MENG 25500 PSET 1: Monte Carlo Simulations
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Due: 2 February 2022

Introduction

This document includes the written responses to each question, plots of the resulting data, as well as a list of files included in this submission.

Included Files

report1.pdf This document.

simulation_main.py The main simulation code with background functions and main functions for each question. Please run this file when checking my code. Note that it relies on an internally defined file structure for i/o operations.

data_analysis A supplementary notebook for some data analysis related to part 4.

seed_log.txt A log of seed used.

(Please also note that figure placements may be further down than their assigned section due to LaTeX automated placement.)

1 Simple Model Bead-Spring Model for Polymer

In the problem statement we are given that the potential is described by

$$V(r) = \frac{1}{2}\epsilon k \left(\frac{r}{\sigma}\right)^2$$

with σ as the length scale for a polymer chain with no pairwise interactions in an infinite vacuum. The unit scaling is chosen to be $\epsilon = k_B T$ and $\sigma = 1$.

Additionally, we have that the expectation value of an observable $\mathcal{O}$ that does not depend on momentum is

$$\langle \mathcal{O} \rangle = \frac{\int_{-\infty}^{\infty} \mathcal{O} e^{-\beta \mathcal{H}} \, \mathrm{d}r}{\int_{-\infty}^{\infty} e^{-\beta \mathcal{H}} \, \mathrm{d}r}$$

Here the Hamiltonian $\mathcal{H}$ of our system is simply the harmonic potential. Then the expectation value of r with this $\mathcal{H}$ is

$$\langle r \rangle = \frac{\int r e^{-\frac{1}{2}k_s r^2} * r^2 \, dr}{\int e^{-\frac{1}{2}k_s r^2} * r^2 \, dr}$$

where both integrals are assumed to be over all space. There is no dependence on θ nor ϕ, so their integrals would both evaluate to the same constant in the numerator and denominator, ultimately canceling to one. This radial symmetry can be further exploited, since we know that the symmetric 3D potential well does not favor particular configurations over others with the same inter-monomer distance. It is also true that the beads may invert their order with respect to the origin (i.e. reading low to high on a given axis, a

configuration may change from AB to BA). Reasoning $\boldsymbol{r}$ as a vector from A to B also supports this, since on average contributions at each iteration i (for a high iteration count) will cancel out $\sum_i \boldsymbol{r}_i \approx \boldsymbol{0}$, or

$$\langle |r| \rangle = 0$$

As a final check, this makes energetic sense, as the lowest point on the symmetric potential curve is when $r = 0$. This however does not serve as an adequate length scale since 0 can not be used as a coefficient or divisor safely.

The next quantity of interest is $\langle r^2 \rangle$,

$$\langle r^2 \rangle = \frac{\int r^2 e^{-\frac{1}{2}k_s r^2} * r^2 \, dr}{\int e^{-\frac{1}{2}k_s r^2} r^2 \, dr}$$

which does not evaluate to zero. The numerator is

$$\int_0^\infty r^4 e^{-\frac{1}{2}k_s r^2} \, dr = \frac{3\sqrt{\pi/2}}{k^{5/2}}$$

if the Gaussian integral table relation

$$\int_0^\infty x^4 e^{-ax^2} \, dx = \frac{3}{8a^2} \left(\frac{\pi}{a} \right)^{1/2}$$

is used. The denominator is

$$\int_0^\infty r^2 e^{-\frac{1}{2}k_s r^2} \, dr = \frac{\sqrt{\pi/2}}{k^{3/2}}$$

using

$$\int_0^\infty x^2 e^{-ax^2} \, dx = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

This gives that the final value for $\langle r^2 \rangle$ is

$$\langle r^2 \rangle = \frac{3}{k_s}$$

In the problem statement we are also told that the spring constant k_s should be chosen to satisfy $\sqrt{\langle r^2 \rangle} = \sigma$

$$\sqrt{\langle r^2 \rangle} = \sigma$$
$$\langle r^2 \rangle = \sigma^2$$
$$\frac{3}{k} = \sigma^2$$
$$k = \frac{3}{\sigma^2}$$

If $k = \frac{3}{\sigma^2}$ and $\sigma = 1$, then $k = 3$ in the reduced units.

2   Simple Displacement Algorithm

The first necessary step for this problem is to create a function that takes N as a parameter as the number of monomers in the chain, and that then returns the coordinates of the initialized chain. The coordinates are randomly generated with Numpy's `random.random()` set with the seed `int(time.time())` which is then recorded to file. The y and z parameters are formulated the same for each monomer, but the x coordinates will be offset by their order i within the sequence multiplied by a scaling factor a. In segments of the code where this is either not needed or would introduce error, it is turned off and all coordinates are generated evenly. A second function is developed to calculate the bond energy between two coordinates that are given as inputs. This is done via calculating $|r - r'|^2$, and passing this value to the formula for V as determined with the constants from problem 1. Next, another function is written to take a sequence as an argument and perform sample trial moves for the Markov chain. A second layer function is written to call this N times, where N is the number of beads in the polymer.

Note on Code Structure: The functions mentioned above, as well as others, are all written separately and then called by main methods `main_n()` where `n` is the number of the problem. This is done so that it is easy to execute tasks specific to each problem in a self contained way while reusing functions across problems.

