Modelling Polymer Dynamics

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Abstract

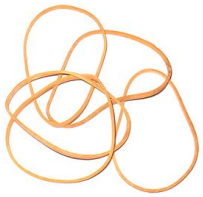
This project explores the dynamics of freely-jointed chain polymers. Starting with 1 degree-of-freedom (1-dimension), we climbed up to 2D and ultimately to 3D. Using MATLAB to simulate the probabilistic behavior of the freely-jointed chain, with one end fixed, we were able to observe the results of how temperature and force affect the end-length. This results matched the experimental observations we saw in class. Keeping temperature constant, as a greater force is applied, the chain will stretch towards the direction of the applied force. Keeping force constant, as temperature increases, we observe that the chain contracts. When we compare a similarly constructed polymer chain between the different dimensions, we observe interesting results. The 2D and 3D cases follow similar behaviors for both a temperature and force change, and the 1D chain remains the most taut compared to the 2D and 3D chain during temperature change.

1 Introduction & Background

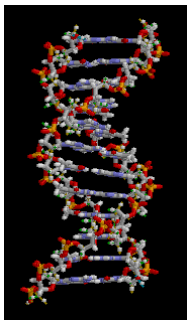
1.1 Basics of Polymers

Polymers are ubiquitous substances with a broad range of material properties. According to Wikipedia, a polymer is defined as a "substance or material consisting of macromolecules composed of repeating subunits" [4]. Because of this, they play an large and an important role in many chemical reactions and come with many variations (Refer to Figure 1 for a couple of examples). Their interesting properties can be understood by looking into their thermodynamics. For instance, by looking at a chain's entropy, we can make predictions about its stretching and compression [5].

However, according to our course lectures, what is interesting about polymer chains is that their movement is probabilistic. For instance, let's say that we fix one end of a polymer chain. We then grab



(a) Rubber band.



(b) DNA molecule.

Figure 1: Examples of polymers. Despite their differences in molecular structure and material properties, both a rubber and DNA molecule are composed of repeating subunits, forming a chain.

the other end of the chain and apply a rightward force. From our observations, the chain will stretch and move towards the right, as we would expect. *However*, if we look at the individual units of the chain, we can see that not all of them move towards the right. Some of them in fact move towards the opposite direction! This behavior is caused by the thermal fluctuations that the individual elements of the chain experience. Understanding how this affects their dynamics is crucial, since polymers play an active role in many chemical processes.

1.2 Tie to PS10

During the early part of the thermodynamics portion of the course, we touched upon polymers and explored how their dynamics can be described by the Boltzmann Distribution. Furthermore, thanks to Daniel, we also saw experimentally how polymers, in this case a rubber band, contract when heat was added to it. This was extremely unintuitive, surprising, and fascinating. I wanted to explore this behavior in greater detail via modelling and see what how each model differs between different dimensions.

In the beginning, I was interested in seeing how this could be applied to soft robotics, an engineering and research interest of mine. However, the underlying physics, specifically continuum mechanics, was outside the scope of the course. Nonetheless, this was a great way to explore the underlying material properties and mechanics that most soft robots are constructed out of. Also, the physics of polymers are just interesting!

2 Model

Truly modelling the dynamics of polymers are complex, but to capture their general physics, we can use a freely-jointed chain model [2]. We want to model how a freely-jointed polymer chain behaves when a force or temperature change is applied to it. Regardless of the dimensionality of the system, the Boltzmann distribution governs its probability distribution, which in turn influences the direction that the chain will move. The general form of the probability distribution function is presented below:

$$P(X) = Ae^{\frac{-\epsilon_i}{k_B T}} \tag{1}$$

X represents the direction that the chain will move, A is the normalization constant, ϵ_i represents the energy associated with X, k_B is the Boltzmann Constant, and T is the temperature of the system. Both A and ϵ_i changes as the dimension increases, and will be explored in greater depth in their respective sections.

Note that this model represents an *individual link* in the chain, so we would need to reapply this model to each link in the chain. However, with computational tools such as MATLAB, we can easily perform this calculations.

