

Exercise_2 Molecular Dynamics Simulation

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1 Introduction

In the context of molecular dynamics simulation, the force field is defined as the complete set of parameters that approximate the real system. Consequently, it may be considered to be potential energy. It is evident that the precision and thoroughness of the forcefield directly correlates with the efficacy of the simulation outcomes. In this exercise, the forcefield for a polymer chain composed of 20 carbon atoms is to be gradually improved by the addition of terms to the potential.

$$U_{tot} = U_{inter} + U_{intra}$$

where U_{inter} consists of the LJ potential and is the intermolecular term, while $U_{intra} = \sum_{bonds} U_b + \sum_{angles} U_\theta + \sum_{dihedrals} U_\phi$ is the intramolecular term.

The objective of this study is to compute a range of quantitative variables from the simulation. These will then be analysed and compared in order to facilitate an informed comparison of the different landscapes used. The objective of this study is to understand how each term impacts the quality of the simulation. To be more precise, the following calculation will be made:

- The mean end-to-end distance $R_e = \sqrt{\langle (b_1 - b_N)^2 \rangle}$
- The gyration radius $R_g = \sqrt{\frac{1}{N} \sum_{i=0}^N \langle (\vec{r}_i - \vec{r}_{CM})^2 \rangle}$
- The distribution and the values of the angles
- The distribution and the values of the dihedrals

2 Methods

The four distinct simulations are executed utilising the GROMACS software. The initial model is predicated exclusively on the bonds between atoms; in contrast, the subsequent models encompass the angles between bonds, dihedrals, and the L-J potential. The addition of terms to the forcefield has been achieved by modifying the top file and incorporating the desired interaction. For each simulation, an analysis was conducted of the mean end-to-end distance and of the distributions of angles and dihedrals by means of the following command:

- **polystat**: to obtain R_e and R_{gyr}
- **mk_angndx**: to obtain the .ndx file of the angles and dihedrals
- **angle**: to obtain the distribution of the angles and dihedrals

Furthermore, a comparison was made between the R_e values obtained and the analytical value. The following lines contain the passages required to derive the analytical formula for R_e from the definitions of the freely jointed chain and the freely rotating chain.

2.1 derivation of R_e in freely jointed chain

Consider a polymer with N segments (bonds), each of fixed length l , and random orientation. The bond vectors are \vec{b}_i , with $|\vec{b}_i| = l$. The end-to-end vector is:

$$\vec{R}_e = \sum_{i=1}^N \vec{b}_i$$

The mean square end-to-end distance is:

$$\langle R_e^2 \rangle = \left\langle \left(\sum_{i=1}^N \vec{b}_i \right)^2 \right\rangle = \left\langle \sum_{i=1}^N \sum_{j=1}^N \vec{b}_i \cdot \vec{b}_j \right\rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \vec{b}_i \cdot \vec{b}_j \rangle$$

For a freely jointed chain, bond vectors are uncorrelated:

$$\langle \vec{b}_i \cdot \vec{b}_j \rangle = \begin{cases} l^2 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

Thus:

$$\langle R_e^2 \rangle = \sum_{i=1}^N l^2 = Nl^2$$

So the root-mean-square end-to-end distance is:

$$\boxed{\langle R_e^2 \rangle = Nl^2 \quad \Rightarrow \quad \langle R_e \rangle = \sqrt{N}l}$$

2.2 derivation of R_e in freely rotating chain

Consider a polymer with N bonds of fixed length l and fixed bond angle θ between successive bonds. The angle between bond vectors \vec{b}_i and \vec{b}_{i+1} is fixed to θ , but torsional angles are random.

The end-to-end vector is:

$$\vec{R}_e = \sum_{i=1}^N \vec{b}_i$$

Then:

$$\langle R_e^2 \rangle = \left\langle \left(\sum_{i=1}^N \vec{b}_i \right)^2 \right\rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \vec{b}_i \cdot \vec{b}_j \rangle$$

Because the bond vectors form a Markov chain with fixed correlation:

$$\langle \vec{b}_i \cdot \vec{b}_j \rangle = l^2 \cos^{|i-j|} \theta$$

Thus:

$$\langle R_e^2 \rangle = l^2 \sum_{i=1}^N \sum_{j=1}^N \cos^{|i-j|} \theta = l^2 \left[N + 2 \sum_{k=1}^{N-1} (N-k) \cos^k \theta \right]$$

This is the exact expression. In the limit of large N , the sum becomes a geometric series and simplifies to:

$$\langle R_e^2 \rangle \approx Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta}$$

So the end-to-end distance is:

$$\boxed{\langle R_e \rangle = \sqrt{Nl^2 \frac{1 + \cos \theta}{1 - \cos \theta}}}$$

3 Results

In order to facilitate the comparison of the various simulations that had been conducted, a preliminary analysis was performed, during which R_e was compared with the analytical values for the freely jointed chain and the freely rotating chain.

