

Molecular Dynamics Exercise II: Polymer Simulation with Different Force Field Terms

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1 Abstract

The aim of this exercise was the MD simulation of a polymer consisting of a chain of 20 bound carbon atoms with varying parts of the force field considered in the simulation. For each configuration the mean end-to-end distance, the radius of gyration as well the mean bond angles and mean torsion angles were recorded. For the MD simulation the software GROMACS was used.

2 Introduction and Procedure

The force field of molecule can be split into intermolecular U_{inter} and intramolecular U_{intra} contributions. The intermolecular force field contribution is given by a Lennart-Jones Potential at every atom:

$$U_{inter} = \sum_m^{Atoms} \sum_{n \neq m}^{Atoms} U_{\sigma, \epsilon}^{Lennart-Jones}(r_{nm}) \quad (1)$$

The intramolecular force field is given by three contributions: the bond potential U_b , the angular potential U_θ and the torsion potential U_ϕ .

$$U_{intra} = \sum_i^{bonds} U_b(b_i) + \sum_j^{angles} U_\theta(\theta_j) + \sum_k^{dihedrals} U_\phi(\phi_k) \quad (2)$$

Here b_i , θ_j and ϕ_k are the respective bond lengths, angles between two bonds and torsion angles of the molecule. Firstly, a simulation of a freely joined chain was conducted. This means that only U_b with $b_0 = 0.1525$ nm was active. Secondly, U_θ with $\theta_0 = 120^\circ$ was added, making the polymer a freely rotating chain. For the third simulation the full intramolecular force field was activated (U_ϕ with $\phi_0 = 180^\circ$). Lastly, the full force field was used by adding the Lennart-Jones Potential with parameters: $\sigma = 0.3401$ nm and $\epsilon = 0.9786$ kJ/mol. All simulations were done for $T = 10000$ ps and a time step of $dt = 0.001$ ps.