1D Model

In this model, the individual links of the chain can move only in two directions. In this project, we chose either the link moves left or right. The underlying probability distribution and normalization constant is represented by the following two equations, respectively (note that cosh in Eq 3 is the hyperbolic cosine function):

$$P(L|R) = A_{1D}e^{\frac{-\epsilon_i}{k_B T}} \tag{2}$$

$$A_{1D} = \frac{1}{2\cosh(\frac{FL}{k_B T})} \tag{3}$$

Now for the energy of the system, represented by ϵ_i, is as follows:

$$\epsilon_i = \pm FL \tag{4}$$

This is the work done onto the chain: how much force we apply to the length of an individual link. In the direction we apply the force, ϵ_i takes on the negative sign, while it takes the positive sign for the opposite direction. A bit counter-intuitive, but mathematically, when plugged into the Boltzmann equation, we can see the that probability moving towards the direction of the force grows exponentially while it exponentially decays when the probability moves towards the opposite direction, matching our expectations.

This probability distribution is simple: x% the chain would move to the left, and y% the chain would move to the right. Another way to think about it is that this is like a coin-flip with changing probabilities for heads and tails.

2D Model

Climbing up to 2 dimensions, we begin to see a more complex but much more interesting probability distribution. This time, the links of the chain can move up and down as well. We use polar coordinates, where we hold the radius (length of the link in this case) to be constant. Therefore, we are interested in the probability distribution of θ's, where θ is the angle between the line from the origin to the point and the x-axis [1]. The probability distribution $P(\theta)$ takes a similar form, but the normalization constant (A_{2D}) and energy (ϵ_i) change due to the increased dimensions, as presented below:

$$P(\theta) = A_{2D} e^{\frac{-\epsilon_i}{k_B T}} \tag{5}$$

$$A_{2D} = \frac{1}{\int_0^{2\pi} e^{\frac{-\epsilon_i}{k_B T}} d\theta} \tag{6}$$

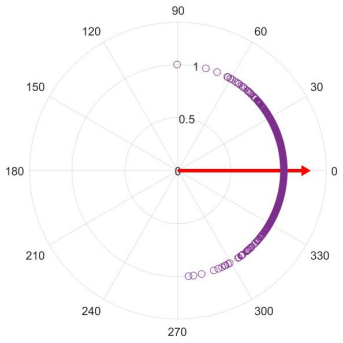
$$\epsilon_i = -\vec{L} \cdot \vec{F} = -L \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} \cdot \begin{bmatrix} F_x \\ F_y \end{bmatrix} \tag{7}$$

Eq. 6 represents the fact that we are getting a range of θ values between 0 to 2π. Eq. 7 uses vector notation to compactly represent the x and y components of the force and length, and shows that the energy of the system is the *dot product* between the length and force. This returns a scalar value, which is what energy is.

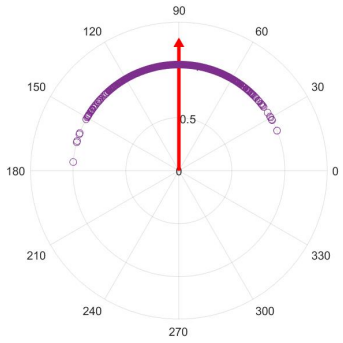
In short, we are applying the Boltzmann distribution to a circle. For a visual representation of this distribution, refer to Fig. 2.

3D Model

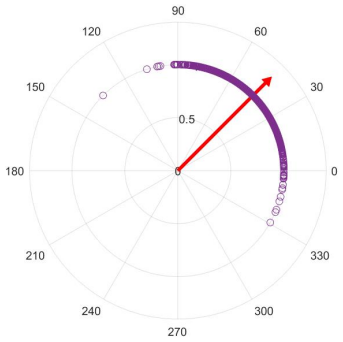
Finally we reach the real world: creating a model for a freely-jointed chain in 3-dimensions. Compared to the 2D model, we can see that this is more complex (yet also more fascinating). We are using spherical coordinates, keeping the radius (length) constant, therefore needing a θ and ϕ value to represent the orientation of the chain. θ's definition remains the same from the 2D case, but ϕ is the angle between



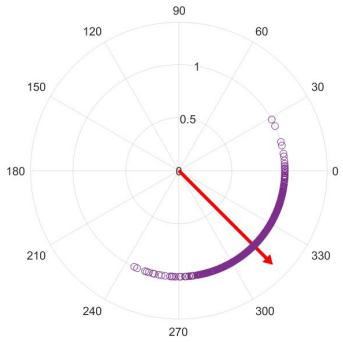
(a) Distribution of randomly-sampled points with rightward force applied.



(b) Distribution of randomly-sampled points with upward force applied.

