

WASHINGTON UNIVERSITY IN SAINT LOUIS

Department of Chemistry

MOLECULAR DYNAMICS SIMULATION OF A POLYMER CHAIN

By

Carlos Roberto Bean Chevez

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- **Introduction**

Polymers are a continuous area of study among many scientific disciplines. Chemists investigate their properties to reveal possible improvements in designing robust materials suitable to multiple environments. This project focuses on exploring the effects of temperature on polymer chains, with the purpose on elucidating the properties in which it can remain unfold at low temperatures.

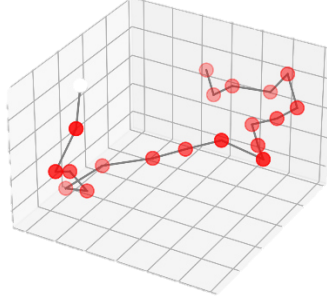


Figure 1: Polymer Chain in 3D space

The polymer chain, e.g. Figure 1, is represented using a bead-spring model, in which each monomer is connected to each other by a harmonic spring. Molecular Dynamics simulations will be implemented to model the changes presented by the polymer chain in light of temperature and interaction strengths.

- **Methodology**

This study was conducted by simulating the dynamics of a polymer chain at constant volume and temperature, controlled using a velocity rescaling thermostat in the programming language “python”. The temperature is calculated using eq. 1, and later the velocities are rescaled using eq.2.

$$T_{inst} = \frac{2K}{3Nk_B} \quad \text{eq.1}$$

$$v_i = v_i \sqrt{\frac{T_{target}}{T_{inst}}} \quad \text{eq.2}$$

A velocity Verlet algorithm was implemented to conserve the energy of the system, in which consist on updating the positions and velocities of the polymer. The interactions in the polymer chain consist on bonded interactions between adjacent beads specified by a harmonic bond potential (eq.3) and the force induced.

$$U_{bond}(r) = \frac{1}{2}k(r - r_0)^2 \quad \text{eq.3}$$

$$F_{bond} = -\frac{dU}{dr} = -k(r - r_0)\hat{r} \quad \text{eq.4}$$

They also consist on non-bonded interactions, in which it is assumed that the interactions of monomers separated by one “spacer” can be modeled by a repulsive Lennard-Jones potential (eq.5), and the attractive interactions by an attractive Lennard-Jones potential (eq.6).

$$U_{LJ,rep}(r) = \begin{cases} 4\epsilon_{rep} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + 0.25 \right], & r \geq 2^{\frac{1}{6}}\sigma \\ 0, & r < 2^{\frac{1}{6}}\sigma \end{cases} \quad \text{eq.5}$$

$$U_{LJ,att}(r) = 4\epsilon_{rep} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{eq.6}$$

To elucidate the conditions in which the polymer chain folds and unfolds many properties such as potential energy, radius of gyration, and end-to-end distance were investigated. The potential energy was tracked by adding all the interactions specified in eq.7

$$U_{Total} = \sum_{bonds} U_{bond}(r_{i,i+1}) + \sum_{|i-j|=2} U_{LJ,rep}(r_{i,j}) + \sum_{|1-j|>2} U_{LJ,att}(r_{i,j}) \quad \text{eq.7}$$

The radius of gyration, which gives information on the overall size of the polymer, effectively capturing the spread of the chain is given by eq.8. End-to-end distance (eq.9), which is a straight line from the start of the chain to the end complements the information given by the radius of gyration.