3 Simulation Results

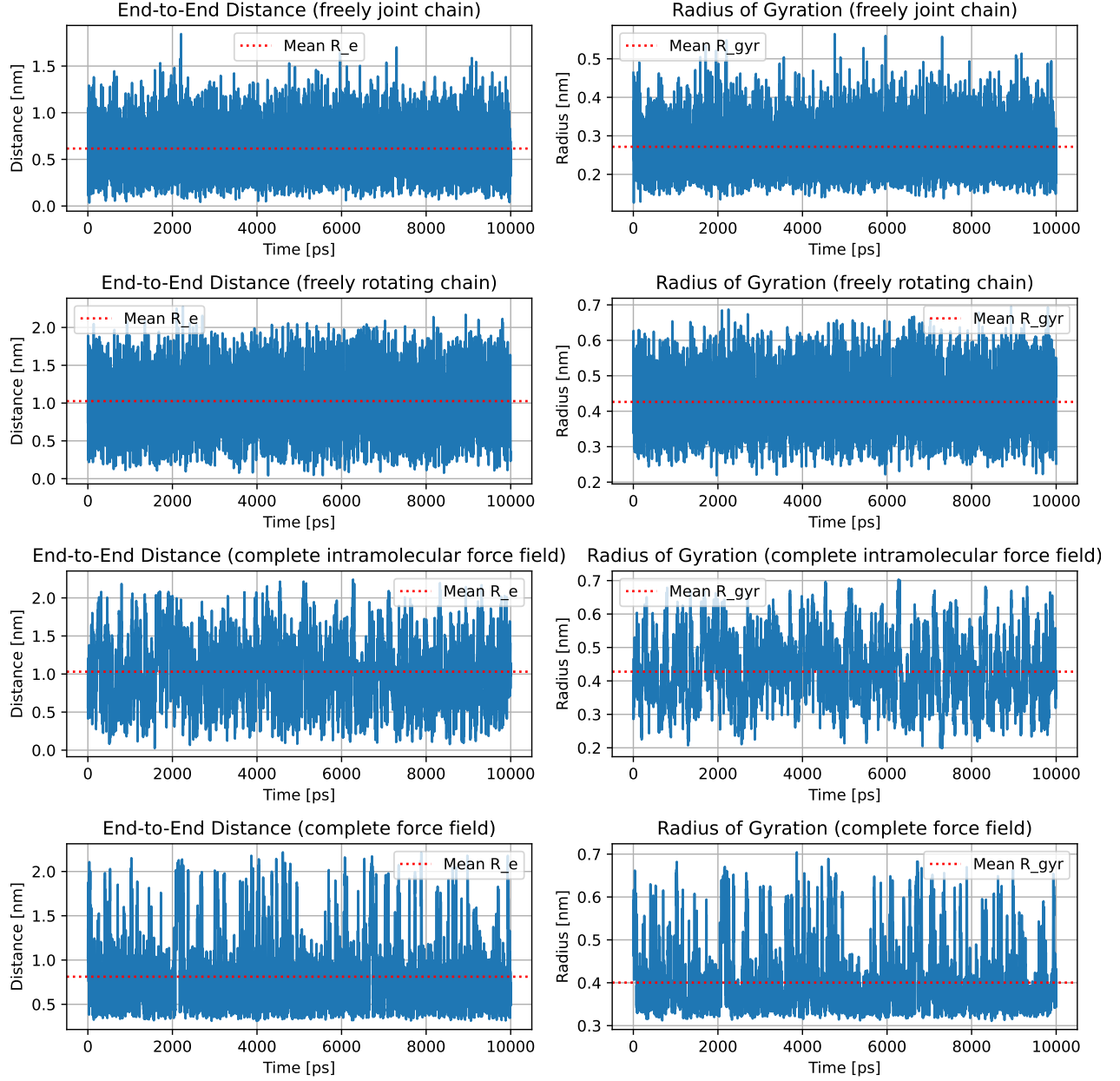


Figure 1: Mean end-to-end distance R_e and radius of gyration as a function of the simulation time.

To get an idea of the extension of the molecule with N atoms, the mean end-to-end distance R_e is defined.

$$R_e = \sqrt{\langle (\vec{b}_1 - \vec{b}_N)^2 \rangle} \quad (3)$$

Here \vec{b}_i are the positions of the N atoms. Similarly, the radius of gyration R_{gyr} is used to describe the amount of torsion of a molecule. In figure 1, both of these quantities are shown as a function of the simulation time. As one can see the addition of further contributions of the intramolecular force field cause the molecule to favour a more extended structure. This can be seen by the increase in R_e . The addition of the intermolecular forces reverses this effect slightly. For the radius of gyration a similar pattern can be observed.

Furthermore, the bond angles were affected by the variations of the force field. Below, the chain average of θ is displayed as a function of the simulation time (figure 2). For a better overview, the average chain angles are also presented as a histogram (figure 3). From the figures one sees that the introduction of the angular potential has the effect of forcing the bond angles to remain close to 120 degrees. The further additions of other force field contributions only cause minor alterations of the distribution.