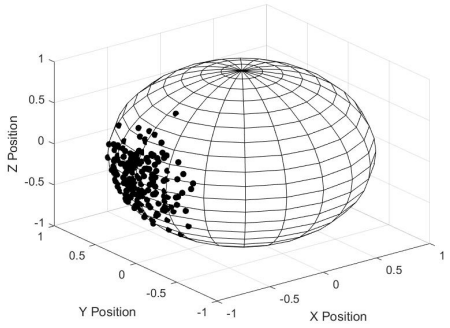


(c) Distribution of randomly-sampled points with upright force applied.

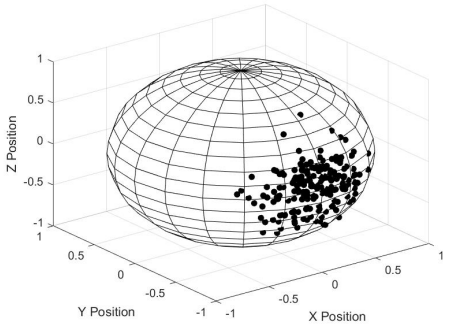


(d) Distribution of randomly-sampled points with downright force applied.

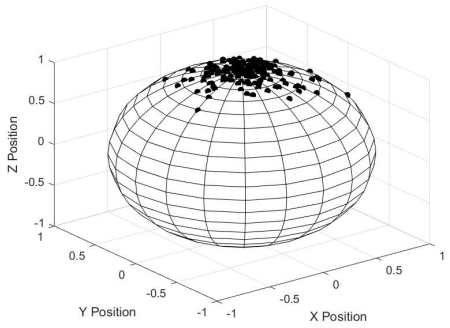
Figure 2: Random sampling of points based on the 1D Boltzmann distribution. These points correspond to a respective θ value. The red arrow represents the direction of the applied force. Note how the points appear to distribute themselves around this arrow.



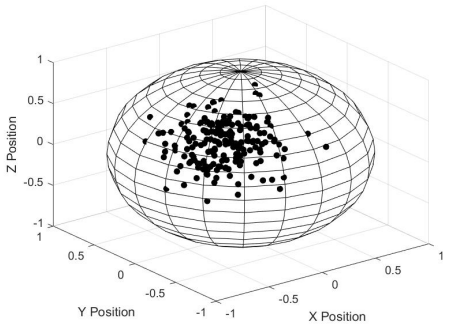
(a) Distribution of sample points when force applied in the negative X direction.



(b) Distribution of sample points when force applied in the negative Y direction.



(c) Distribution of sample points when force applied in the positive Z direction.



(d) Distribution of sample points when force applied in the negative X, negative Y, and positive Z direction.

Figure 3: Random sampling of points based on the 2D Boltzmann distribution. These points correspond to respective θ and ϕ values.

the line formed from the points from the origin to the radius and the z-axis. This new information is represented by the three equations below:

$$P(\theta, \phi) = A_{3D} e^{\frac{-\epsilon_i}{k_B T}} \tag{8}$$

$$A_{3D} = \frac{1}{\int_0^{\pi} \int_0^{2\pi} e^{\frac{-\epsilon_i}{k_B T}} d\theta d\phi} \tag{9}$$

$$\epsilon_i = -\vec{L} \cdot \vec{F} = -L \begin{bmatrix} \sin(\phi)\cos(\theta) \\ \sin(\phi)\sin(\theta) \\ \cos(\phi) \end{bmatrix} \cdot \begin{bmatrix} F_x \\ F_y \\ F_z \end{bmatrix} \tag{10}$$

Eq. 9 includes another integral, representing the fact that the ϕ values range from 0 to π. Eq. 10 represents the fact that we are now in 3D space, however, the use of the dot product still remains the same.

Essentially, in the 3D case, we are applying the Boltzmann distribution to the sphere, and are sampling from this sphere. Refer to Fig. 3 for a visual representation of the probability distribution.

3 Simulations & Results

Now that the underlying physics has been established, we can start to simulate the dynamics of each chain. The core of the simulations is to create a random walk, where the randomness is influenced by the model's respective Boltzmann distribution. To do this and ensure that the chain remains connected, the core algorithm was obtained from user Torsten's post on MATLAB Answers webpage [6].

For each case, we perform two simulations on a constructed 10-point chain, where each link is $L = 1$ unit long. The first one is where the temperature is kept constant (298 K), but the applied force increases, starting from 0 up to the maximum possible value (more on this later). The second one is where the force is kept constant at its maximum possible value, but the temperature increases, starting from 298 K up to 1×10^5 K. Truth be told, there is no specific reason why this maximum temperature value was chosen, other than showcasing behavior at extreme temperature scales.