The output for the recorded energy is given in the following figure. Independent calculations performed via plugging in coordinates at the end of the trial move period to the harmonic potential confirmed that the energy changes were self consistent. The value obtained for $\langle r^2 \rangle$ is also consistent with the analytical prediction of 1. Please see the corresponding table for question 2 for the relevant data.
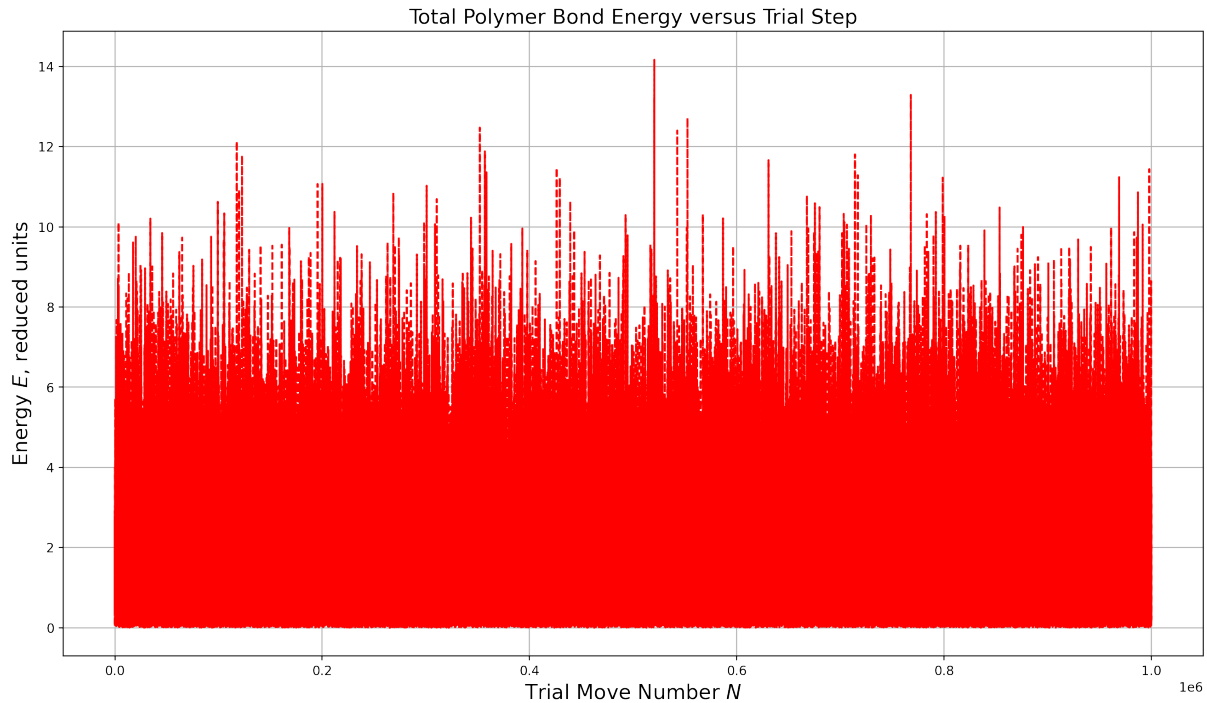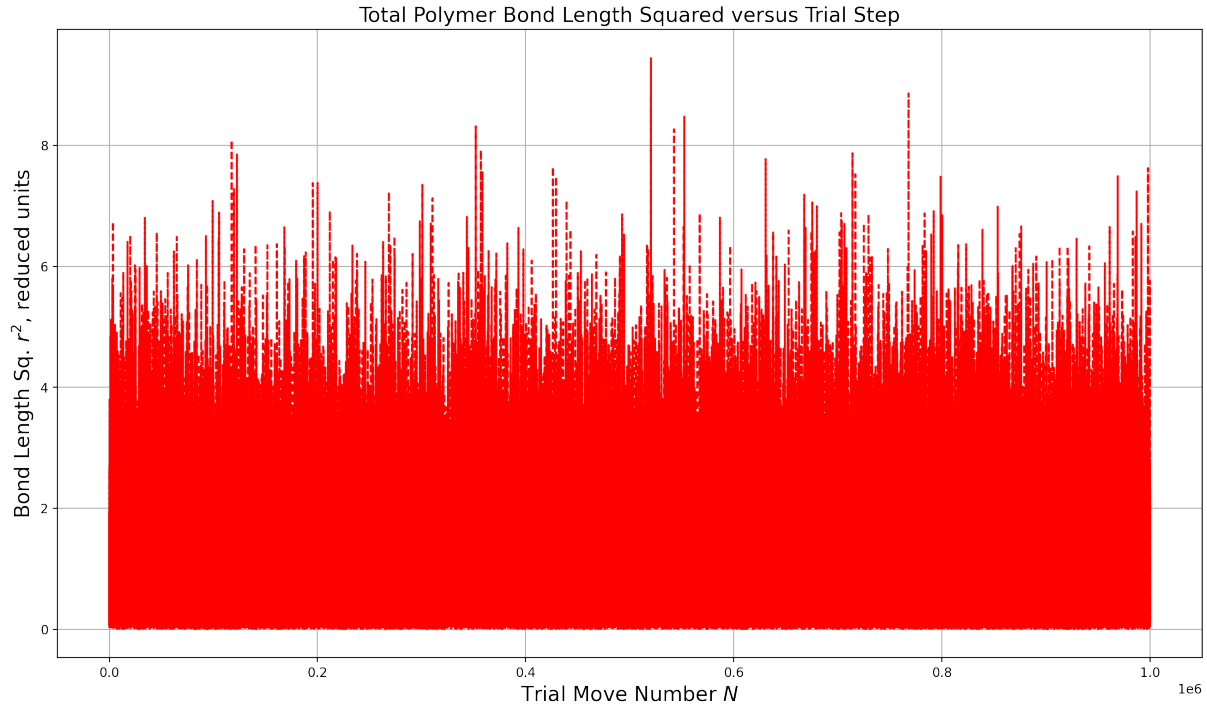

Figure 1: (Q2) The energetic results for an $N = 2$ simple system over approx. 10^6 trial steps

Quantity	Value (Unit)
Starting Energy:	2.108162978864724 (En)
Final Energy (from Log):	3.5160048227986183 (En)
Final Energy (ind. Calc):	3.5160048227986183 (En)
$\langle E \rangle$	1.4980882198713585 (En)
$\langle r^2 \rangle$	0.9987250731977336 (σ^2)

Table 1: Output Data for Question 2

Figure 2: (Q2) r^2 over approx. 10^6 trial steps ($N = 2$)

3 Optimizing the Performance of the MC Simulation

Now, a chain length of $N = 32$ will be chosen for the purposes of finding an optimal value for the displacement constant a. In the previous section, this value was assumed to be equal to 1.0 Here we are asked to find the MSD of the polymer chain at each iteration compared to the initial state of the polymer. At equilibrium, one would expect that this value would settle around a certain value. For this question, a function is needed that will take two geometries, the current and the initial, and report back the following quantity

