a result, a noticeable change in polymer's structure occurred at $T=0.75$, which indicates the transition point between the folded and unfolded states. **Figure 1A** shows how the radius of gyration (Rg) changes with temperature. At low temperatures ($T < 0.75$), Rg remains small and stable, meaning the polymer stays folded. However, at $T=0.75$, Rg increases sharply, showing that the polymer starts unfolding. The red curve highlights this transition clearly, with a sigmoidal shape typical of such structural changes. **Figure 1B** denotes the end-to-end distance of the polymer versus temperature.

Although there is some variation, the trend matches the R_g data. At lower temperatures, the polymer has a shorter end-to-end distance, confirming its folded structure. After the transition, the distance increases as the polymer unfolds. **Figure 1C** shows the potential energy of the polymer as the temperature increases. The energy rises gradually with temperature, reflecting more thermal movement. Unlike R_g , there is no sudden jump at $T=0.75$. However, at $T=0.75$, the standard deviation of the potential energy was larger than at other points, indicating that $T=0.75$ is the transition point. **Figure 1D** compares the configuration of polymer at $T=0.7$ and $T=0.75$. At $T=0.7$, the polymer remains tightly folded. At $T=0.75$, it begins to unfold, spreading out into a more extended structure. This transition highlights how temperature influences polymer behavior. Below $T=0.75$, the polymer folds to minimize interactions with its surroundings. As the temperature rises, thermal energy dominates, causing the polymer to unfold.

3.2. Finding optimal spring constant (k) and $\epsilon_{\text{repulsive}}$ conditions to prevent polymer folding at low temperature ($T=0.1$)

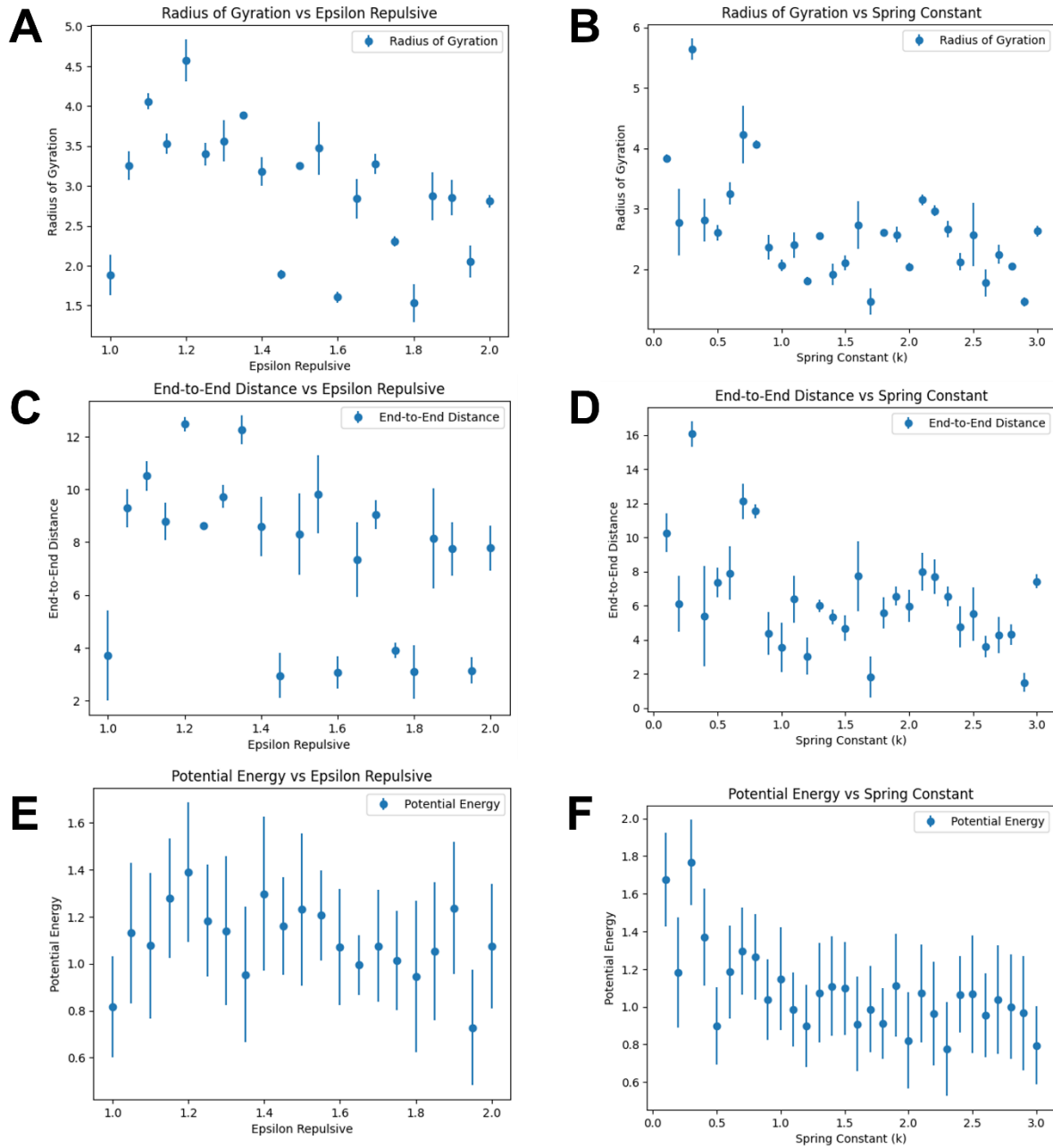


Figure 2. (A) Radius of Gyration vs. Epsilon Repulsive, (B) Radius of Gyration vs. Spring Constant, (C) End-to-End Distance vs. Epsilon Repulsive, (D) End-to-End Distance vs. Spring Constant, (E) Potential Energy vs. Epsilon Repulsive, (F) Potential Energy vs. Spring Constant. Total 20,000 steps were applied.