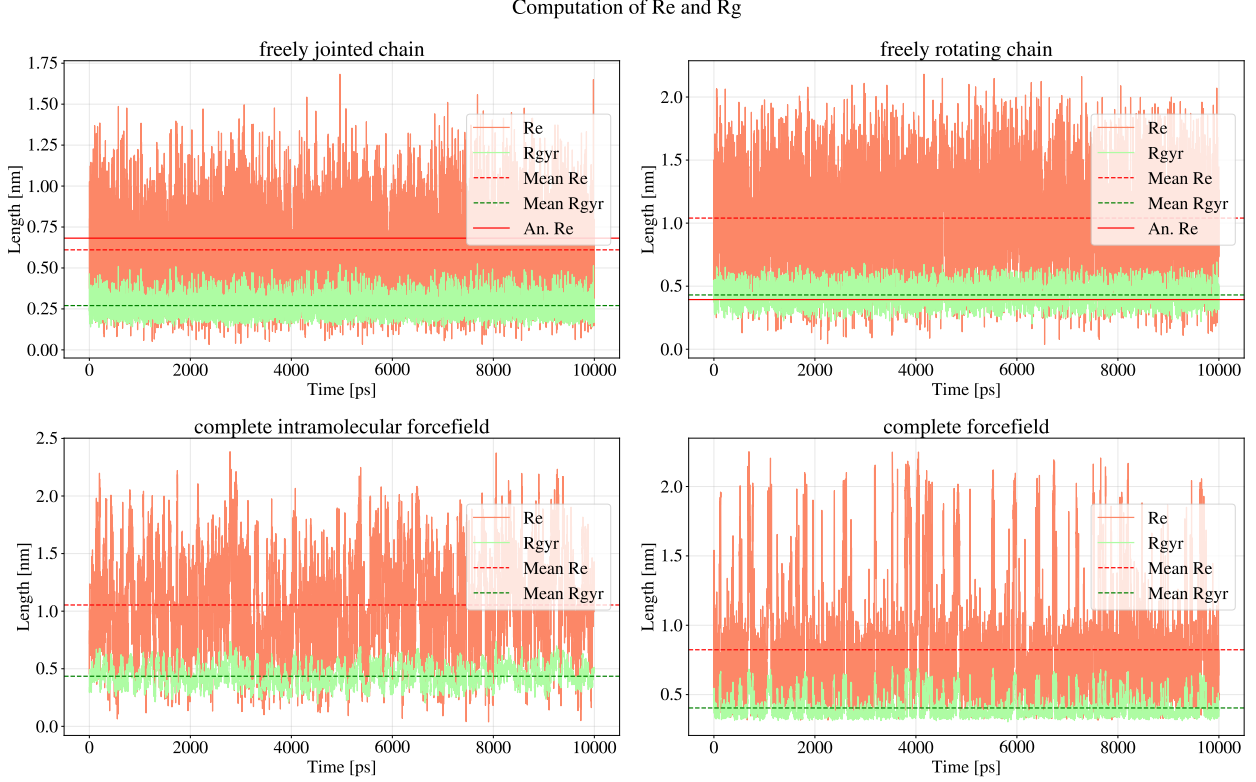


Figure 1: R_e and R_{gyr} values for the four different forcefield, compared with the analytical values.

As demonstrated, the values of the freely jointed chain correspond with the analytical values, while the freely rotating chain underestimates the R_e .

This may be attributable to the fact that the geometric series approximation is not applicable in this instance.

It is evident from the Figure 2 that the entirety of the freely rotating chain, the complete intramolecular force field, and the complete force field exhibit analogous time series and angular distribution. This congruence can be attributed to the presence of a term that corrects for angles in all three cases.

Conversely, the freely jointed chain exhibits greater uniformity and encompasses all values between 0 and 180, as it does not regulate the angular parameter.