In order to reduce programming errors and computational inaccuracies, from the advice of the course staff, the representation of the parameters have been modified. The Boltzmann Constant, k_B, is represented as 1.38 instead of its whole value of $1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$. The applied force representation has also been modified, being on the scale of 10^{-23} Newtons.

Since the chain's movement is probabilistic, we want to capture its general movement. Thus, for each force or temperature value, we simulated the chain 100 times and calculated the average position of the elements in the chain.

As will be noted in their respective sections, the quality of our simulation is limited by the computational constraints imposed by MATLAB. One example is the maximum force values. Although realistically we can apply an extremely large force, at some point, the probability density values either becomes extremely large (1D case), or the sample points converge to the same point, which would raise errors in MATLAB (2D and 3D case).

1D Model

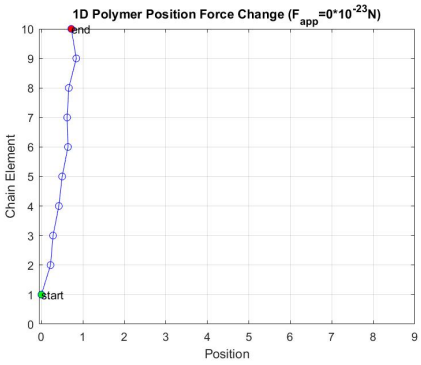
Our simulations starts with the simple 1D case. Referring to Fig. 4 and 5, we can see the behavior of the freely-jointed chain. It matches our expectations: holding temperature constant, as the force increases in a certain direction, more of the units will move towards that direction, in our case, rightwards. When temperature increases, we expect the opposite, that the chain will start to contract, holding the applied force constant.

Here, the value of 6700×10^{-23} N was selected as the maximum value because the chain quickly converges to it's full, extended length. For the temperature, 1×10^5 K was the selected max temperature at the time of the simulations.

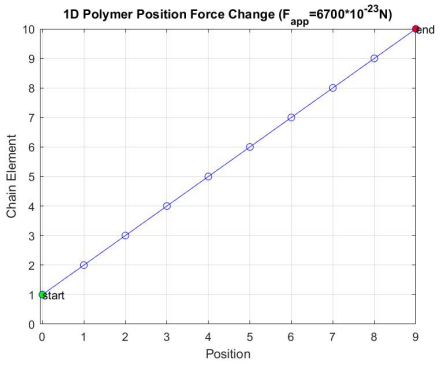
2D Model

In the 2D case, we observe similar overall behaviors when the force and temperature is varied from the 1D case, matching our analytical predictions and experimental observations. Here, the maximum force value applied was 7200×10^{-23} N. Refer to Fig. 6 and Fig. 7 for the force and temperature simulation results, respectively.

In order to perform the simulation, we needed to sample a random θ value from the changing distribution. Unfortunately, due to the increased complexity, it wasn't as simple as drawing a random number and seeing if it falls in a certain threshold, as in the 1D case. To do this, we needed to construct a new probability distribution, one that follows the model given in the **2D Model** section of this paper, and randomly sample from that distribution. From his online book *Advanced Statistical Computing*, Professor Roger Peng describes the following algorithm [3]:

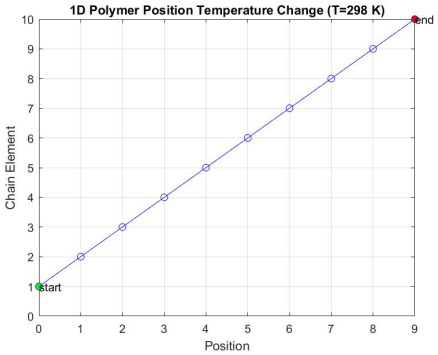


(a) Start of force-change simulation at 0 N.

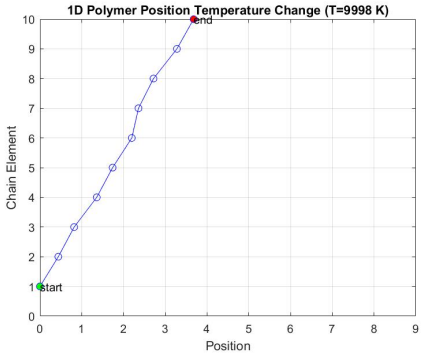


(b) End of force-change simulation at 6700×10^{-23} N.