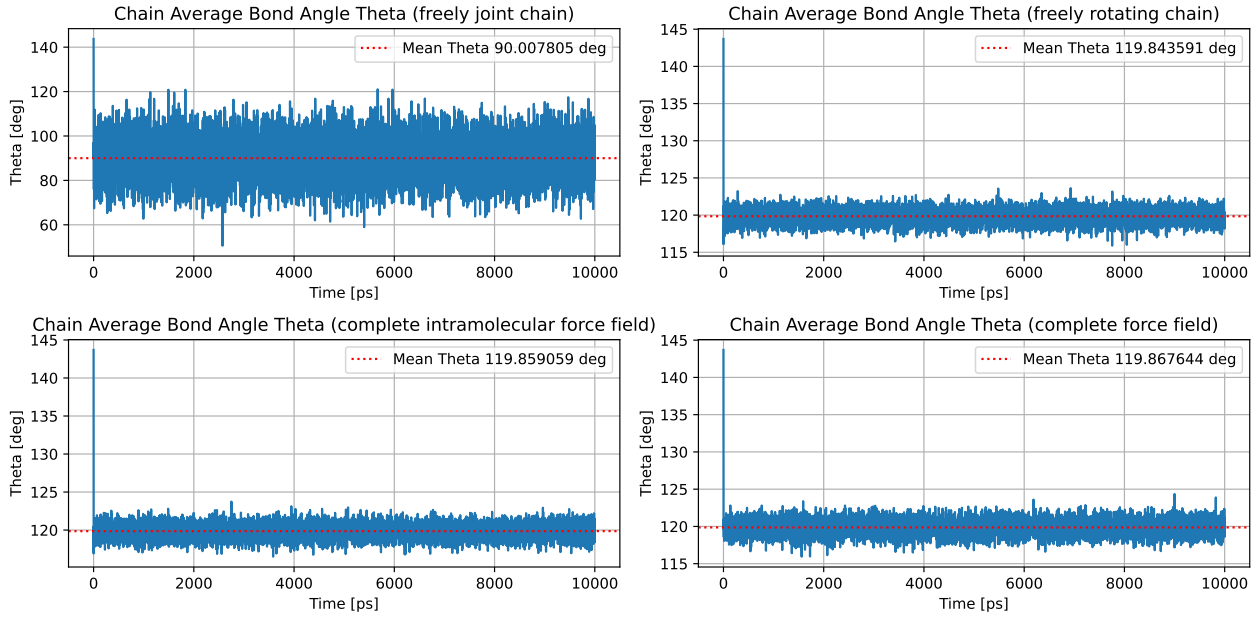


Figure 2: Chain Average of the bond angle θ for the different variation of the force field.

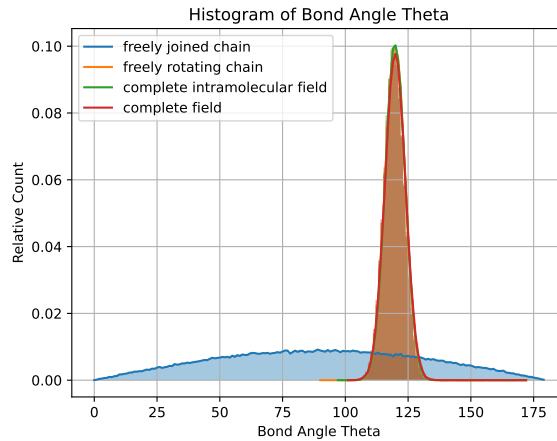


Figure 3: Histogram of the chain average of the bond angle θ

Similarly, the effect of the force field variations of the torsion angles ϕ was investigated. In figure 4, the average chain torsion angles ϕ are shown as a function of the simulation time. Again also a histogram is provided (see figure 5). While the development of the dihedral angle over time for all force field looks more or less the same, further details can be spotted in the histogram. Here one finds that without the dihedral potential the angles are uniformly distributed. Upon activating this potential, angles around 180 degrees and 0 degrees are favoured. While without intermolecular forces, the state with 180 degrees seems to be favoured over the 0 degree state, this seems to even out once the Lennart-Jones potential is activated.