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \left[\vec{r}_i(t) - \vec{r}_i(0) \right]^2$$

To test this, a few differing values of a were tested. In a preliminary run, several orders of magnitude were tested (10^{-2} to 10^2). Lower orders of magnitude did not see a high degree of coordinate movement, and higher orders of magnitude, especially 10^2 did not give adequate opporutiny for coordinate change, as their results for MSD appeared to never stray far from zero. This is because at higher magnitudes of displacement, it is more than likely the initial displacement of the bead from its orginal coordinate r_0 will
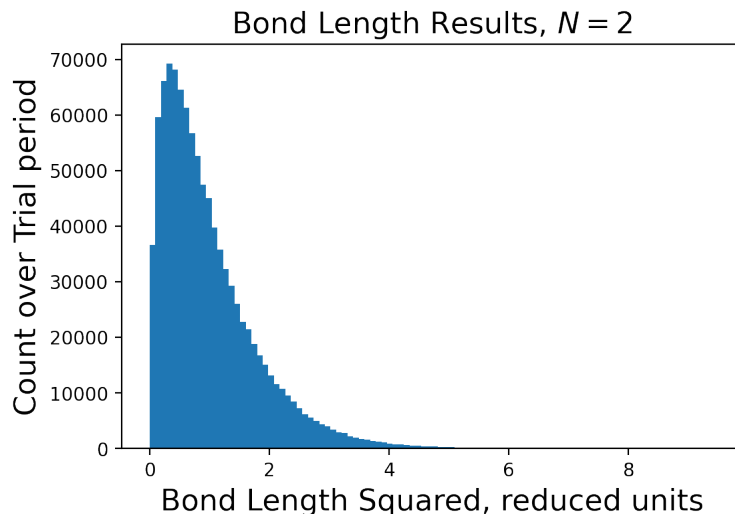
Figure 3: $(Q2)$ r^2 over approx. 10^6 trial steps

be too high in energy to ever be accepted. The values which fell in-between are reported below, namely $a \in \{0.1, 0.15, 0.25, 0.50, 1.0, 2.0\}$.

Ideally, one would expect the value of a which results in the highest MSD over a given period, meaning the molecule may diffuse the most, to be the optimal choice for a production run. In office hours, it was suggested that this value of a should lie around 0.5. Per my results, it appears that 1.0 is the strongest candidate, outperforming 0.5 over an averaged series of 100 runs. This may be due to an error in the code, though it is unknown what it could be, as results for the second question are in perfect agreement with what is expected, meaning the scaling of the simulation should be correct. A possible explanation includes that my definition of a is different than intended. In the textbook, it is suggested to define displacements in terms of $\Delta/2$,[1] where as I have opted to define the constant in terms of a unity instead of a fraction. This may responsible for the factor of two discrepancy.

4   End to End Distance of Rouse Model

For this section, a function is developed that will report the following quantity for a given input geometry `C`

$$\vec{R}_{ee} = \vec{r}_0 - \vec{r}_{N-1}$$

where N is the length of the chain. The values of N considered are $\{8, 16, 32, 64\}$. The square of this quantity is then found and recorded to file. Before moving forward, it was decided to research the literature on the Rouse model. It was found that the standard Rouse model will exhibit a relaxation time of

$$\bar{\tau} = \frac{\gamma N^2 b^2}{3\pi^2 k_B T}$$

with γ as the damping constant and b as the size of the monomer, as given by Osmanović and Rabin.[2] For our purposes, we will just assume that

$$\bar{\tau} \sim N^2$$

Additionally, this portion of the code should be run so that the chain starts off in a non-automatically linearised state (i.e. `C_0` not initialized in a linear fashion) so that relaxation time can be measured in a
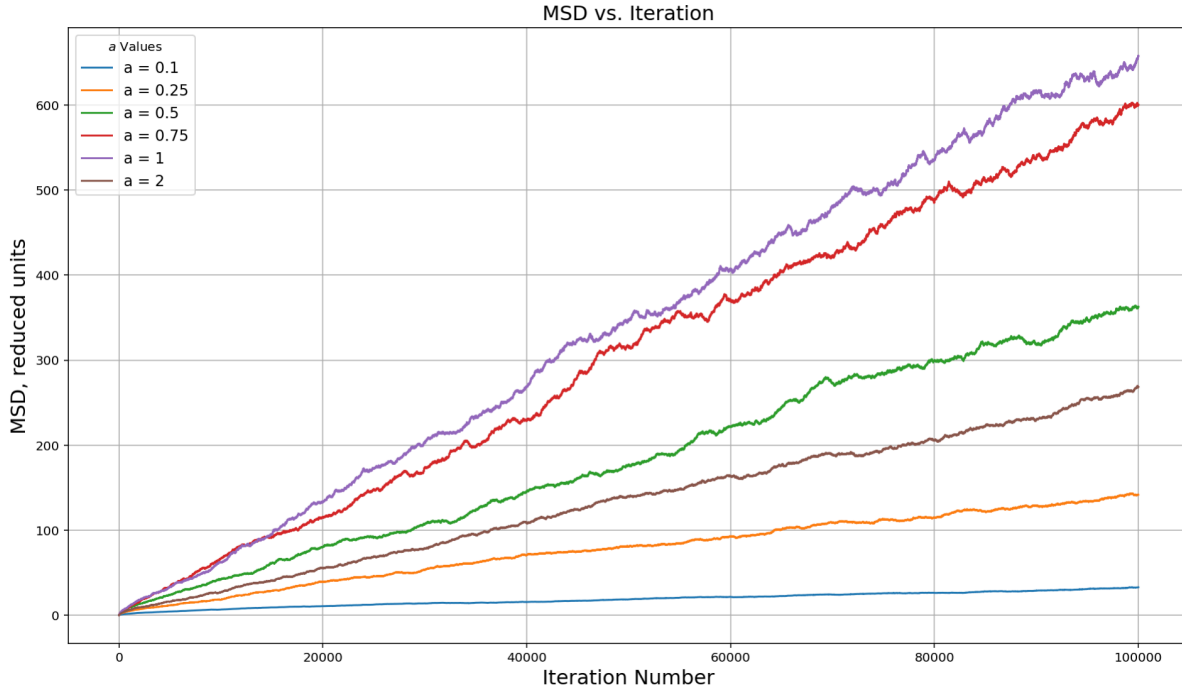
Figure 4: (Q3) Averaged MSD over several values of a over 1.0e5 trials

