Molecular Dynamics Simulations of a Polymer Chain

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December 2024

1   Introduction

We are a space technology company dedicated to developing advanced materials for spacecrafts. One of the challenges that we face in space is extreme temperatures, which can cause polymer materials to fold or become brittle, compromising their mechanical properties and reliability. Our team aims to design polymer materials that remain unfolded and maintain structural integrity at low temperatures encountered in space environments.

Our task is to simulate a polymer chain using molecular dynamics to understand how temperature affects the polymers conformational behavior, with a focus on preventing folding at low temperatures. We will model the polymer chain as a series of beads connected by harmonic springs and include non-bonded interactions using Lennard-Jones potentials (Figure 1). By performing simulations at various space-relevant temperatures, many relevant properties will be further analyzed such as the radius of gyration, end-to-end distance, and potential energy to assess the linearity and stability of the polymer chain. Our findings will contribute to the design of polymers suitable for use in space technology.

This report summarizes the findings and discusses the implications for material design in the context of space applications.
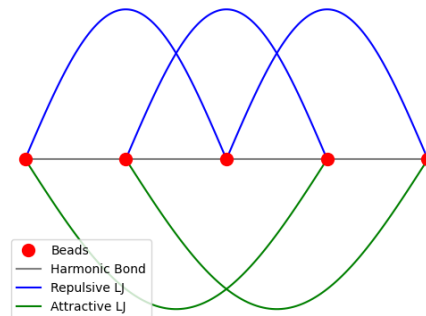

Figure 1: Basic representation of polymer chain and forces considered.

2 Polymer Chain Simulation Methods

The bead-spring model is a basic model that represents a chain of beads, in this case monomers, attached by bonds. Though this model is a simple representation of a polymer, it can provide insightful dynamics of the system studied. Important interactions to be considered for the system are bonded (harmonic potentials) and non-bonded (Lennard-Jones potentials) interactions between the monomers. Non-bonded interactions are further split into attractive (separated by more than one bead) and repulsive (beads next to each other) interactions. The harmonic potentials are defined by

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

where k is the spring constant, r is the distance between beads next to each other, and r_0 is equilibrium bond length.

Next the Lennard-Jones potentials are split into both attractive (2) and repulsive (3):

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

$$U_{\text{LJ,att}}(r) = 4\epsilon_{\text{att}}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

where ϵ_{rep} and ϵ_{att} are the depth of the repulsive and attractive potentials, respectively, and σ is the LJ potential parameter. Repulsive potentials are calculated between monomers that are adjacent and attractive potentials are calculated for all monomers that are separated by one or more other monomers. Total potential energy of the system adds all of the potentials together, making sure none are double counted.

$$U_{\text{total}} = \sum_{\text{bonds}} U_{\text{bond}}(r_{i,i+1}) + \sum_{\substack{i,j \\ |i-j|=2}} U_{\text{LJ,rep}}(r_{ij}) + \sum_{\substack{i,j \\ |i-j|>2}} U_{\text{LJ,att}}(r_{ij}) \tag{4}$$

To simulate at a constant temperature, a velocity rescaling thermostat will be utilized. Instantaneous temperature is calculated by

$$T_{\text{inst}} = \frac{2K}{3Nk_B} \tag{5}$$

where K is the total kinetic energy, N is the number of particles, and k_B is the Boltzmann constant. Velocity is then rescaled using

$$\mathbf{v}_i \leftarrow \mathbf{v}_i\sqrt{\frac{T_{\text{target}}}{T_{\text{inst}}}} \tag{6}$$

This is a simple form of a thermostat and does not provide true canonical ensemble sampling. More advanced thermostats can be used for better temperature control measures.

With the goal of avoiding folding of the polymer chain at lower temperatures, the spring constant and depth of the repulsive well, ϵ_{rep}, will be varied. Other variables used are listed below. Note, temperature is varied between simulations but kept low to determine suitable conditions for space.

Parameter	Value
N	20 beads
T	0.1-1.0 K
ϵ_{att}	0.5 eV
σ	1 eV
r_0	1 $\overset{\circ}{A}$

3 Results

Several simulations at temperatures varying between 0.1 to 1 Kelvin were run in order to determine optimal values of k and e_{rep} to avoid folding. 3 simulations give an idea of how the polymer acts differently at low, medium, and high temperatures.