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^N (r_i - r_{cm})^2} \quad \text{eq.8}$$

$$R_{ee} = |r_N - r_1| \quad \text{eq.9}$$

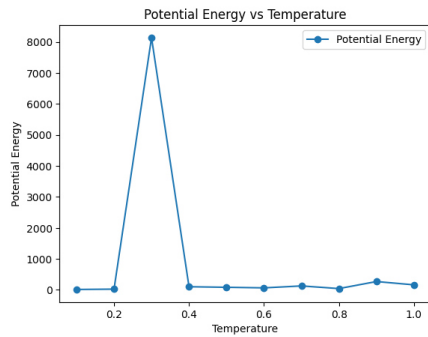


Figure 2: Pre-equilibration potential energy as a function of Temperature

The simulation consisted on a polymer chain of 20 monomers reacting to different temperatures, repulsion forces in the harmonic spring, and spring constants. In order to ensure an equilibrium state, rather than the random initial configuration, an equilibration procedure was implemented. First, the system was simulated for 53,000 time steps to allow it to reach equilibrium. This equilibration phase allowed the polymer chain to reach a steady state which is statistically meaningful. Figure 2 shows the potential energy by taking the average of the first 10,000 steps. This can be compared to Figure 3C to see the importance of equilibration. After this phase, the simulation was run for an additional 2,000 time steps which

were recorded and the data was used to plot the different polymer configurations and analysis of the different parameters.