more meaningful way. In office hours, it was clarified that

$$\tau_{\text{est}} = \frac{n_B}{2} \frac{\left\langle \delta \mathcal{O}^{B^2} \right\rangle}{\left\langle \delta \mathcal{O}^2 \right\rangle}$$

where n_B is the number of steps per block in the block analysis. A below figure contains the results for the chain length versus averaged end to end distance over 10^6 iterations. As expected, the equilibrated chains show an average end to end distance that is close to $N - 1$, the distance that a straightened out polymer would have with the square of average bond length being 1. The results are more obtuse, however, when block analysis is considered. Instead of the observing an N^2 scaling relation as predicted, instead a N^{-2} relation is found. This may be due to the way in which the variances were sampled.

5   Lennard-Jones Potential and Minimum Image Boxes

For the last section of the homework, we are asked to implement the minimum image convention along with replacing the harmonic potential with the Lennard-Jones potential, given by

$$V_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

with a cutoff distance of $r_c = 2^{1/6}\sigma$. The energy of the system will be found with the image of each particle as it would be in the original box. As beads of the polymer propagate through space, it is kept track of how many times the particle has crossed the boundary of the $L = 10\sigma$ box (cube) and in which direction. For example, a bead which is still truly located in the box will be associated with the tracking coordinates
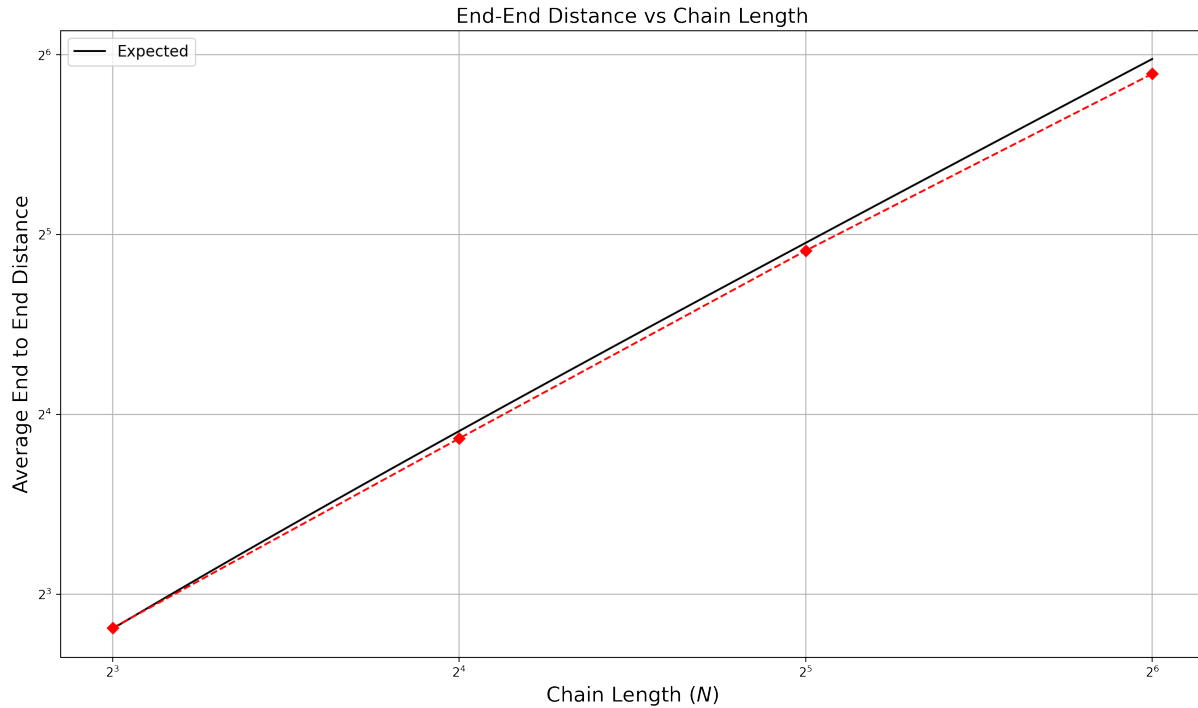
Figure 5: (Q4) Chain length and average end to end distance. 10^6 iterations.

Quantity	Value (Unit)
Starting Energy:	75766581.74231693 (En)
Final Energy (from Log):	0.8326479776871623 (En)
Final Energy (ind. Calc):	0.8326479776871623 (En)
$\langle E \rangle$	77.81609165727221 (En)
$\langle r^2 \rangle$	1.5227595822651132 (σ^2)

Table 2: Output Data for Question 5.2. Two bead system.

$[0, 0, 0]$, while a bead that is located at $(15, 25, 35)$ will have a tracking coordinate $[1, 2, 3]$ and a virtual coordinate $(5, 5, 5)$. It is for the full set of virtual coordinates that the pairwise LJ potential energy is found at each time step.