As demonstrated in Figure 3, the mean value for all four dihedral time series is zero. However, while the freely jointed chain and the freely rotating chain exhibit a uniform distribution along dihedral angles, the distribution for the complete intramolecular force field and the complete force field differ significantly (see Figure 2). The distribution under consideration exhibits three local maxima at $-180, 0$, and 180 degrees.

4 Conclusion

The following table summarises the results of the study.

As we can notice the addition of the dihedral term is the less relevant respect the others that change more the different results.

In polymer modeling, the total potential energy U of the system is typically decomposed into contributions from bond stretching, angle bending, and dihedral torsions:

Angles analysis

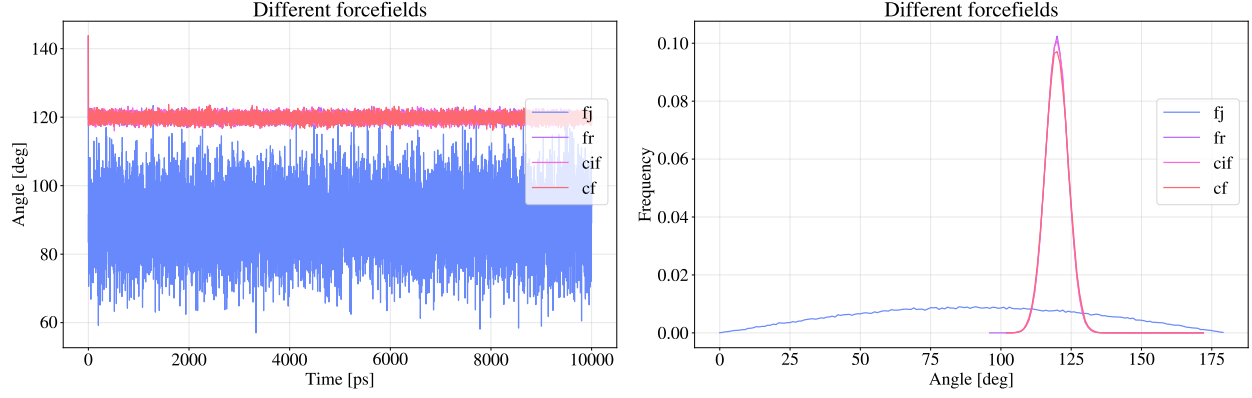


Figure 2: On the left the values values of the angles over the time. On the right their distribution.

Dihedral Analysis

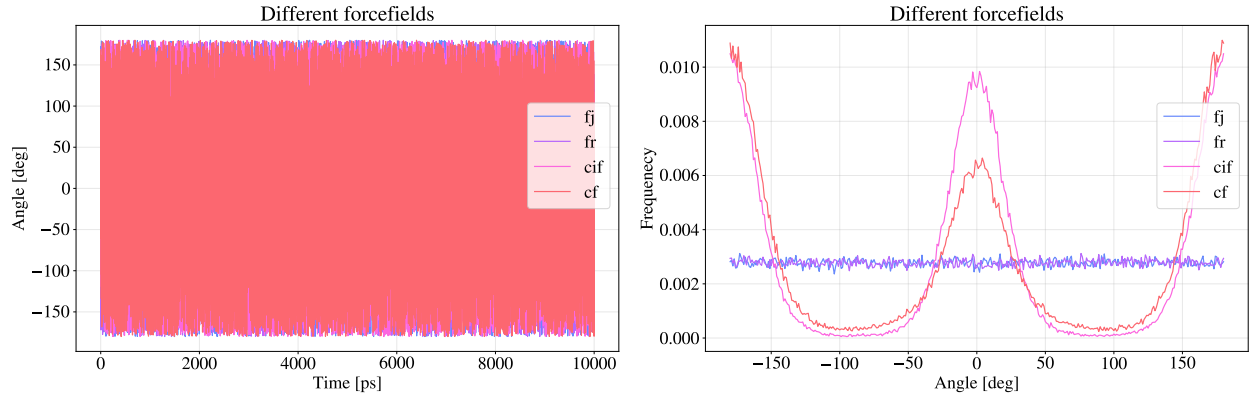


Figure 3: From the left plot apparently the dihedral time series appears coherent, because the mean value is equivalent to zero for both the force field with and without the dihedral term. However, upon closer examination of the distribution (right plot), it becomes evident that the distributions exhibit significant disparities.