• Results and Discussion

Temperature Dependence

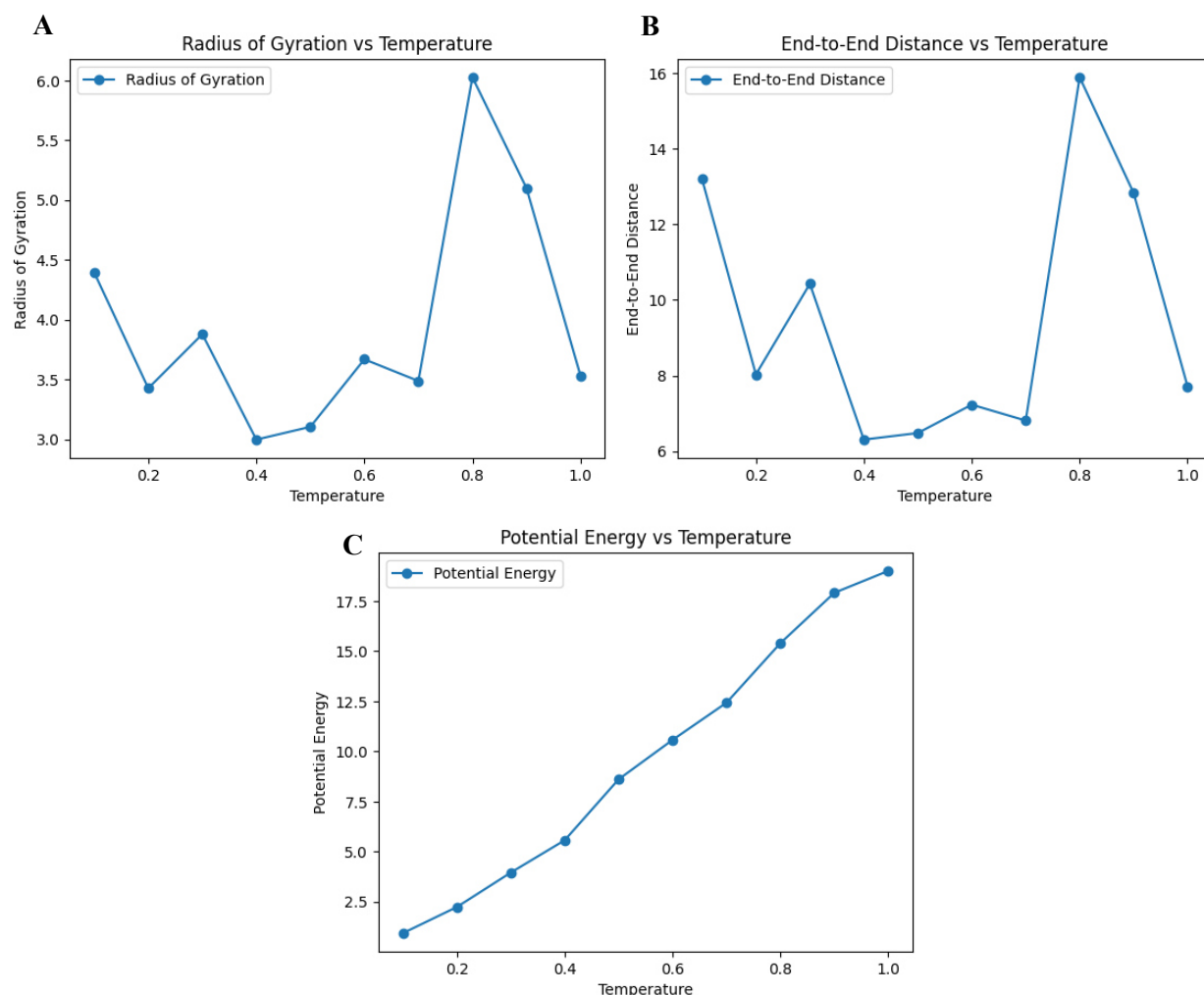


Figure 3: Temperature Dependence. A) Radius of gyration. B) End-to end distance. C) Potential Energy

An exploration of temperatures between 0.1 and 1 resulted in the plots in Figure 3, which shows the radius of gyration, end to end distance, and potential energy. The depth of the potential well for attractive interactions was 0.5, and for repulsive interactions 1.0. Figure 3A and Figure 3B present similar results, with spikes around $T=0.70$. At temperatures below this spike, the radius of gyration and end-to-end distance fluctuates modestly. However, the spike presents evidence of temperature-driven phase transition between the globular and extended states.