5.1   Question 5 Part 2: Trial Polymer

The resulting data for question 2 done with the LJ/Image method is, as would be expected, different from the original harmonic potential Rouse model. Firstly, the observed starting energy is quite high due to the particles being generated very closely together. From there, it is almost certain that the two beads will drift apart due to the energy sampling from the Metropolis scheme favoring lower states in energy. Once the particles have drifted a certain distance, they are liable to cross the cutoff boundary, at which the pair wise interaction is discarded and only the harmonic interaction between sequential beads remains. It is noted that both the average energy and the expectation value are increased, with the energy rising by an order of magnitude and $\langle r^2 \rangle$ gaining a factor of approximately 3/2. This makes qualitative sense, as the Lennard-Jones interaction is primarily repulsive, leading to higher energies and higher inter-bead distances on average. Please see the corresponding tables and graphs for the resultant data.
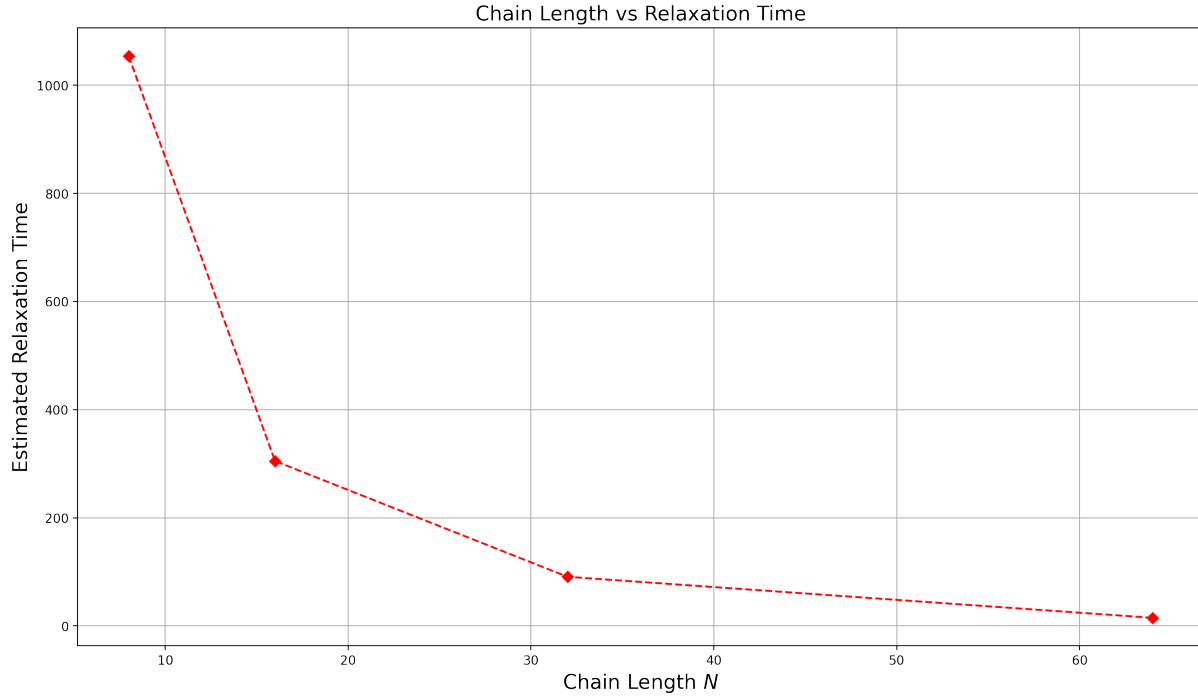
Figure 6: (Q4) Predicted Relaxation times per length of polymer N. Values are scaled by the block length $n_B = 1000$.

5.2 Question 5 Part 3: Optimization via MSD

In this question we return to the optimization to the displacement parameter a via the same equation for MSD as given in section 3.

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \left[\vec{r}_i(t) - \vec{r}_i(0) \right]^2$$

This is evaluated in *real space* to measure the actual distance traveled by the polymer chain away from its starting point. The same set of a values was tested as was in the first version of this problem. The computational demand of the Lennard-Jones calculations was more intensive that that of their plain harmonic counterparts, and as such the number of iterations was decreased to complete the averaged runs in a timely manner. The final averages display that an a value of approximately 1.0 will give the highest displacement across the trial period, with $a = 0.75$ achieving a similar performance. Again, these values may be liable to the scaling discrepancies discussed in the harmonic potential MSD section above. Though, these results may make qualitative sense for the system that they correspond to, as they are each less than the overall magnitude of the cutoff distance for the Lennard-Jones Potential $(2^{1/6} \approx 1.12)$, meaning that they would not have to cross the energy hurdle that is associated with transitioning from the $V = V_H + V_{LJ}$ to the $V = V_H$ region of space.

5.3 End to End Distance with Lennard-Jones

The investigation into end-to-end distance is repeated with the use of the Lennard-Jones model. Again, this is a quantity that must be found in *real*, not *virtual* space. It should be expected that the chain length squared should on average be more than than the number of the beads in the chain, as the value predicted for $\langle r^2 \rangle$ in question 5.2 is approximately 1.5. This is consistent with what is seen in the results.
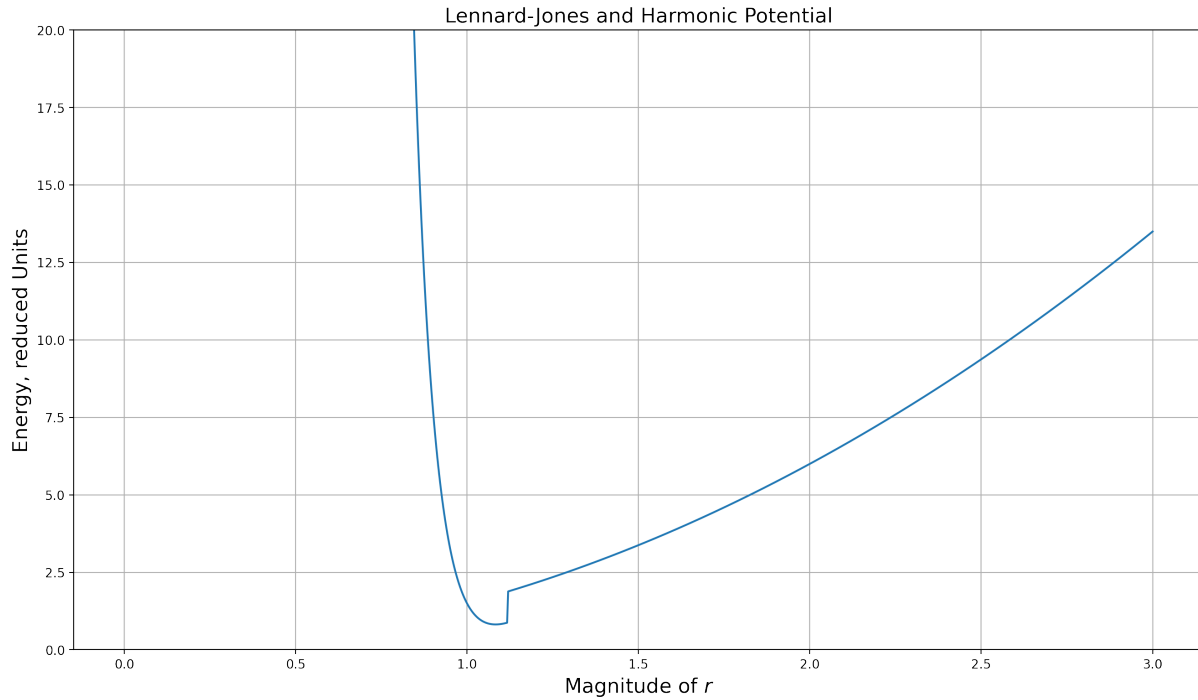
Figure 7: (Q5) A graphic representation of the potential curve $V = V_{\mathrm{H}} + V_{\mathrm{LJ}}$