The results from the low step (total 20,000 steps) show how the polymer behaves when changing $\epsilon_{\text{repulsive}}$ and the spring constant (k). These two parameters were treated independently: $\epsilon_{\text{repulsive}}$ was varied while fixing $k=1.0$, and k was varied while keeping $\epsilon_{\text{repulsive}}=1.0$. As $\epsilon_{\text{repulsive}}$ increased, both the radius of gyration and end-to-end distance increased, as shown in **Figures 2A and 2C**. However, the increasing trend was stopped early, and the largest values for both radius and end-to-end distance were observed at $\epsilon_{\text{repulsive}}=1.1-1.2$. Beyond this point, further increases in $\epsilon_{\text{repulsive}}$ had little effect, suggesting that the contribution of $\epsilon_{\text{repulsive}}$ had reached its limit. The potential energy, shown in **Figure 2E**, also stabilized around $\epsilon_{\text{repulsive}}=1.1-1.2$, indicating this is the point where the polymer reaches a stable and stretched fully with the contribution of $\epsilon_{\text{repulsive}}$.

When varying the spring constant k , the radius of gyration and end-to-end distance decreased steadily, as shown in **Figures 2B and 2D**. The largest values for the radius of gyration and end-to-end distance appeared at $k=0.2$, where the bonds were less restricted, allowing the polymer to stretch out. **Figure 2F** shows that the potential energy dropped quickly in the initial phase as spring constant (k) increased, then reached equilibrium. It reflects a more stable and tightly controlled bond structure at higher k values.

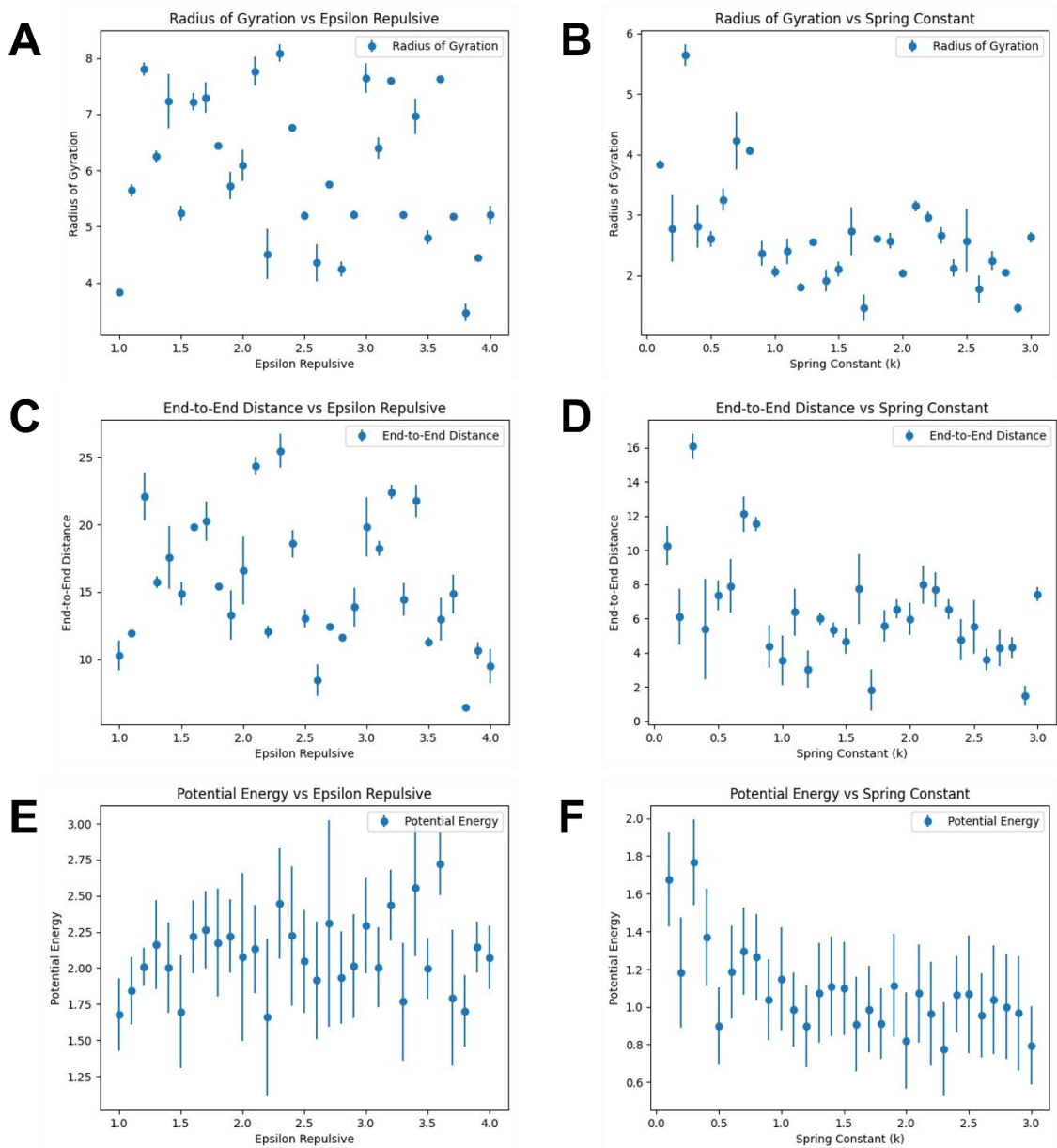


Figure 3. (A) Radius of Gyration vs. Epsilon Repulsive, (B) Radius of Gyration vs. Spring Constant, (C) End-to-End Distance vs. Epsilon Repulsive, (D) End-to-End Distance vs. Spring Constant, (E) Potential Energy vs. Epsilon Repulsive, (F) Potential Energy vs. Spring Constant for optimizing the k and $\epsilon_{\text{repulsive}}$. Simulations were conducted with varying $\epsilon_{\text{repulsive}}$ and fixing k as 0.2 for A, C, and E and varying k and fixing $\epsilon_{\text{repulsive}}$ for B, D, and F.