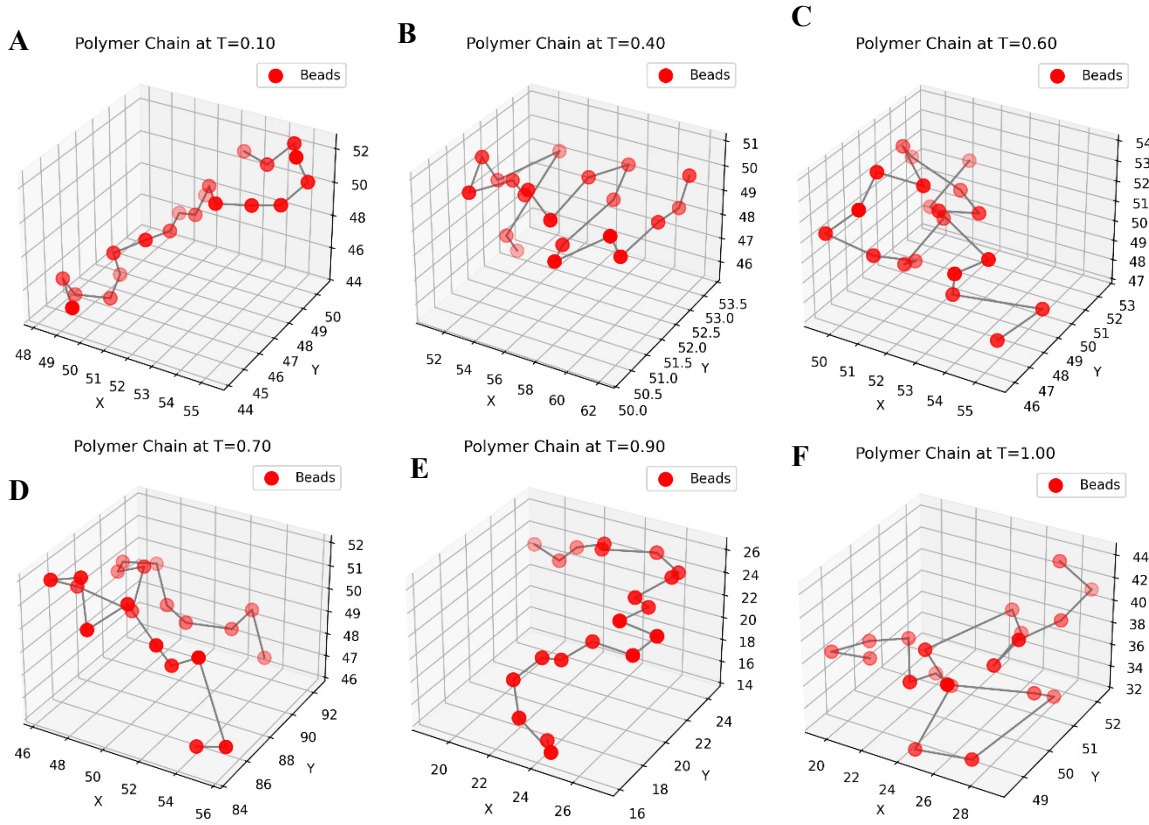


Figure 4: Last trajectory Polymer chains configuration at different temperatures

Figure 4 shows some plots of the polymer chains at the end of the dynamic simulation, in which it shows that at low temperatures, the polymer chain seems to be more compact than at high temperatures. The spike in the radius of gyration and end-to-end distance can be mildly observed in figure 4C to 4D, while the tendency to unfold at high temperatures can be easily visualized in figure 4E.

Figure 3C shows that the potential energy generally increases with temperature. This is an expected result as the thermal energy of the system increases. This presents some evidence that the polymer chains are able to increase their motion as temperature increases. At low temperatures, the polymer seems to settle into more energetically favorable states. At high temperatures, it has enough thermal energy to overcome energy barriers associated with less favorable conformations. This is certainly an issue for the material properties of the polymers for the space industry, as it should remain unfold at the extremely low temperatures of space. An exploration of different values for

the spring constant (k), and the repulsive depth well (ϵ) is used to determine the suitable values that will overcome the natural tendency of the polymer chain to fold at low temperatures.

Spring Constant (k) Dependence and Repulsive Interactions (ϵ) Dependence

Figure 5A and 5B presents evidence that low spring constant values (k) increase both the radius of gyration and end-to-end distance. A value around $k=0.25$ presents the highest value in which the polymer remains unfolded. Low k values can be physically interpreted as more flexible bonds, allowing the polymer to adopt extended configurations as it can go beyond their equilibrium length.