5.3.1   Block Analysis

Similar to the previous attempt with Block Analysis with

$$\tau_{\mathrm{est}} = \frac{n_B}{2} \frac{\left\langle \delta \mathcal{O}^{B^2} \right\rangle}{\left\langle \delta \mathcal{O}^2 \right\rangle} \ ,$$

a non-conclusive result was obtained for the estimation of relaxation time with chains that were introduced to to Lennard-Jones potential. A negatively-correlated relation was obtained with an increase in the chain length N. This issue could be due to an incorrect implementation of the formula, or other problems with the data. Please see the corresponding graph below.

References

[1] Frenkel, D.; Smit, B. In *Understanding Molecular Simulation (Second Edition)*, second edition ed.; Frenkel, D., Smit, B., Eds.; Academic Press: San Diego, 2002; pp 23–61.

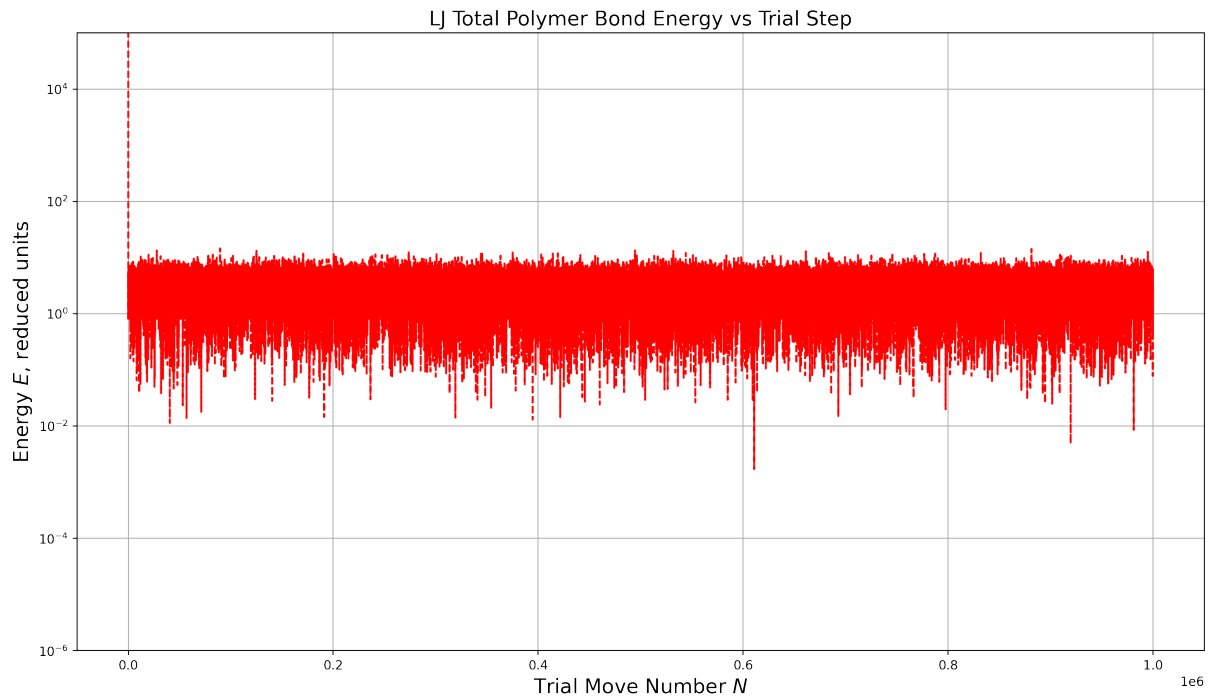[2] Osmanović, D.; Rabin, Y. *Soft Matter* **2017**, *13*, 963–968.

LJ Total Polymer Bond Energy vs Trial Step

Figure 8: (Q5.2) Energy by step with N=2 chain (LJ potential) . 10^6 iterations.