To optimize the k , $\epsilon_{\text{repulsive}}$ and obtain the most unfolded polymer configuration, simulations with 20,000 steps while varying $\epsilon_{\text{repulsive}}$ and the spring constant (k) was also conducted. In this

case, when varying $\epsilon_{\text{repulsive}}$, k was fixed at 0.2, and when varying k , $\epsilon_{\text{repulsive}}$ was fixed at 1.2. The trends observed in the results were consistent with the previous results. As shown in **Figure 3A** and **Figure 3C**, increasing $\epsilon_{\text{repulsive}}$ caused the radius of gyration and end-to-end distance to increase initially. **Figure 3E** shows that the potential energy fluctuated slightly as $\epsilon_{\text{repulsive}}$ increased but stabilized after reaching a balance at higher values.

When varying k , the radius of gyration and end-to-end distance showed a decreasing trend as shown in **Figure 3B** and **Figure 3D**. The potential energy, shown in **Figure 3F**, dropped sharply at lower k values and then reached equilibrium. It indicates that higher k stabilizes the bond energy while constraining the polymer configuration.

To understand the trend, we need to figure out the effect of each factor ($\epsilon_{\text{repulsive}}$ and k). Increasing $\epsilon_{\text{repulsive}}$ helps prevent folding by keeping monomers apart, but after $\epsilon_{\text{repulsive}} = 1.2$, the repulsion is already strong enough to fully expand the polymer. On the other hand, reducing k allows the polymer bonds to stretch more freely, promoting an extended structure. At very low k , the harmonic potential weakens, making the polymer more flexible. This explains why low k value ($k=0.2$) can cause the most stretched configuration without destabilizing the bonds. These results suggest that $\epsilon_{\text{repulsive}} = 1.2$ and $k=0.2$ are the best conditions to prevent folding. These conditions provide a balance between repulsive interactions and bond flexibility, allowing the polymer to remain extended and prevent folding, even at low temperatures ($T=0.1$).

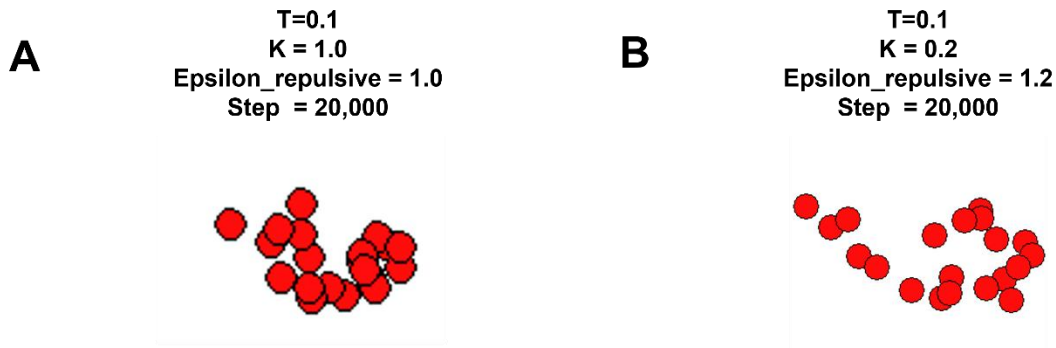


Figure 4. polymer configurations (A) at $T=0.1$, $K=1.0$, and $\epsilon_{\text{repulsive}}=1.0$ and (B) at $T=0.1$, $K=0.2$, and $\epsilon_{\text{repulsive}}=1.2$. Total steps were 20,000.

Under the conditions of $k=0.2$ and $\epsilon_{\text{repulsive}}=1.2$, the polymer demonstrated a more stretched structure compared to lower repulsive interaction parameters. The spring constant $k=0.2$, which determines the stiffness of the bonds, allowed for greater flexibility in the polymer chain, enabling it to adopt extended configurations. Simultaneously, the increased $\epsilon_{\text{repulsive}}$ enhanced the non-bonded repulsive forces between beads, pushing them further apart and reducing the overall compactness of the structure. As a result, the polymer chain showed more stretched configuration (**Figure 4A and 4B**). This behavior highlights the influence of the balance between elastic and repulsive forces on the structural transition of polymer.