3.1 Folded and Unfolded states

When determining whether certain parameters are suitable or not, an important consideration is where the polymer becomes folded or unfolded. Our goal is to make a configuration that does not become folded at lower temperatures so the overall character does not change at temperatures prevalent in space. Consider these 2 configurations:

(a) Unfolded state at low temperature   (b) Unfolded state at high temperature
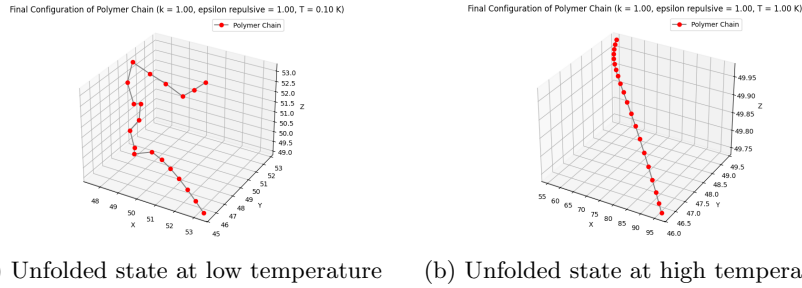
Figure 2: Configurations of the same parameters. The left is at low temperature and right is at high temperature.

Though both figures above are both unfolded they show the difference of 2 unfolded states at varying temperatures. The left is an example of an unfolded state at low temperature and the right shows a unfolded state at high temperature, both shown at differing conditions. Additionally, values such as

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radius of gyration, end-to-end distance, and total potential energy of the chain are important characteristics of the chain that will help further determine if the polymer with given conditions is suitable for space.

Figure 3 is an example of a fully folded state, which is clear in the image. Therefore, the conditions stated from this simulation are not ideal for a polymer being used in space.

3.2   Determining spring constant

In order to determine a spring constant that works at low temperatures, k is varied from 0 to 2 while holding $T = 0.1$ K to represent lower temperature in space. Figures of configurations of $k = 0$ and $k = 2$ are shown below. It is

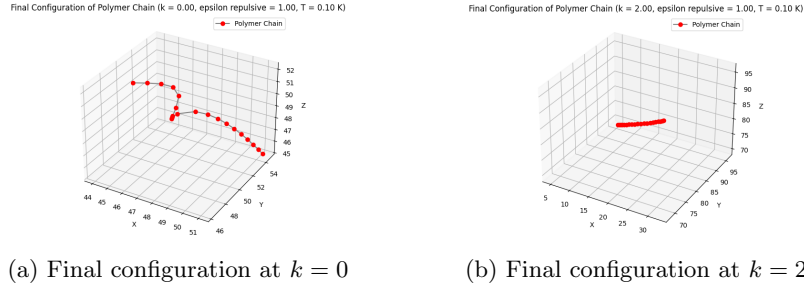(a) Final configuration at $k = 0$ (b) Final configuration at $k = 2$

Figure 3: Configurations at different spring constants at low temperature ($T = 0.1$ K)

important to note that even though the left configuration is not 'folded' there is a kink in which there is a slight folding occurring, which we do not want to be present in our final polymer. Similarly, note that a spring constant of 2 is likely too high as the particles are all very closely attached and not able to move in the system because the stiffness of there bonds. Therefore, creating a polymer with a spring constant of $\tilde{1}$ seems to be the best course. To check this evaluation, consider radius of gyration, end-to-end distance, and potential energy as a function of increasing spring constant. Further explanation of these analysis techniques will be described in the discussion.

Based on these results, a value of 1 for the spring constant will be used for further analysis. This is because there seems to be an increase fo all analysis techniques around this value, which is evident in Figure 4-6.
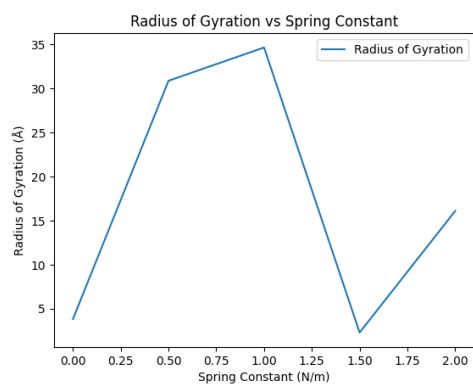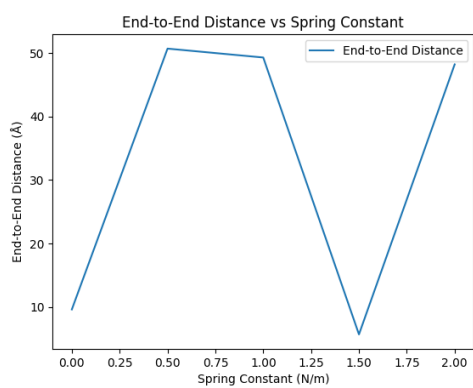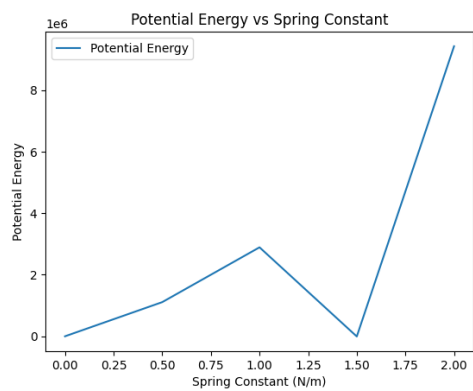
Figure 4

Figure 5

Figure 6

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3.3   Determining ϵ_{rep}

A similar model for how spring constant was determined is used for determining ϵ_{rep}.