Model	θ	ϕ	R_e	R_g
FJC	90	0	0.61	0.27
FRC	120	0	1.04	0.43
CIF	120	0	1.05	0.43
CF	120	0	0.82	0.40

Table 1: Summary of parameters and characteristic lengths for different forcefields.

$$U = \sum_{\text{bonds}} U_{\text{bond}} + \sum_{\text{angles}} U_{\text{angle}} + \sum_{\text{dihedrals}} U_{\text{dihedral}} + U_{\text{non-bonded}}.$$

The **bond length** interactions (e.g., harmonic potentials) are responsible for keeping covalent bonds at their equilibrium distances, and thus involve high energy penalties for deviations. These are typically the stiffest terms.

The **bond angle** interactions maintain the geometry of chemical groups and constrain the local direction of the chain. These are also energetically significant, especially in semiflexible polymers.

In contrast, the **dihedral** interactions control the relative orientation of planes formed by four consecutive atoms. While they influence the *conformation* and folding of chains, their energetic contribution is often smaller than that of bond and angle terms.

Therefore, in many idealized polymer models like the *freely jointed* or *freely rotating chain* the dihedral interactions can be neglected or treated as less significant compared to bond stretching and angle bending.

As is evident, the freely jointed chain exhibits excessive self-folding, resulting in aberrant behaviour of corners and dihedrals. Furthermore, the absence of repulsive interactions is notable. In the case of the freely rotating chain, the angles are fixed, thus resulting in a more natural behaviour. However, the addition of the term on the dihedrals leads to a slight enhancement in geometrical realism for the polymer. Nevertheless, the chain tends to collapse excessively on itself, as illustrated in Figure 5. It is evident that, under normal circumstances, the polymer does not tend to bring the atoms too close together in order to minimise the potential due to the repulsive terms of the Lennard-Jones potential. However, this tendency is counteracted by the full force field.