3.3. Polymer behavior with different chain length

3.3.1. Polymer behavior trend with short chain length (particles = 5)

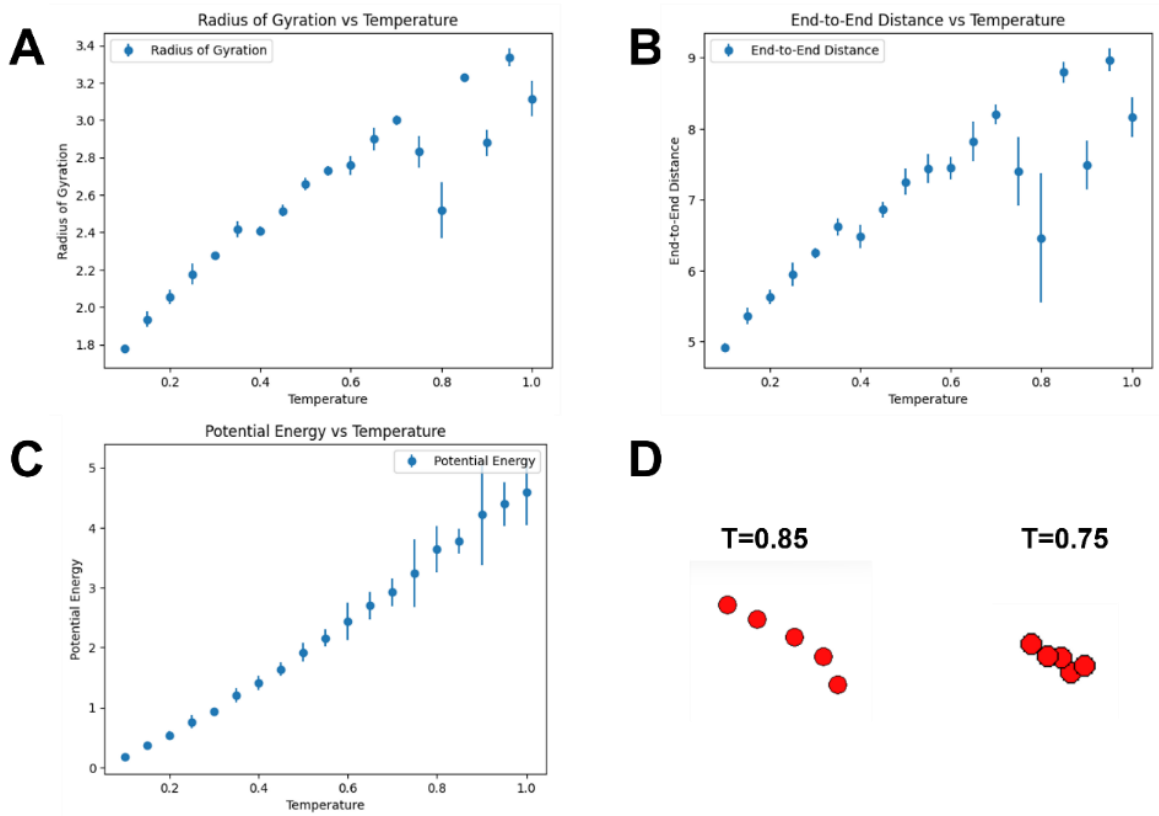


Figure 5. (A) Radius of Gyration, (B) End-to-End Distance, (C) Potential Energy, and (D) Polymer configurations before and after transition state. Total particle numbers were 5.

The short chain length simulation was performed with $k=1.0$, $\epsilon_{\text{repulsive}}=1.0$, and 20,000 steps for a system with 5 particles. The results show a significant reduction in the standard deviation of measured properties, including the radius of gyration, end-to-end distance, and potential energy. This is likely due to the small number of particles, which allowed the system to achieve stable configurations within a relatively short simulation time. At $T=0.8$, a noticeable inflection point was observed, accompanied by a large standard deviation. This suggests that $T=0.8$ represents the transition phase for this system, where the polymer shifts from a folded to an unfolded state. The transition is evident in the radius of gyration, which increases steadily with temperature and shows a sharp change near $T=0.8$ (**Figure 5A**). Similarly, the end-to-end distance follows a similar trend,

with significant variation at $T=0.8$, indicating a structural change to a more stretched configuration (**Figure 5B**). The potential energy also rises smoothly with temperature, but the deviation at $T=0.8$ highlights the energy cost associated with breaking cohesive interactions during the transition (**Figure 5C**). **Figure 5D** shows the polymer configuration at different temperature. Due to the limited number of particles, the polymer shape looks similar. However, the bond length between two atoms is longer at $T=0.85$, indicating that a stretched configuration has been achieved. The small number of particles in this system likely simplified the interaction dynamics, allowing for rapid equilibration and clearer thermodynamic transitions even with fewer simulation steps and short simulation time. These results suggest that the particle number and simulation steps have a significant impact on the stability and transition behavior of the system.

3.3.2. Polymer behavior trend with long chain length (particles = 100)

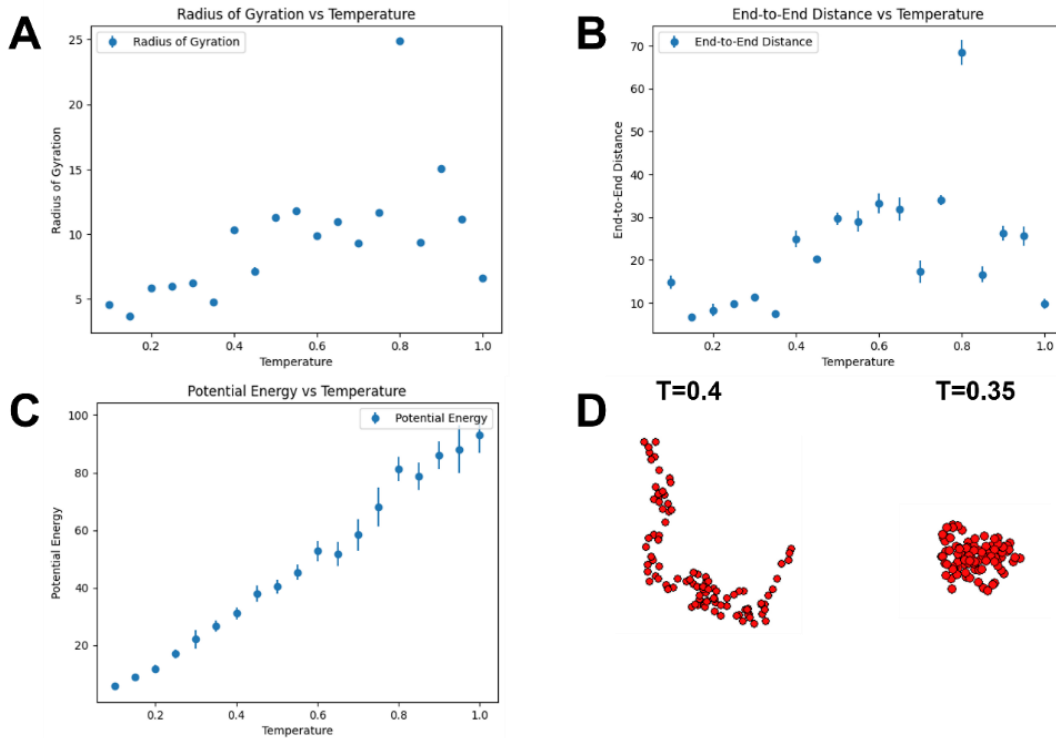


Figure 6. (A) Radius of Gyration, (B) End-to-End Distance, (C) Potential Energy, and (D) Polymer configurations before and after transition state. Total particle numbers were 100.

The results for the system with 100 particles are shown in **Figures 6**, highlighting the trends in radius of gyration, end-to-end distance, potential energy, and the polymer configuration at $T=0.4$ and $T=0.35$. In **Figure 6A**, the radius of gyration increases steadily with temperature, with a sharp rise observed between $T=0.35$ and $T=0.4$. This indicates that the polymer undergoes a significant structural transition in this temperature range, expanding from a compact to a more stretched configuration. In **Figure 6B**, the end-to-end distance shows more variability compared to the radius of gyration. While the polymer becomes stretched at higher temperatures, the end-to-end distance can remain relatively small if the polymer bends such that the distance between the first and last atoms is reduced. This highlights how end-to-end distance can be influenced by local chain bending, even when the overall size of the polymer increases. In **Figure 6C**, the potential energy increases gradually with temperature, reflecting the thermal energy input and the energetic cost of overcoming cohesive interactions as the polymer unfolds. This gradual rise is consistent across the temperature range, including the transition region between $T=0.35$ and $T=0.4$. **Figure 6D** shows the polymer configuration at $T=0.4$, where the chain is visibly more stretched compared to configurations at lower temperatures. This stretched state confirms that the temperature range of $T=0.35$ to $T=0.4$ represents the transition phase for this system.