LJ Rsq vs Trial Step
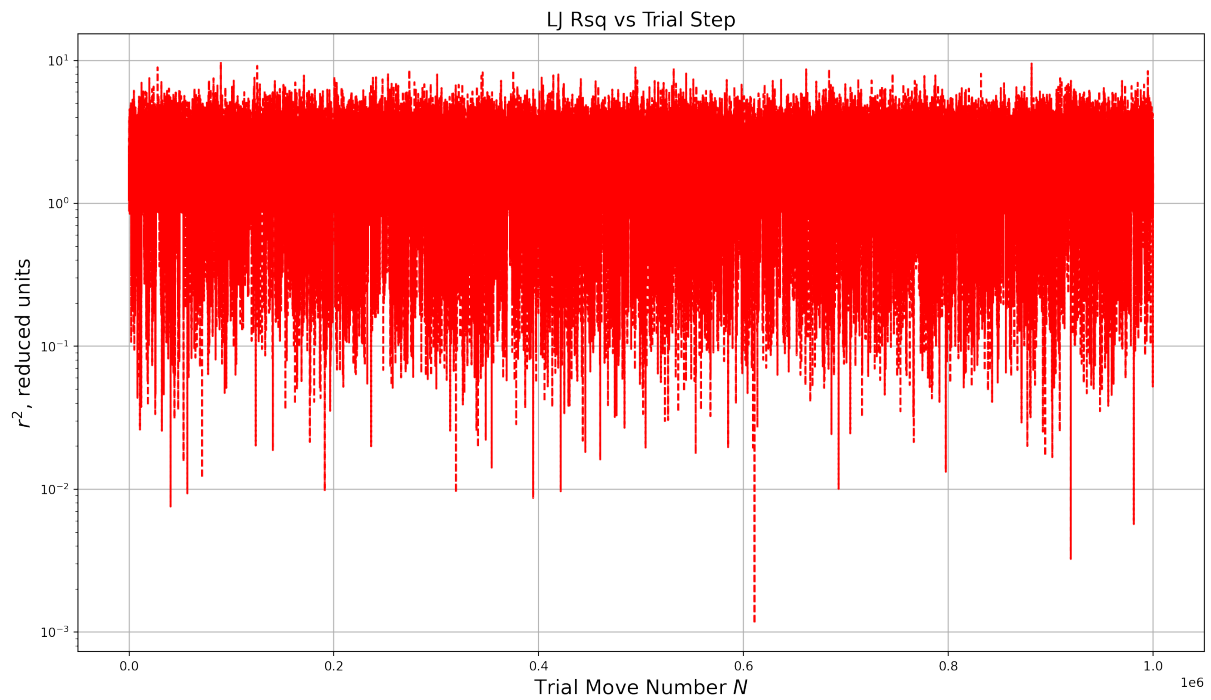
Figure 9: (Q5.2) r^2 in *real space* by step with N=2 chain (LJ potential) . 10^6 iterations.
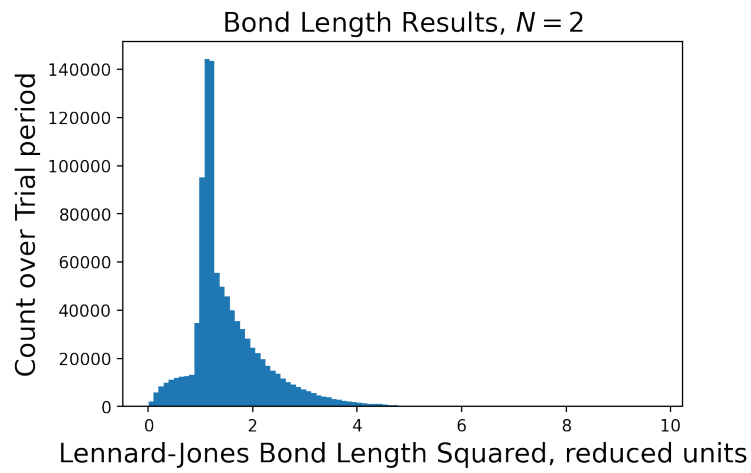
Bond Length Results, $N = 2$