Figure 4: 2D simulation results for polymer with an increasing force applied right. The polymer has 10 units, with 9 links in the chain. The temperature was held constant at 298 K.

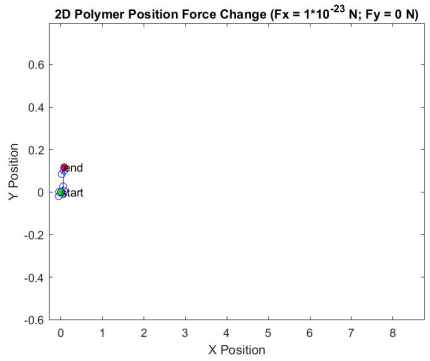


(a) Start of temperature-change simulation at 298 K.

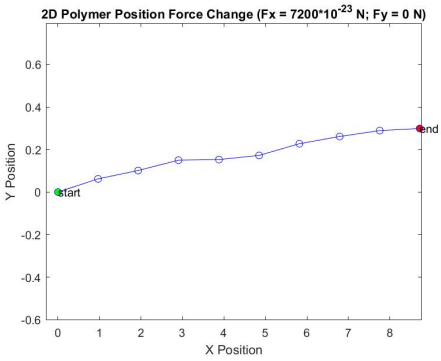


(b) End of temperature-change simulation at 9998 K.

Figure 5: 2D simulation results for polymer with varying temperature, starting from 298 K to about 1×10^5 K. The polymer has 10 units, with 9 links in the chain. The force was held constant at 6700×10^{-23} N.

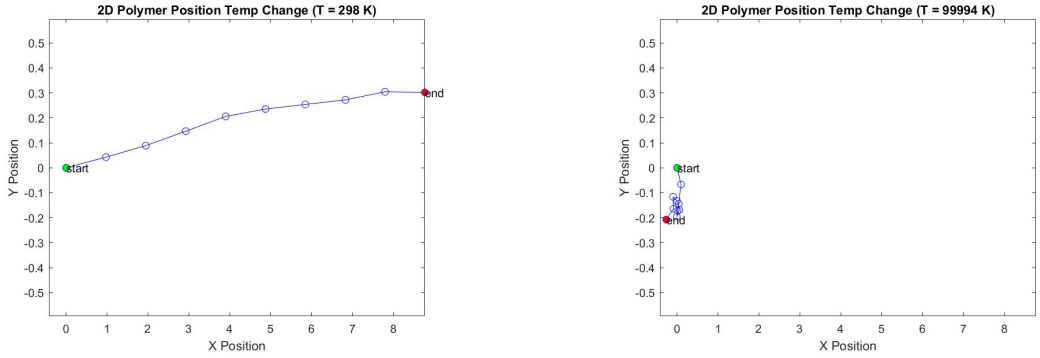


(a) Start of force-change simulation at 0 N.



(b) End of force-change simulation at 7200×10^{-23} N.

Figure 6: 2D simulation results for polymer with an increasing force applied rightward ($\theta = 0$ rad). The polymer has 10 units, with 9 links in the chain. The temperature was held constant at 298 K.



(a) Start of temperature-change simulation at 298 K. **(b)** End of temperature-change simulation at 99 994 K.

Figure 7: 2D simulation results for polymer with varying temperature, starting from 298 K to about 100 000 K. The polymer has 10 units, with 9 links in the chain. The force was held constant at 7200×10^{-23} N.

Algorithm 1 Random Sampling from Non-Uniform Distribution [3]

1: Construct probability density function $\rightarrow PDF(X)$
2: Create cumulative density function (CDF) from PDF $\rightarrow CDF(PDF)$
3: Take the inverse of the CDF $\rightarrow CDF^{-1}$
4: Generate a random number U
5: Feed U into the inverse function to get out a random θ value $\rightarrow \theta = CDF^{-1}(U)$

Thanks to MATLAB's `interp1` function, we were able to create this mapping from random numbers ranging from 0 to 1 to θ values ranging from 0 to 2π, respecting the underlying probability distribution. Refer to the attached code for the implementation.