By varying the particle number, the effect of chain length was identified. It was observed that the transition temperature point differed compared to the results for a particle number of 20 (where the transition temperature point was $T=0.75$). This indicates that the polymer chain length influences the transition temperature point of the polymer, and it was confirmed that this influence decreases the transition temperature as the chain length increases. However, if the chain length decreases, the transition temperature increases.

3.4. Performing energy minimization before starting the MD simulation

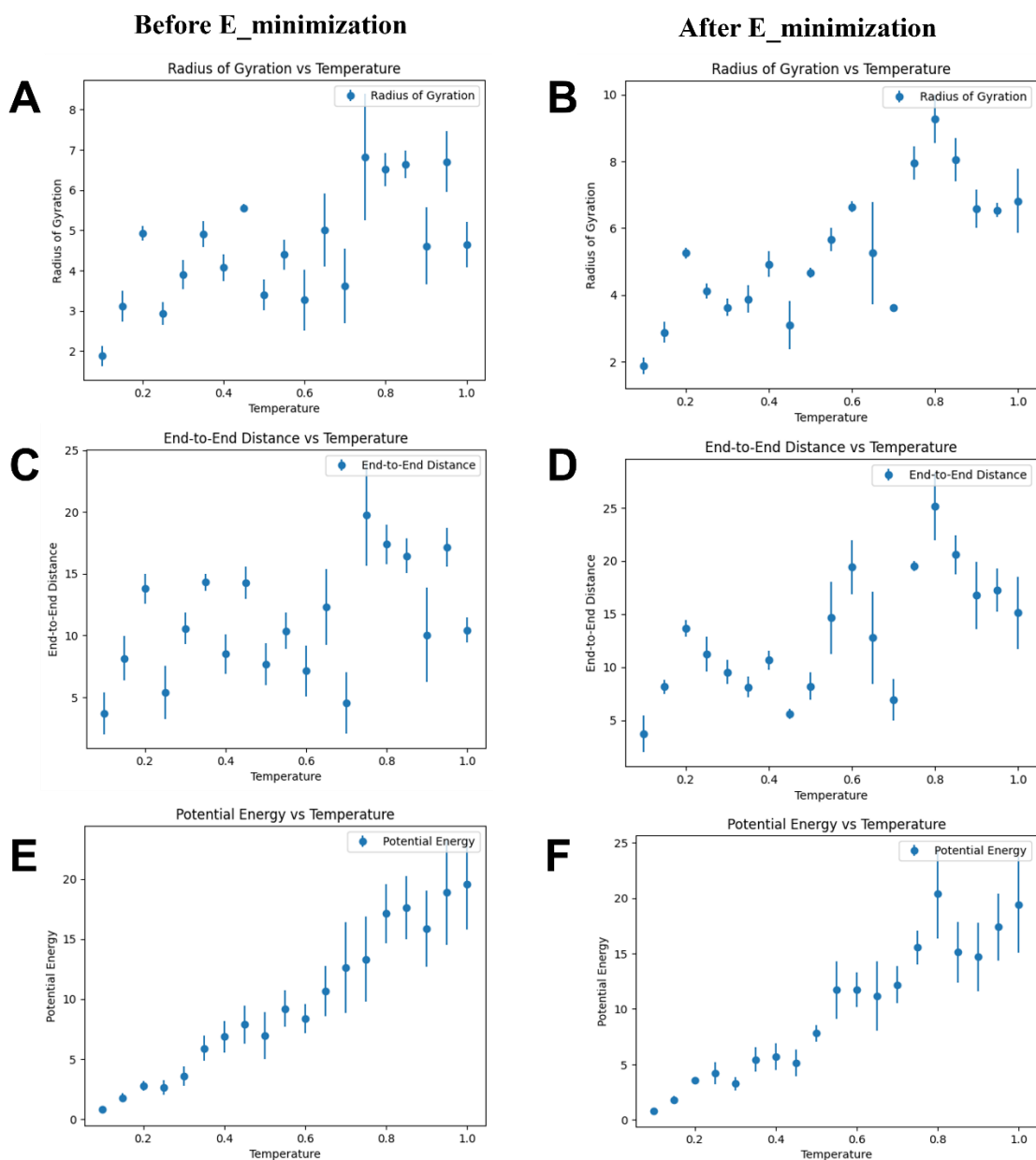


Figure 7. (A) Radius of Gyration vs. temperature before energy minimization, (B) Radius of Gyration vs. temperature after energy minimization, (C) End-to-End Distance vs. temperature before energy minimization, (D) End-to-End Distance vs. temperature after energy minimization, (E) Potential Energy vs. temperature before energy minimization, (F) Potential Energy vs. temperature after energy minimization.

Minimizing the potential energy simulations were performed with $k = 1.0$, $\epsilon_{\text{repulsive}} = 1.0$, and 20,000 steps for a system of 20 particles. This was done after initializing the chain and achieving potential energy minimization. The radius of gyration, end-to-end distance, and potential energy as functions of temperature are shown in **Figure 7**. Specifically, **Figures 7A, C, and D** present the results before potential energy minimization, while **Figures 7B, D, and F** show the results after potential energy minimization. Regarding the transition state point, it remained unchanged at $T = 0.75$. However, when we applied energy minimization to the initial chain, the standard deviation decreased. As a result, the fluctuations in the data points were smaller compared to those without energy minimization. Therefore, incorporating potential energy minimization helps in obtaining more stable results.