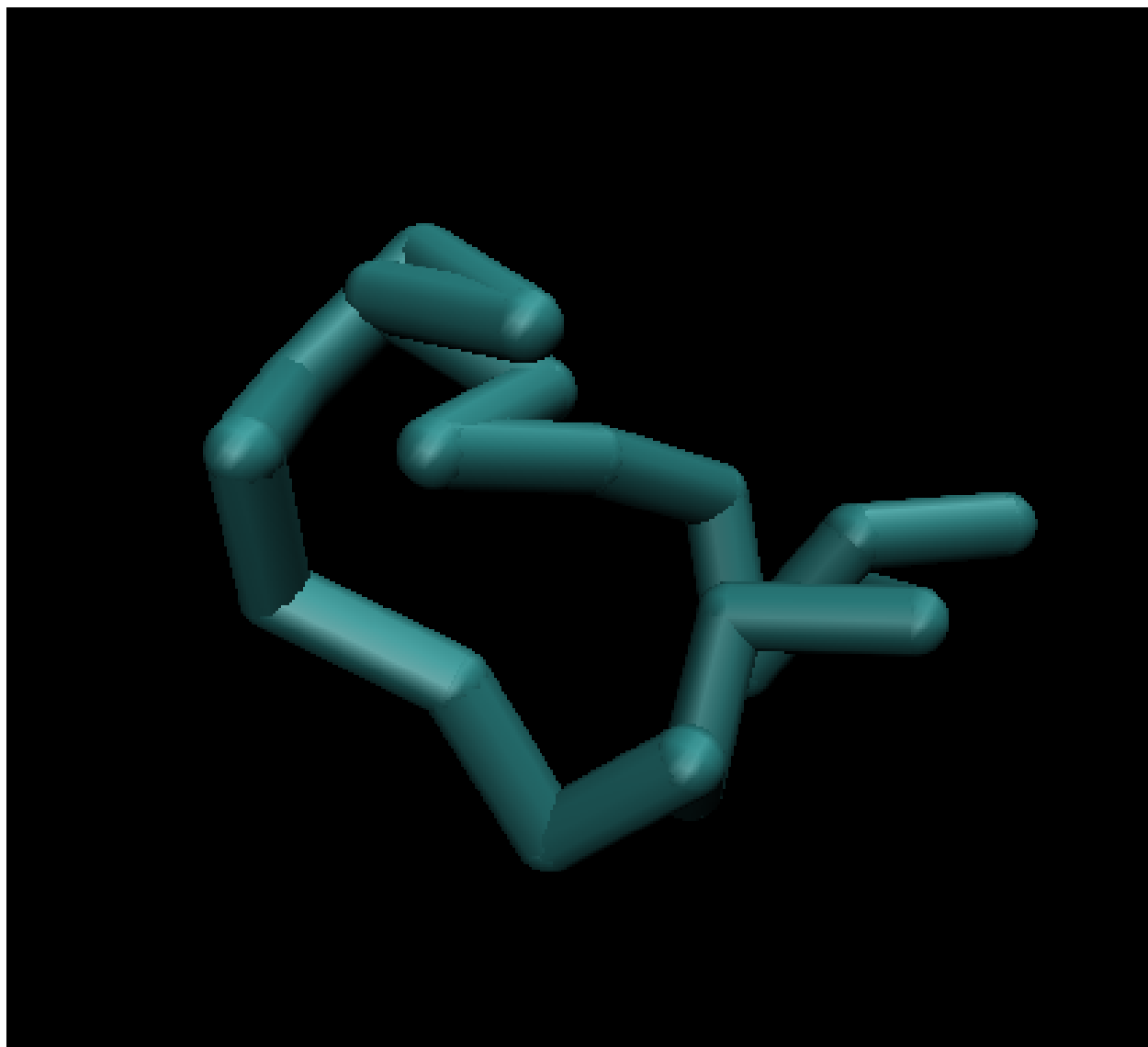


Figure 4: Image of the freely jointed chain.