Figure 10: (Q5.2) Histogram of r^2 in *real space* by step with N=2 chain (LJ potential) . 10^6 iterations.
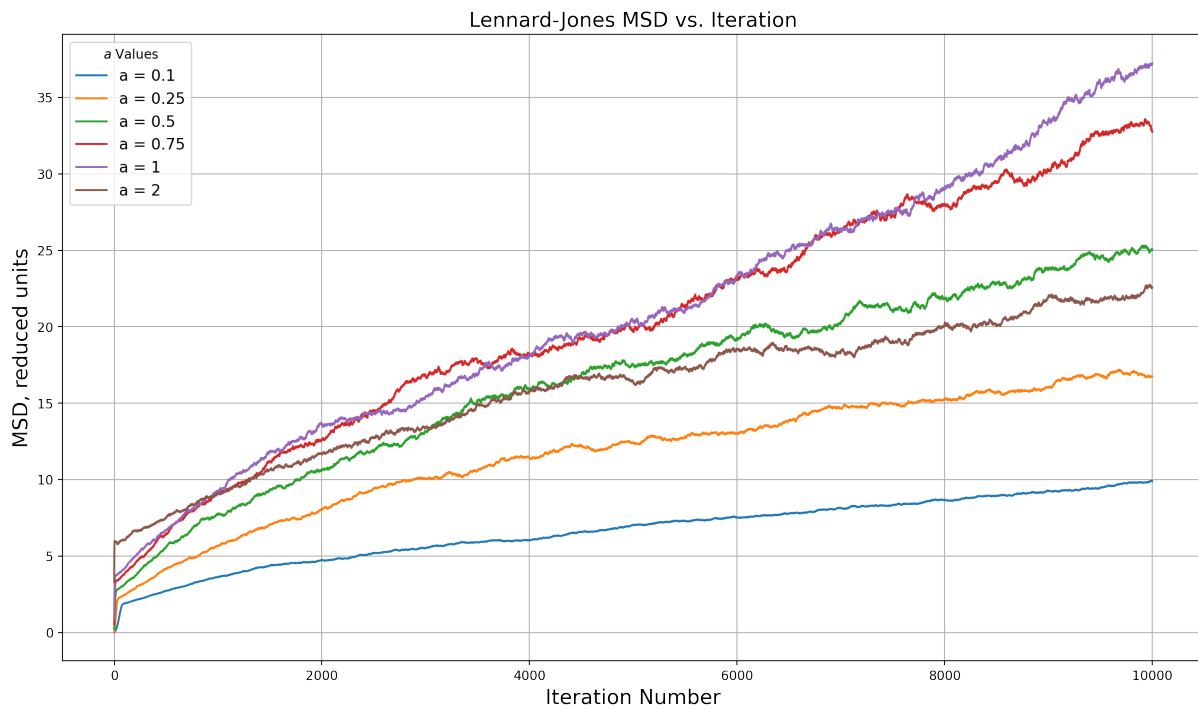
Figure 11: (Q5.3) Averaged MSD over several values of *a* over 1.0e5 trials
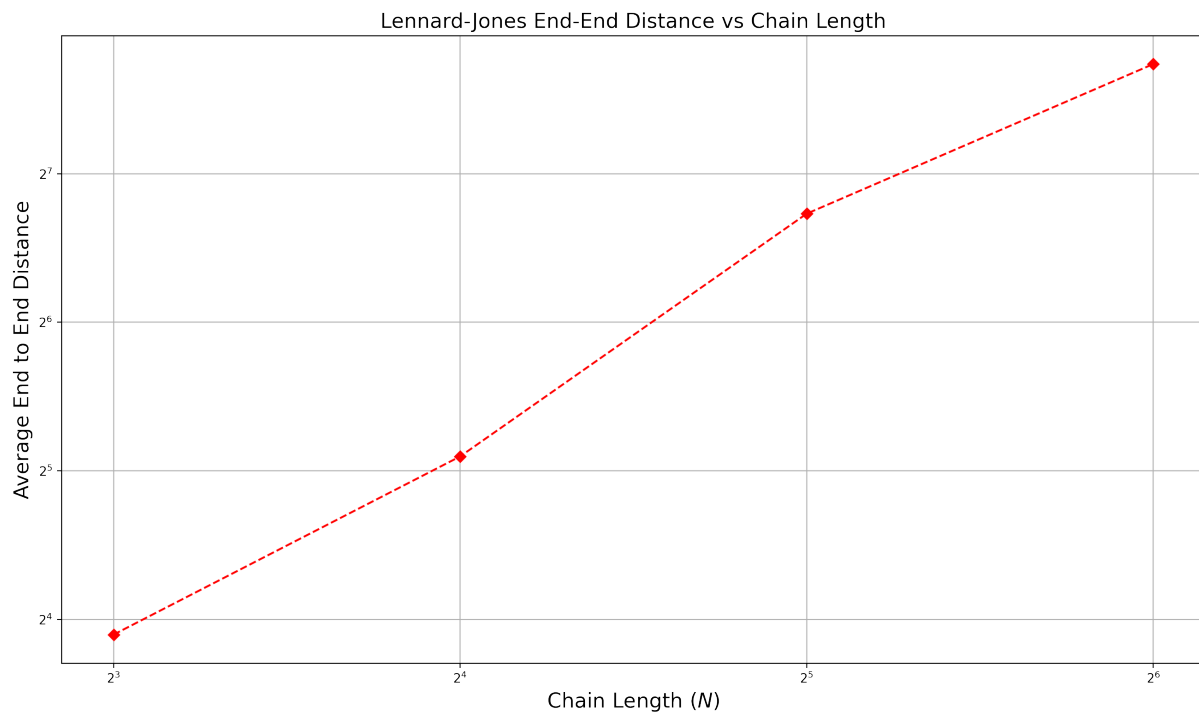
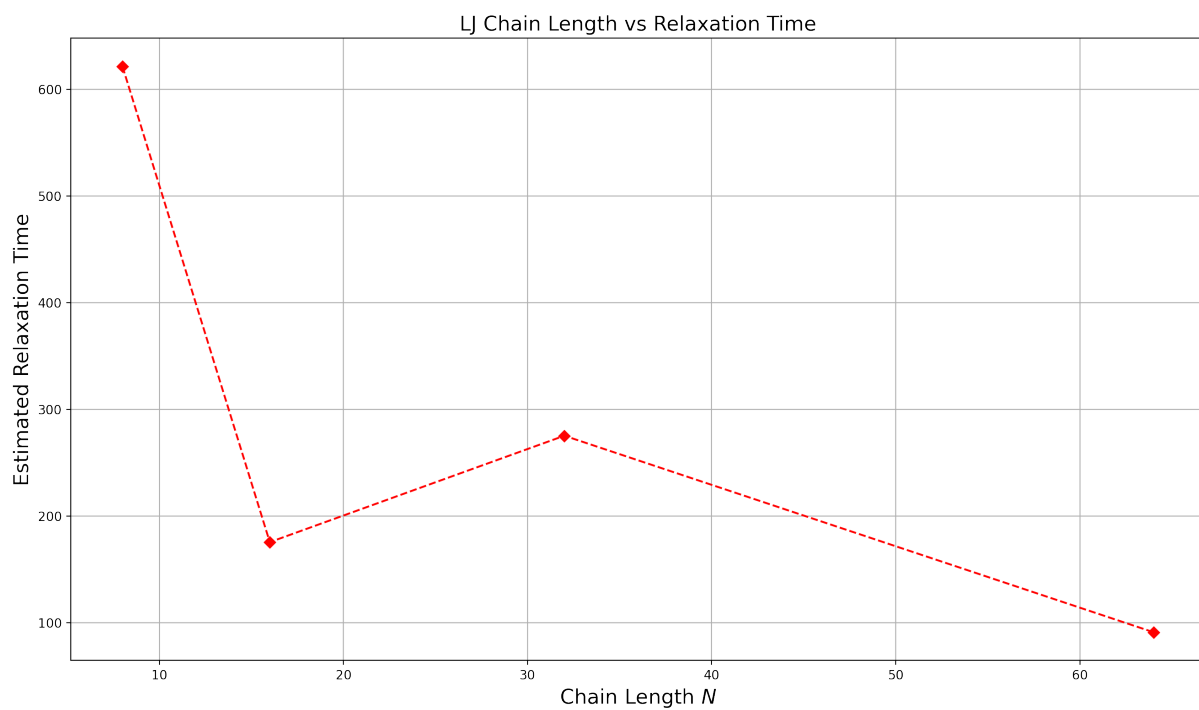Figure 12: (Q5.4) Chain length as a function of N with the LJ potential addition.

Figure 13: (Q5.4) Estimated relaxation time τ with respect to chain length. Values are scaled by $n_B = 1000$.