3.5. Stabilization strategy before simulation

3.5.1. Stabilization process for robust analysis

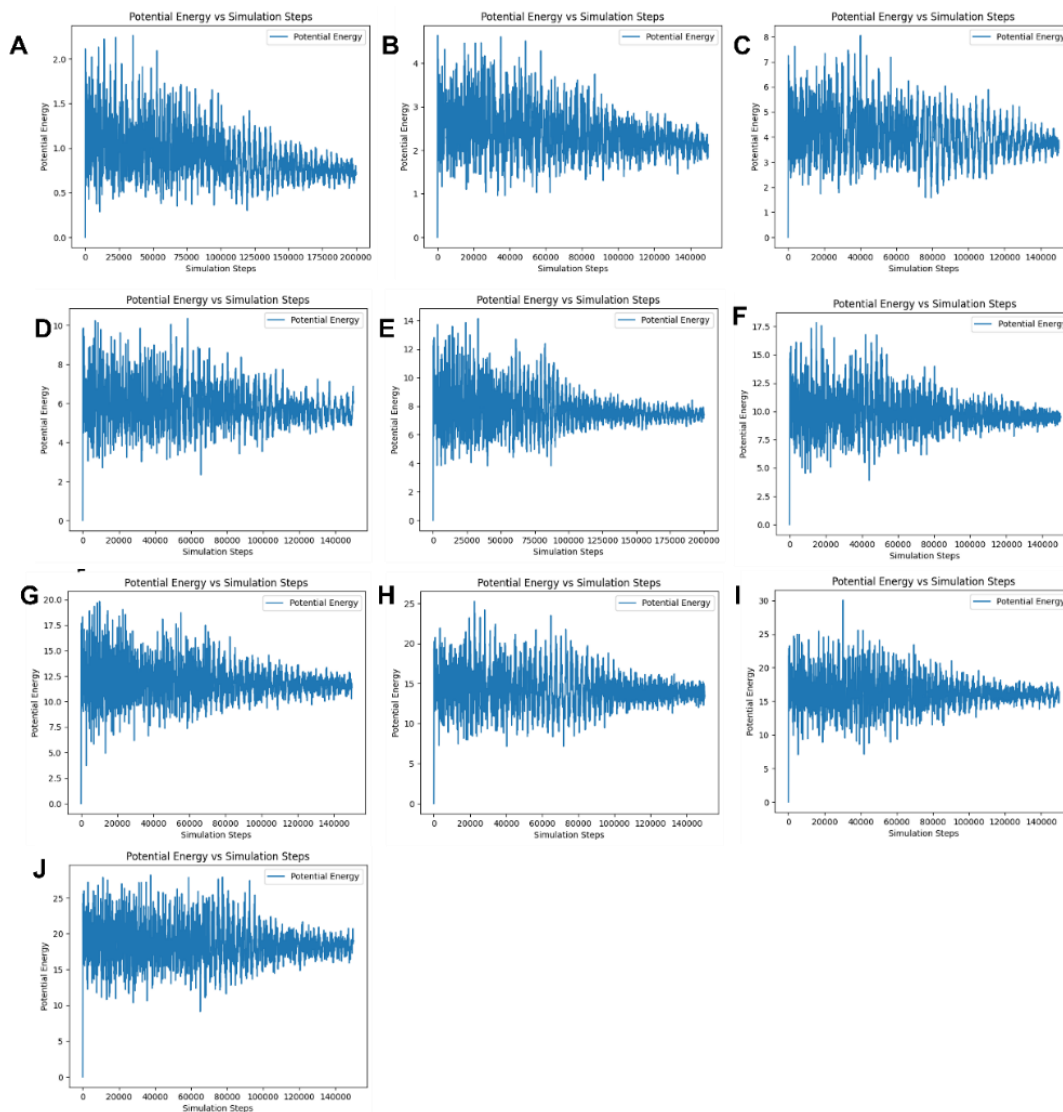


Figure 8. Potential energy vs. simulation steps at (A) $T=0.1$, (B) $T=0.2$, (C) $T=0.3$, (D) $T=0.4$, (E) $T=0.5$, (F) $T=0.6$, (G) $T=0.7$, (H) $T=0.8$, (I) $T=0.9$, and (J) $T=1.0$.

The stabilization process in molecular dynamics simulations is important to ensure that the system reaches equilibrium and that subsequent data collection represents the true steady-state behavior of the polymer chain. The stabilization was achieved through an equilibration phase, followed by a sampling phase, designed to provide reliable and robust results. For minimizing the

energy, the equilibration phase was conducted for 140,000 steps to allow the polymer system to reach equilibrium. During the simulation, the potential energy was monitored throughout the total steps to confirm that the system had stabilized and that there were no significant fluctuations. Following equilibration, a sampling phase of 10,000 steps was conducted. During this phase, data of structural properties of polymer, including the radius of gyration, end-to-end distance, and potential energy, were collected. The simulations were performed at ten different temperatures, ranging from 0.1 to 1.0 (**Figure 8A-J**). As a result, we confirmed that 150,000 steps were sufficient to achieve stabilization, as indicated by the convergence of potential energy and the absence of significant fluctuations. This provided confidence that the collected samples represented a stable configuration of the polymer chain, allowing for a robust analysis of its conformational behavior under different interaction strengths. Based on the results, polymer behavior at different temperatures and the determination of the spring constant (k) and repulsive potential were obtained through simulations conducted under two conditions: partial equilibration with 20,000 steps and full equilibration with 150,000 steps.