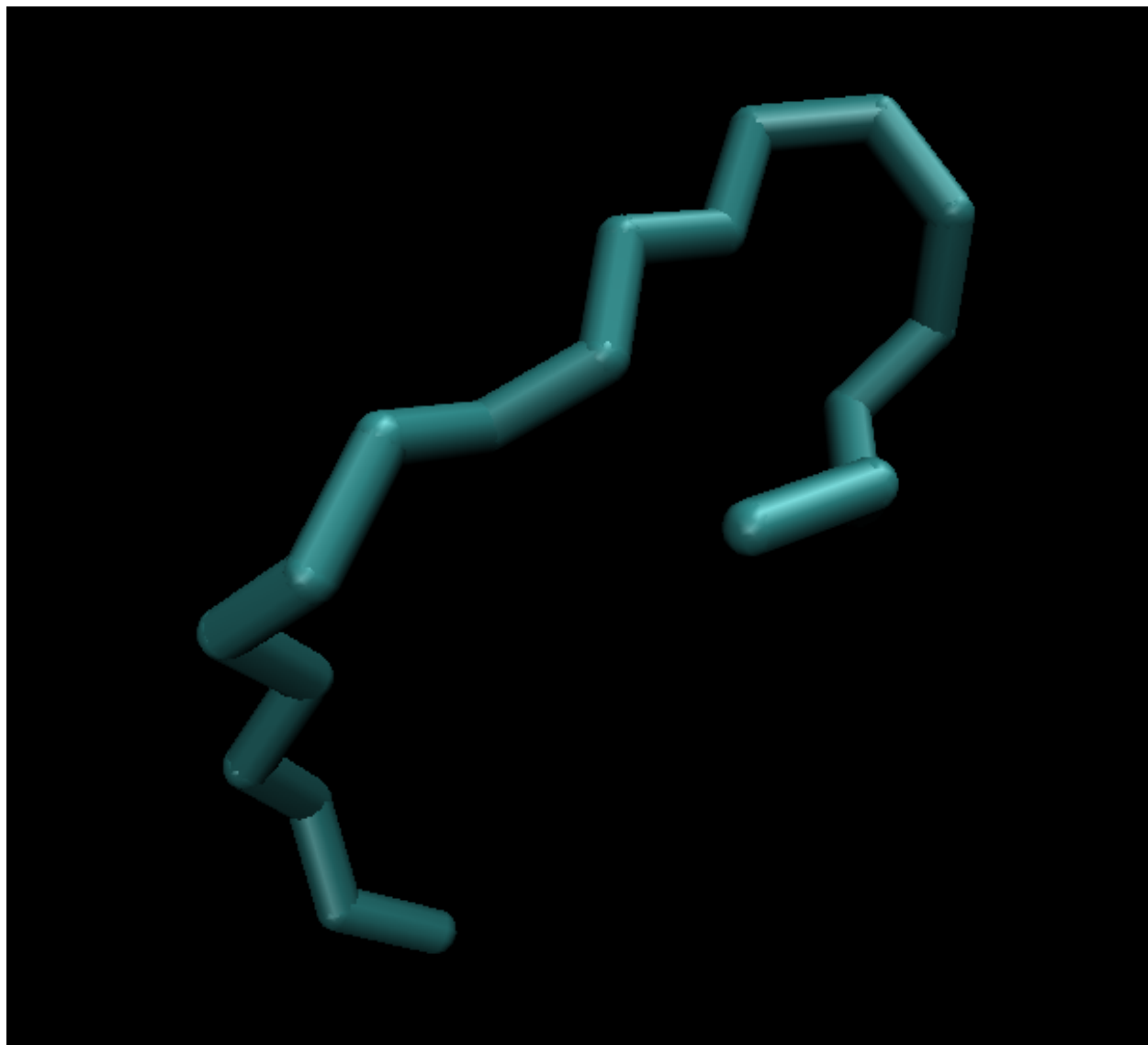


Figure 5: Image of the freely rotating chain.