(a) Final configuration at $k = 0$
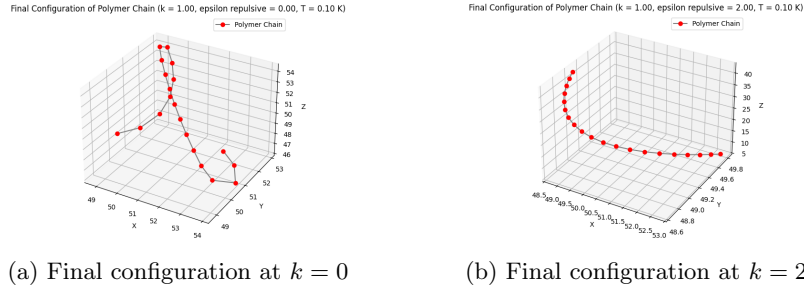

(b) Final configuration at $k = 2$

Figure 7: Configurations at different spring constants at low temperature ($T = 0.1$ K)
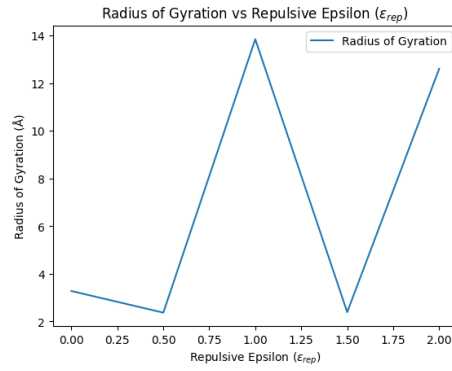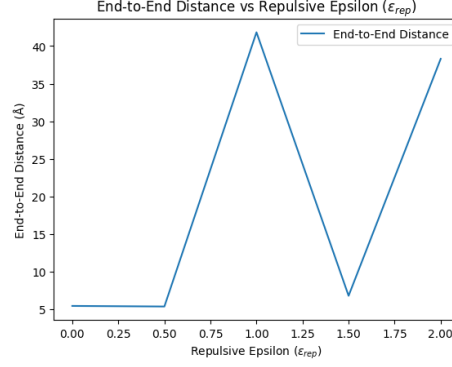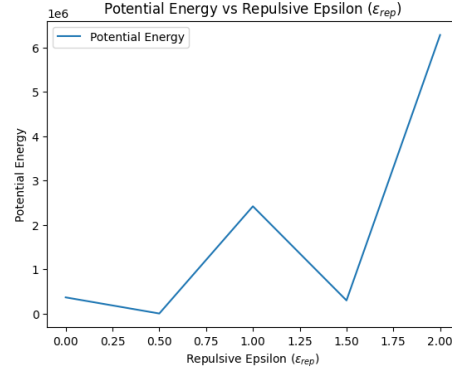

Figure 8

Figure 9

Figure 10

These results clearly show higher value of ϵ_{rep} will lead to better conditions and less folding in space. Because of this, we will let ϵ_{rep} be 2.0

4 Discussion

Now that optimal values for k and ϵ_{rep} have been determined, these values can be tested over a range of temperature from 0.1 to 1 K to see if these conditions are suitable for space polymers. It is important to notice folding is still occurring under these conditions sometimes. Determining the phase transition under these conditions (i.e. when the polymer chain becomes unfolded) will thus help us determine how to make the polymer more likely to not fold at lower temperatures.

4.1 Radius of Gyration R_g

Radius of gyration is connected to the moment of inertia and basically determines the average distance of the beads on the particle from the center of mass of the polymer. The equation used to calculate the radius of gyration is given below:

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{r}_{\mathrm{cm}})^2} \tag{7}$$

where $\mathbf{r}_{\mathrm{cm}}$ is the center of mass of the polymer. R_g over increasing temperatures for $k = 1$ and ϵ_{rep} is given below.
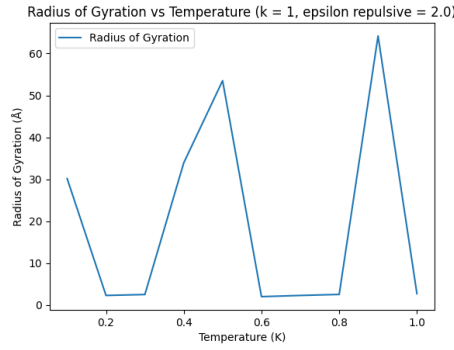