3.5.2 Polymer behavior at different temperature after equilibrium phase

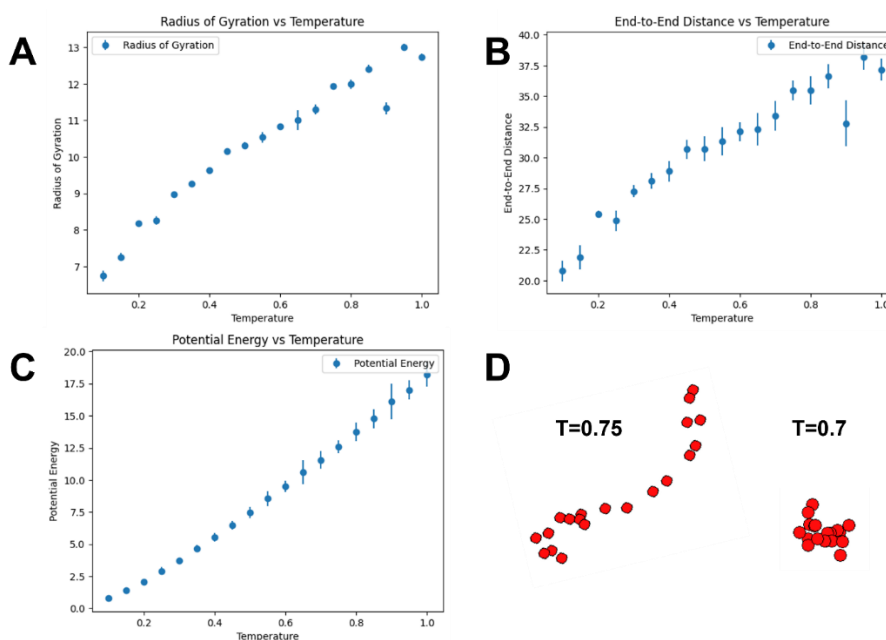


Figure 9. (A) Radius of Gyration, (B) End-to-End Distance, (C) Potential Energy, and (D) Polymer configurations before and after transition state. Total steps were 150,000.

The polymer was simulated for 150,000 steps, and the system reached equilibration. After equilibration, the standard deviations were very small (around 0.1–0.3), showing that the results were consistent and reliable. The radius of gyration, end-to-end distance, and potential energy all increased steadily with temperature, as seen in **Figure 9A–C**. This is because the polymer expands and becomes more flexible as the temperature rises. However, at $T=0.75$, both the radius of gyration and the end-to-end distance showed sudden jump into larger value. This shows that $T=0.75$ is the transition temperature where the polymer transitions from folded to fully unfolded. This result matches what was observed in simulations with lower steps (20,000 steps). **Figure 9A** shows how the radius of gyration changes with temperature. At low temperatures, it increases steadily as the polymer expands. At $T=0.75$, it shows a large increase of radius, meaning the polymer has fully unfolded and expand further. This trend was also shown in **Figure 9B**, the end-to-end distance. **Figure 9C** indicates the potential energy as a function of temperature and shows different trend compared to the gyration and end-to-end distance because the potential energy keeps increasing even after $T=0.75$. This reflects the increase in thermal motion and flexibility, even though the polymer has already unfolded. **Figure 9D** shows the polymer configurations at $T=0.7$ and $T=0.75$. At $T=0.7$, the polymer appears more stretched compared to the same temperature condition, but lower steps shown in **Figure 9D** (20,000 steps). This suggests that the simulation steps can also influence the degree of polymer stretching. At $T=0.75$, the polymer is fully unfolded and stretched out compared to the $T=0.7$ condition. These configurations clearly illustrate the transition from a folded to an unfolded state.

3.5.3. Finding spring constant (k) and $\epsilon_{\text{repulsive}}$ conditions to prevent polymer folding at low temperature ($T=0.1$) after equilibrium phase