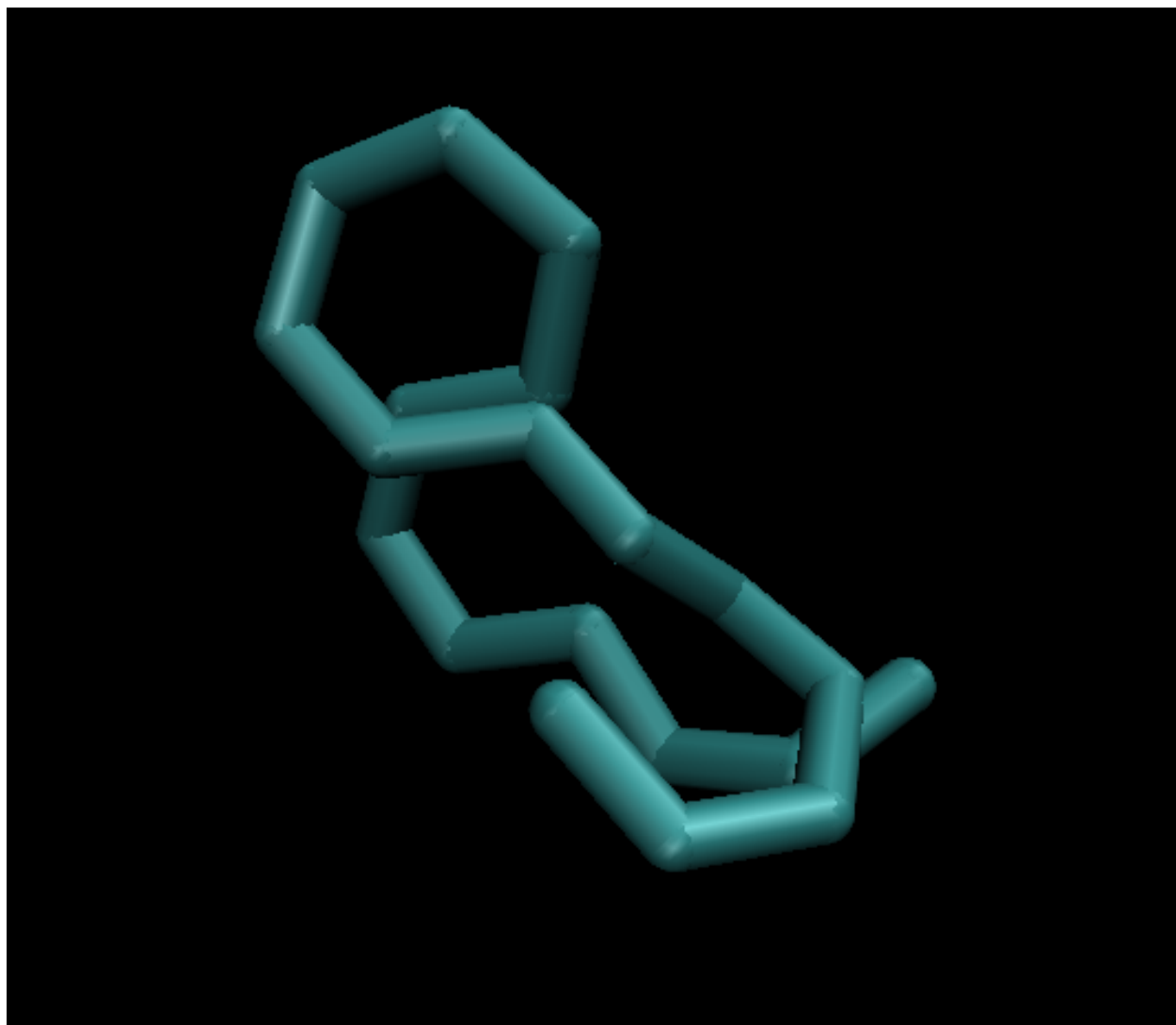


Figure 6: Image of the chain with complete intermolecular forcefield

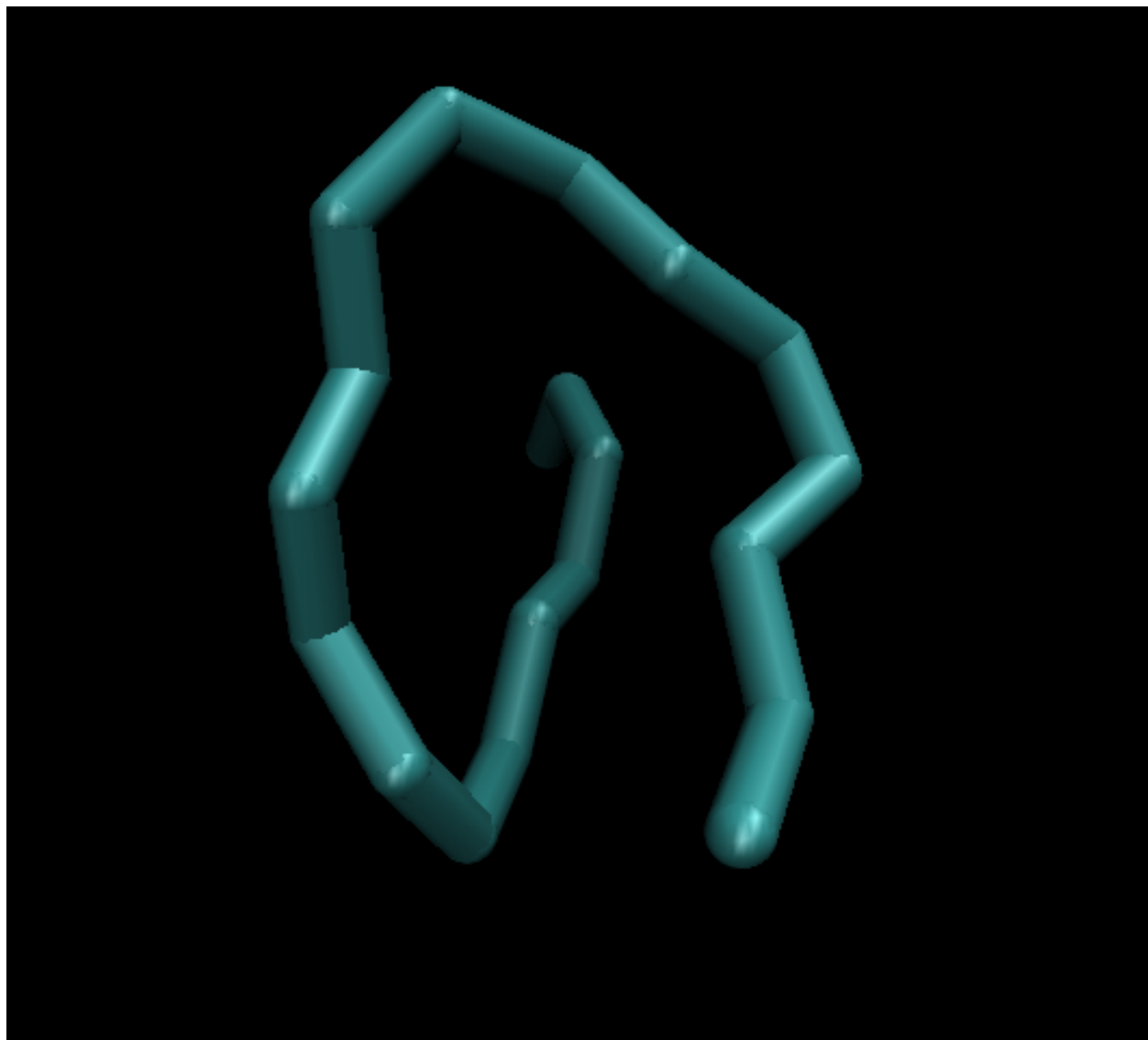


Figure 7: Image of the chain with complete forcefield