3D Model

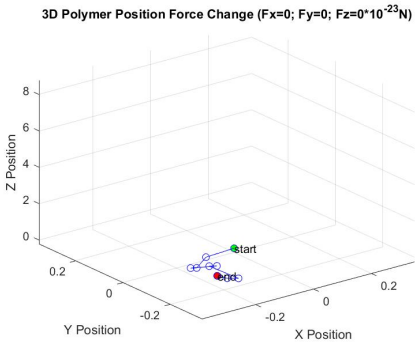
Finally in the 3D case, we observe similar overall behaviors when the force and temperature is varied from the previous two cases, therefore matching our analytical predictions and experimental observations. This time, the maximum force value applied was 6700×10^{-23} N. For the force and temperature results, refer to Fig. 8 and Fig. 9, respectively.

It must be noted here that implementing the sampling for the 3D model was much more difficult than the 2D process, namely since MATLAB doesn't have any built-in functions that can map from 1 data point to 2 distinct points (in this case, it would be a CDF value to a θ and ϕ value). To get around this, what was done was that a random θ value was generated, and from that θ value, constructed a probability distribution function of ϕ values based on that θ value. Refer to the attached code for the implementation.

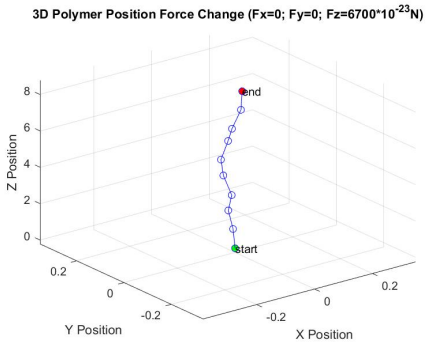
Comparison Between Dimensions

A final exploration that we did was to compare how the chains in each dimension reacted to the changing force and temperature. To do this, the simulation was ran with the same number of elements in the chain (10 in this case), ranges where held the same, and the constant force or temperature was held the same as well.

For the force simulation, it went from 0 N to 6700×10^{-23} N and the temperature was held constant at

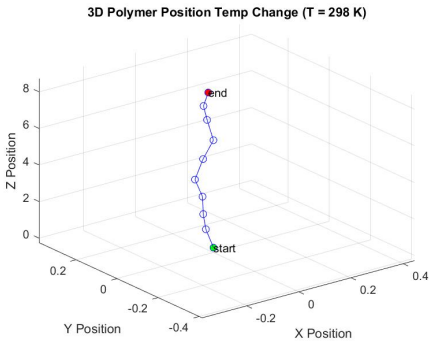


(a) Start of force-change simulation at 0 N.

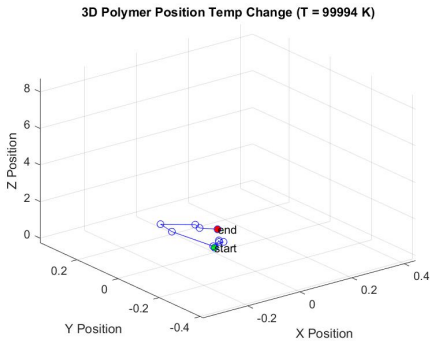


(b) End of force-change simulation at 6700×10^{-23} N.

Figure 8: 3D simulation results for polymer with an increasing force applied upward ($\phi = 0$ rad). The polymer has 10 units, with 9 links in the chain. The temperature was held constant at 298 K.



(a) Start of temperature-change simulation at 298 K.



(b) End of temperature-change simulation at 99 994 K.

Figure 9: 3D simulation results for polymer with varying temperature, starting from 298 K to about 100 000 K. The polymer has 10 units, with 9 links in the chain. The force was held constant at 6700×10^{-23} N.

298 K (Refer to Fig. 10). For the temperature, the range went from 298 K to 1×10^4 K, and the applied force was held constant at 6700×10^{-23} N (Refer to Fig. 11).

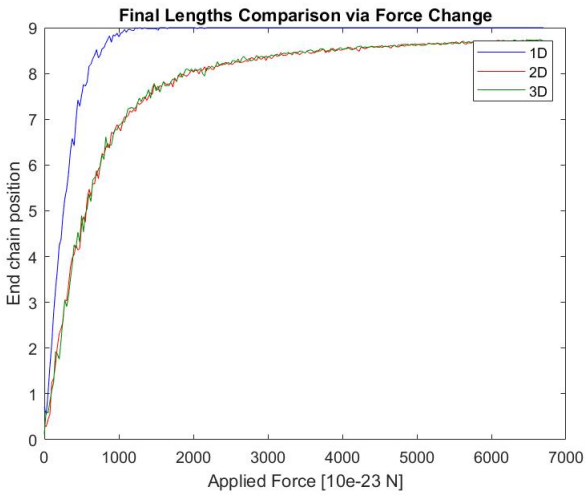


Figure 10: Graph showcases the length of the polymer chain as the applied force increases. The length is measured as the distance from the origin to the end-point of the chain. All chains are composed of 10 units, have the same applied force, and held at the same temperature of 298 K.