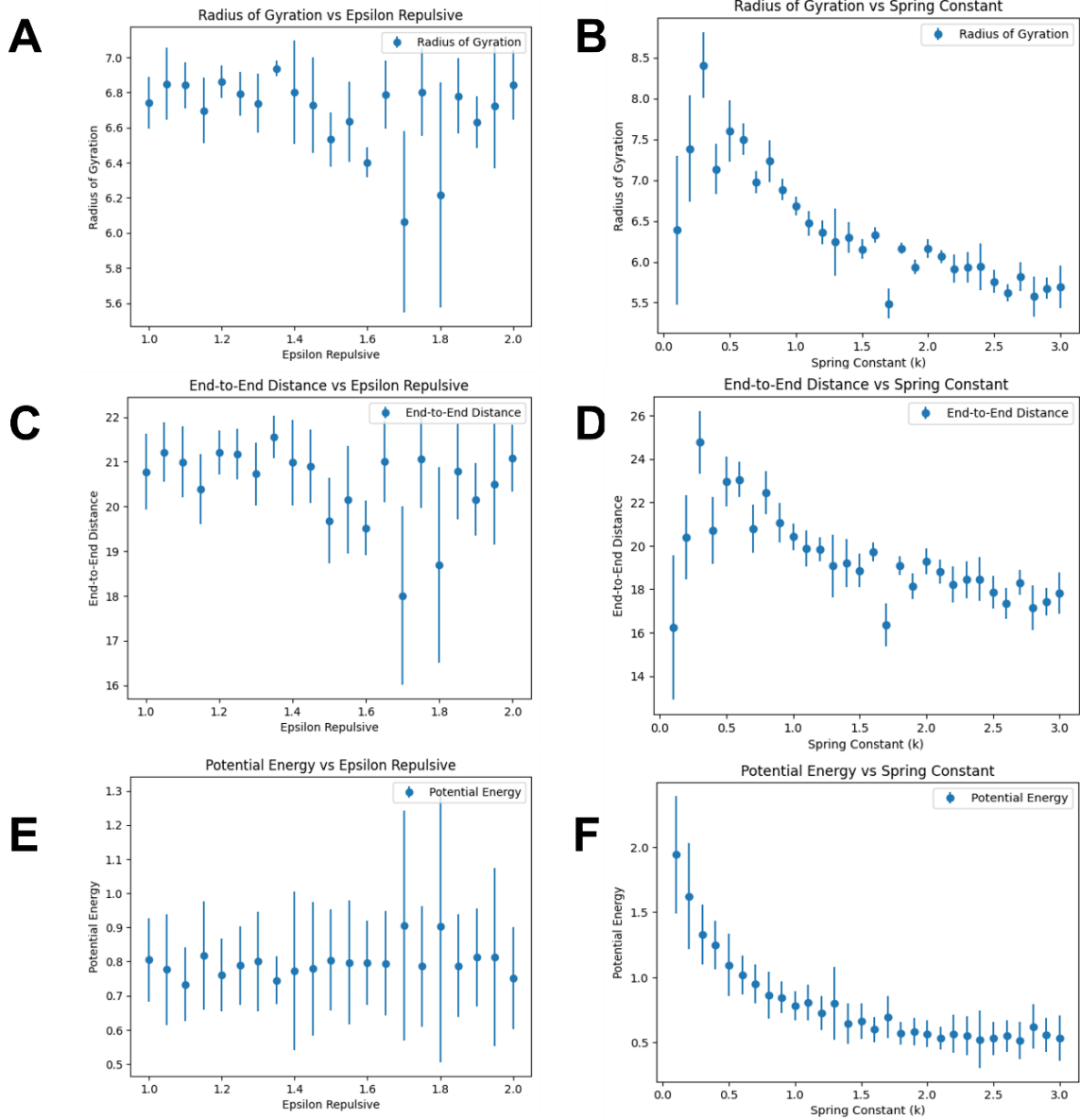


Figure 10. (A) Radius of Gyration vs. Epsilon Repulsive, (B) Radius of Gyration vs. Spring Constant, (C) End-to-End Distance vs. Epsilon Repulsive, (D) End-to-End Distance vs. Spring Constant, (E) Potential Energy vs. Epsilon Repulsive, (F) Potential Energy vs. Spring Constant. Total steps were 150,000.

To confirm the exact trends with varying $\epsilon_{\text{repulsive}}$ and k and to obtain robust results, simulations were conducted for 150,000 steps to ensure equilibrium. The overall trends observed were consistent with the results from the low-step conditions (20,000 steps). As shown in **Figure 10A** and **Figure 10C**, increasing $\epsilon_{\text{repulsive}}$ led to slight increases in the radius of gyration and end-to-end distance before stabilizing. Similarly, **Figure 10E** shows that the potential energy remained stable with $\epsilon_{\text{repulsive}}$. For the spring constant k , **Figure 10B** and **Figure 10D** confirm the same decreasing trend in the radius of gyration and end-to-end distance as k increased, consistent with the low-step results. **Figure 10F** shows that the potential energy decreased rapidly at first and then stabilized at higher k , reinforcing the trends observed previously. These results confirm the reliability and consistency of the trends after reaching equilibrium.

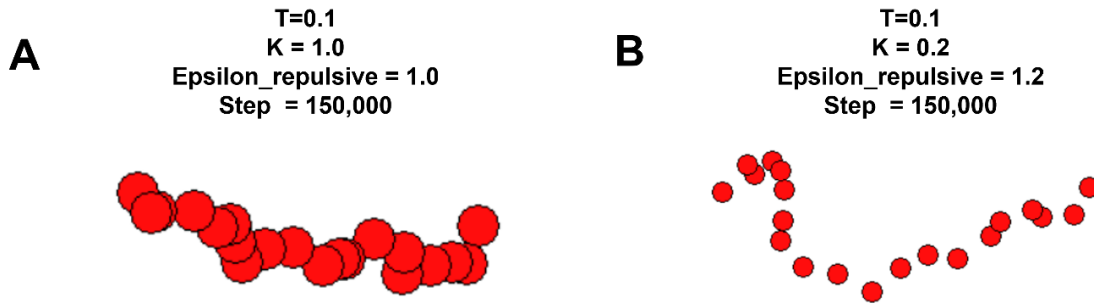


Figure 11. polymer configurations (A) at $T=0.1$, $K=1.0$, and $\epsilon_{\text{repulsive}}=1.0$ and (B) at $T=0.1$, $K=0.2$, and $\epsilon_{\text{repulsive}}=1.2$. Total steps were 150,000.

When we observe the polymer configuration, they are clearly different between the base condition ($k=1.0$, $\epsilon_{\text{repulsive}}=1.0$) and the optimized condition ($k=0.2$, $\epsilon_{\text{repulsive}}=1.2$) in high step condition as well. In the base condition, the polymer is more compact because the higher spring constant ($k=1.0$) keeps the bonds tight, and the repulsive force ($\epsilon_{\text{repulsive}}=1.0$) is not strong enough to fully stretch the polymer (**Figure 11A**). In the optimized condition, the polymer is much more extended. The lower spring constant ($k=0.2$) allows the bonds to stretch, and the stronger repulsive interaction ($\epsilon_{\text{repulsive}}=1.2$) prevents the polymer from folding back on itself.

4. Conclusion

This research explored how polymer folding is affected by changes in the spring constant (k), repulsive interaction strength ($\epsilon_{\text{repulsive}}$), and temperature using molecular dynamics simulations. The results showed that polymer behavior is strongly influenced by these parameters, and adjusting them can control whether the polymer remains folded or unfolds.

Simulations across different temperatures revealed that $T=0.75$ is the transition point where the polymer transitions from a folded to an unfolded state (for 20 particles). Below $T=0.75$, the polymer stays compact, while above this temperature, it fully unfolds due to higher thermal energy. This highlights how temperature affects polymer structure.

However, at the low temperature condition such as $T=0.1$, we can also obtain the unfold polymer by adjusting k and $\epsilon_{\text{repulsive}}$. Increasing $\epsilon_{\text{repulsive}}$ helped prevent folding by keeping monomers apart, with the best results at $\epsilon_{\text{repulsive}}=1.2$. Reducing k made the polymer more flexible by weakening the bond stiffness, with $k=0.2$ allowing the polymer to stretch into its most unfolded state. Comparing the base condition ($k=1.0$, $\epsilon_{\text{repulsive}}=1.0$) to the optimized condition ($k=0.2$, $\epsilon_{\text{repulsive}}=1.2$) showed clear differences. Under the base condition, the polymer was more compact, while under the optimized condition, it was fully extended.

In addition, energy minimization, the effect of particle number, and the effect of phase equilibration were investigated. After energy minimization, the overall trend remained similar, but the standard deviation decreased. Regarding the particle number effect, a smaller particle number can increase the transition temperature, while a longer chain length can decrease it. Finally, phase equilibration before simulation significantly reduced the standard deviation, but the transition temperature and the optimal k and $\epsilon_{\text{repulsive}}$ values remained unchanged.

These results show how balancing k and $\epsilon_{\text{repulsive}}$ can significantly affect polymer structure. This study provides useful insights for controlling polymer folding and designing materials with desired properties. The findings are especially important for applications like aerospace, drug delivery, and smart materials, where polymer stability and functionality are critical.