Figure 11: Radius of Gyration

4.2 End-to-End Distance R_{ee}

End-to-end distance describes exactly what its name is. The equation used it calculate it is:

$$R_{\mathrm{ee}} = |\mathbf{r}_N - \mathbf{r}_1| \tag{8}$$

Note, there is a prevalent relationship between the radius of gyration and end-to-end distance values. This makes sense because both of these values are determining distance from one 'area' of the polymer to another outside point. It would be expected that a larger radius of gyration would mean the polymer is more spread out, thus the end-to-end distance is larger. Though they may not always have this relationship, there is a strong correlation, which is noted.
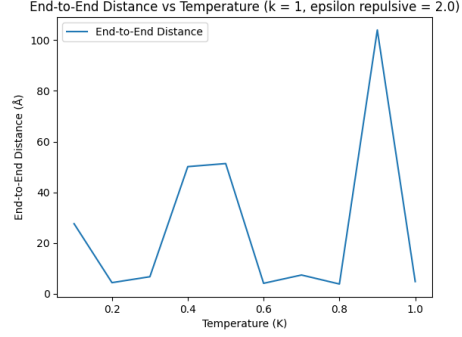
Figure 12: End-to-End Distance

4.3 Potential Energy

The final analysis technique that will be used for this model is the total potential energy, which will be calculated by finding the sum of all potential energy components:

$$U_{\text{total}} = \sum_{\text{bonds}} U_{\text{bond}}(r_{i,i+1}) + \sum_{\substack{i,j \\ |i-j|=2}} U_{\text{LJ,rep}}(r_{ij}) + \sum_{\substack{i,j \\ |i-j|>2}} U_{\text{LJ,att}}(r_{ij}) \qquad (9)$$

where r_{ij} is the distance between beads i and j and $U_{\text{LJ,rep}}$ and $U_{\text{LJ,att}}$ are the repulsive and attractive LJ potentials, respectively. Potential energy also follows a similar pattern noted in radius of gyration and end-to-end distance, but a notable difference is that the largest peak on the distance calculations was at 0.9 K and the largest peak for potential energy is at 0.5 K.
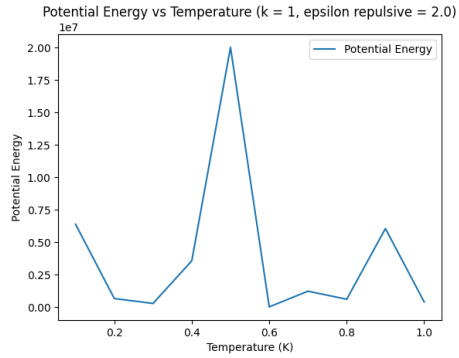

Figure 13: Total Potential Energy

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4.4 Phase Transition

It is tricky to determine the phase transition from the above analysis techniques, as it seems like two may have occurred. First, consider from 0.3 to 0.4 K. There is likely a transition here as the polymer goes from being folded to unfolded. This is hypothesized because the radius fo gyration and end-to-end distance both increase largely here, indication the polymer is more spread out in the box. A similar artifact is present from 0.8 to 0.9 K. Oppositely, there seems to a transition to folding occurring from 0.5 to 0.6 K. Because ti is known that polymers are more likely to fold at lower temperature, it may be noted that this specific polymer is most probable to not fold at temperature of 0.9 K and above, however may additional simulations would need to be performed to make sure these results are reproducible.

5 Conclusion

We have concluded a polymer with high ϵ_{rep} and k values will work better in space as higher spring constant means the polymer is more rigid and less folding occurs and higher ϵ_{rep} means the LJ potential well is deeper. This study is far from being completed, however, as many additional characteristics may need to be further studied to determine what may be the best polymer to use in space.

Important factors to consider is that first, each simulation of a specific k and ϵ_{rep} value over a temperature span take 15-20 minutes, which is considerably long. That is each individual simulation of 10,000 steps takes anywhere from 1-3 minutes, and over 30 of these were computed. This unexpectedly cut the potential of this project short. With further time availability or HPC availability, more characteristics of the polymer could be explored and a more accurate analysis of what could be used in space may become available. Though that was not determined in this project, this gives a good starting point of where to go further to determine how factors of what polymers types may work best in space conditions. Because of this, future considerations on decreasing this time by increasing efficiency in the code would be valuable. Additionally being able to visualize the particle over time in a gif would be a valuable addition to this project in the future; however, time constraints made this tricky. This project can easily be further extended to determine real polymers that may work out in space-like conditions.