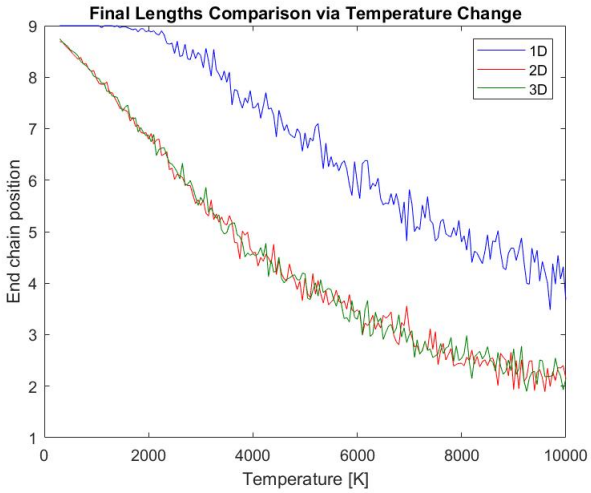


Figure 11: Graph showcases the length of the polymer chain as the temperature increases. The length is measured as the distance from the origin to the end-point of the chain. All chains are composed of 10 units and the applied force was held constant at 6700×10^{-23} N. The temperature varied from 298 K to 1×10^4 K.

Looking at the results, we can see some interesting findings. For the force comparison, it follows our intuition that for the 1D case, it takes a lot less force to reach the final length because the probability threshold exponentially increases faster to move in the direction of the applied force. This corresponds to the chain's stiffness constant being lower than that of the 3D case. However, what is interesting to note is that the behavior between the chain in 2D and 3D are similar. Initially, it was expected to see a difference between these two: when a force is applied, it would be easier to stretch the 2D chain to the final length than the 3D chain because there are less degrees of freedom that it could move towards.

However, we don't observe this behavior, and instead see that they have the same trend. This might be attributed to our algorithm.

Temperature was even more surprising. Not only did the 2D and 3D case match up, they also contracted faster than the 1D chain. This is surprising, especially noting the fact that the 2D and 3D chain are much more stiff than the 1D chain. One theory to explain this observation is taking note of the fact how "responsive" the 1D chain is to the applied force. Since the 1D chain moves towards the direction of the force faster than the other two chains, even though the temperature increases, it will more likely move towards the direction of the force thanks to the high value of it's probability density function at that direction.

4 Conclusion

Overall, this project expanded upon the polymer dynamics that we have explored in the course. Starting of from the 1D model, we were able to create, expand upon, and simulate the dynamics of the freely-jointed polymer chain, climbing up to 3D. For all cases, as the applied force increases and temperature increases, the behavior of extending and contracting follows our expectations, respectively. However, when comparing across dimensions, it seems that the 2D and 3D model seem to have the same behavior, while the 1D chain under temperature change surprisingly remains taut despite the lower stiffness.

This work is just the beginning, and can be expanded in many ways. One way that this work could be expanded is to apply the molecular-bond constraints to the chain. For instance, the links in the chain of a silicone rubber polymer can't fully rotate around the chain, due to the bond between the elements of the chain. This would make it a much more realistic simulation.

Another way that this project could be expanded upon is by explicitly tying the thermodynamic concepts to it. As was mentioned in the beginning, entropy and the Gibb's free energy is tied to the configuration of the chain. It would be worthwhile to dive deeper into this relation and quantify the relations.

5 Special Thanks

I wanted to take this time to thank the people who helped me accomplish this project. Most notably, I want to thank Alvin for guiding me throughout the programming process, helping me develop the algorithms, and advising me throughout the project. On an equivalent note, I also want to thank Phil for helping me figure out how to implement the random sampling algorithm; without it, this project would have not been done. I also want to thank Adam for helping me during office hours better understand the physics of polymers and sharing about it. I also want to thank Janet for walking me through the first parts of the project. Finally, I want to thank Carolyn for being a sounding board and her feedback on my ideas throughout the process of the project.

References

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