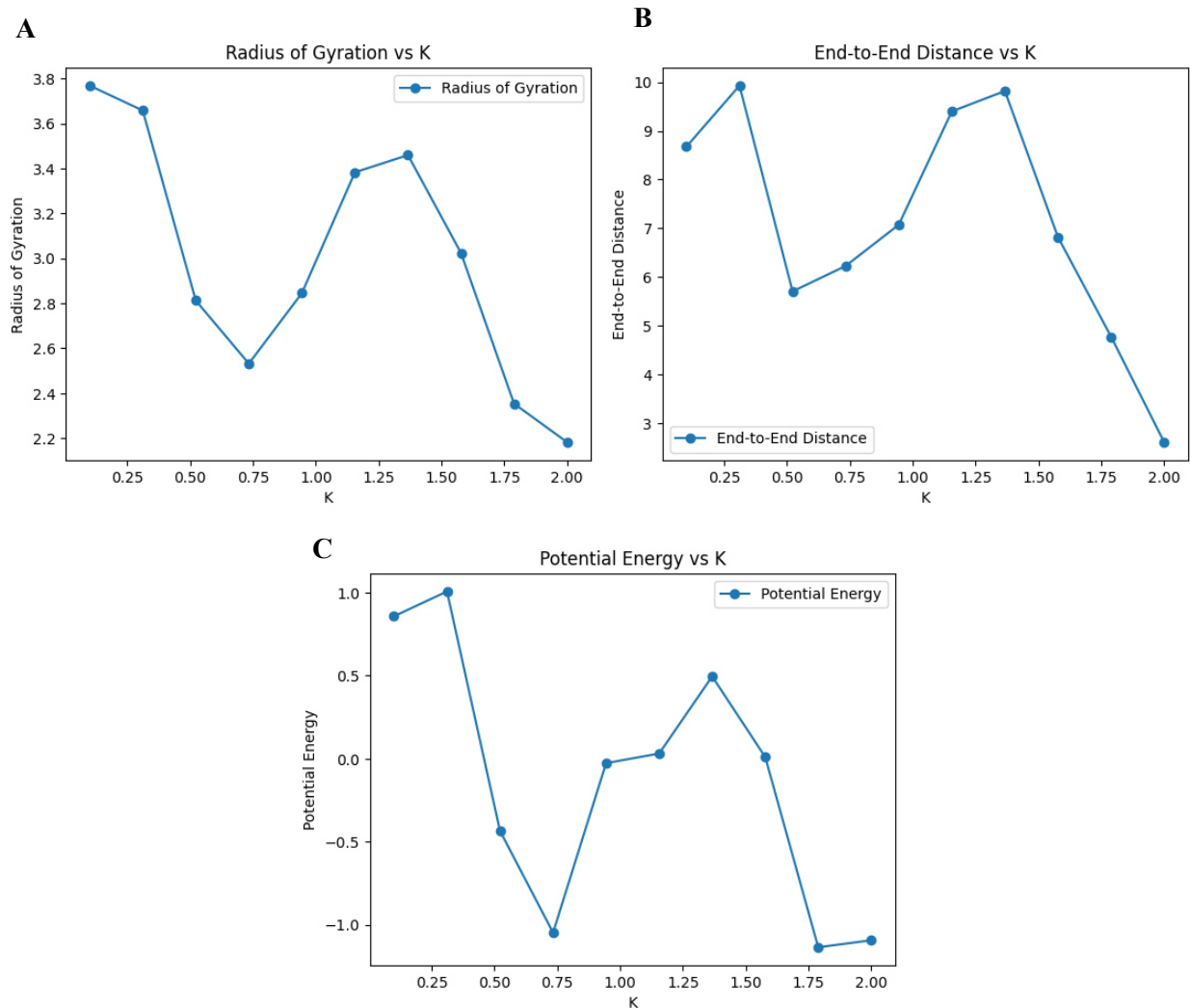


Figure 5: Spring Constant Dependence

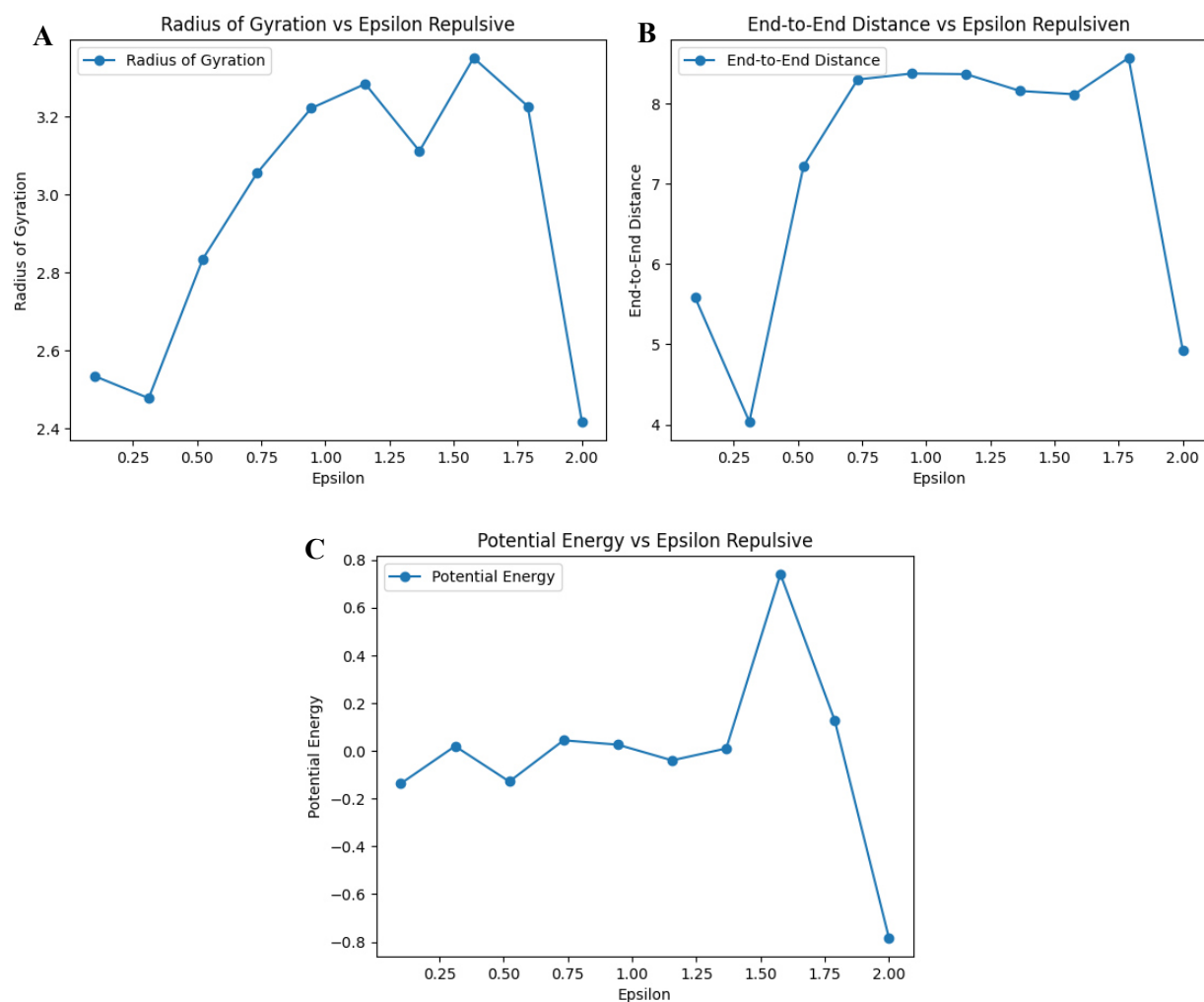


Figure 6: Repulsive interactions Dependence

Figure 6A and 6B shows that the repulsive interactions need to increase in order to keep the polymer chain unfolded as possible. At low ϵ values, the polymer chain will remain somehow folded, as expected due to the attractive interactions overcoming the repulsive interactions. However, as the repulsive interactions start dominating during the $\epsilon = 1.0$ - 1.5 regime, the polymer chain seems to have a more unfolded structure. It is interesting to notice that too large repulsive interactions (>1.8) the polymer becomes folded again. This might be due to the system balancing the harmonic bond force between the monomers. Moderate repulsive strengths are preferred, especially the ones that overcome attractive interactions. In this case, it seems that $\epsilon=1.75$ seems to yield the best value to ensure an unfold polymer.

The potential energy in Figure 5C and 6C presents a peak at the suitable values for k and ϵ that maximizes a unfold state. This suggests that maintaining a polymer in an unfolded state prevents energy minimization. As a result, the unfolded configuration is less energetically stable. However,

a right combination of repulsive forces and bond stiffness could stabilize the extended state to prevent it from collapsing into a compact form.

- **Conclusion**

The simulations demonstrate that as temperature decreases, polymer chains naturally tend toward globular, more compact, conformations as it lowers their potential energy. This tendency poses a challenge for maintaining mechanical integrity and flexibility in the cold of space. To counteract this tendency, the spring constant and repulsive interactions can be optimized to ensure an unfolded state for the polymers. In this case, low k values with moderate ϵ present the best parameters to do so.

In the future, it might be appropriate to examine the effects of oscillating temperatures in the polymer's ability to remain extended because in space, materials experience fluctuating temperatures.