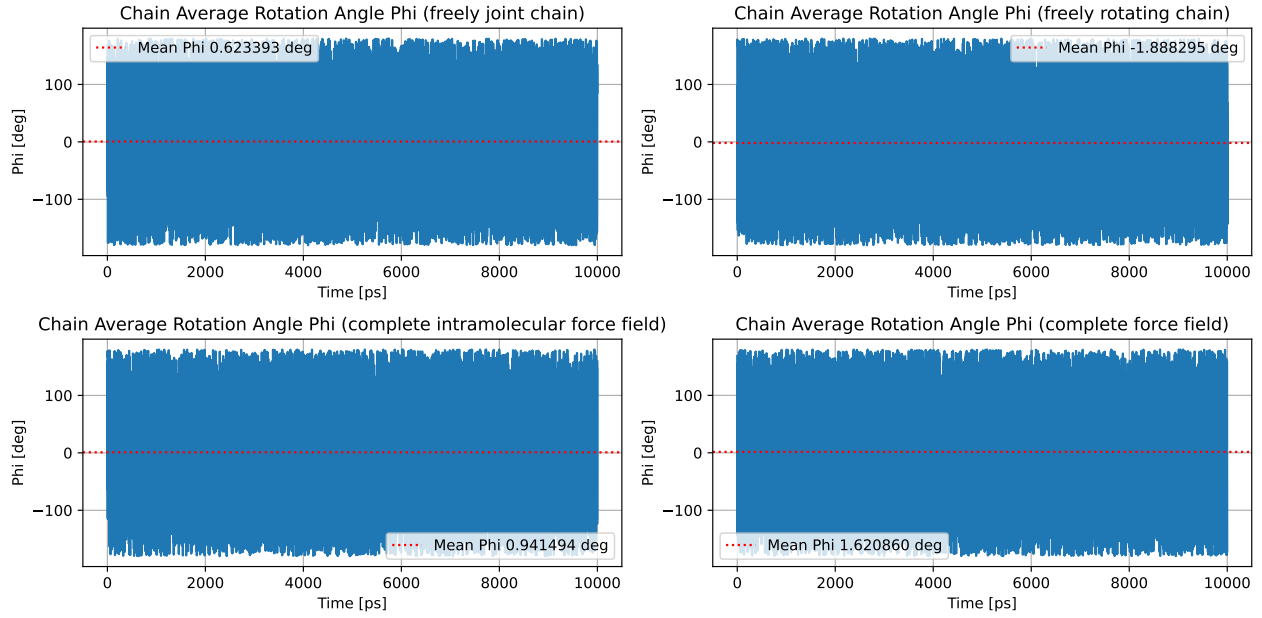


Figure 4: Average chain torsion angle ϕ as a function of the simulation time for different variations of the force field.

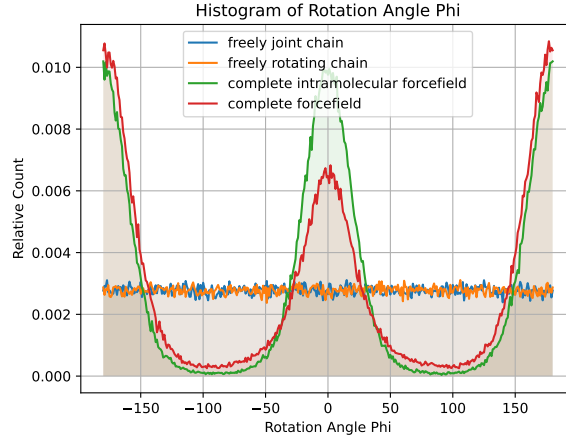


Figure 5: Histogram of the chain average of the bond angle ϕ

For a complete overview of the results of this report the respective values have been added to the table below. The analytic values for R_e of the freely jointed and freely rotating chain have been computed using the formulas from [1].

	freely jointed chain	freely rotating chain	full intram. force field	full force field
Analytic R_e	0.6820 nm	1.1812 nm	—	—
Result R_e	0.6158 nm	1.0255 nm	1.0306 nm	0.8118 nm
Result R_{gyr}	0.2715 nm	0.4263 nm	0.4277 nm	0.4004 nm
Result $\langle\theta\rangle$	90.0078°	119.8436°	119.8591°	119.8676°
Result $\langle\phi\rangle$	0.6234°	-1.8883°	0.9415°	1.6209°

4 Discussion

As seen above the mean end-to-end distance is clearly increasing after the activation of the angular potential U_θ . This is not surprising as the fact that a bond angle close to 120° has to be maintained means that the molecule cannot form a closed shape so easily. Without the bond potential states such as the one presented in figure 6 are possible. Here one recognizes all sorts of bond angles allowing the molecule to be in a very dense configuration. Furthermore, one can observe the effect of the absence of the Lennart-Jones Potential as some atoms overlap. With

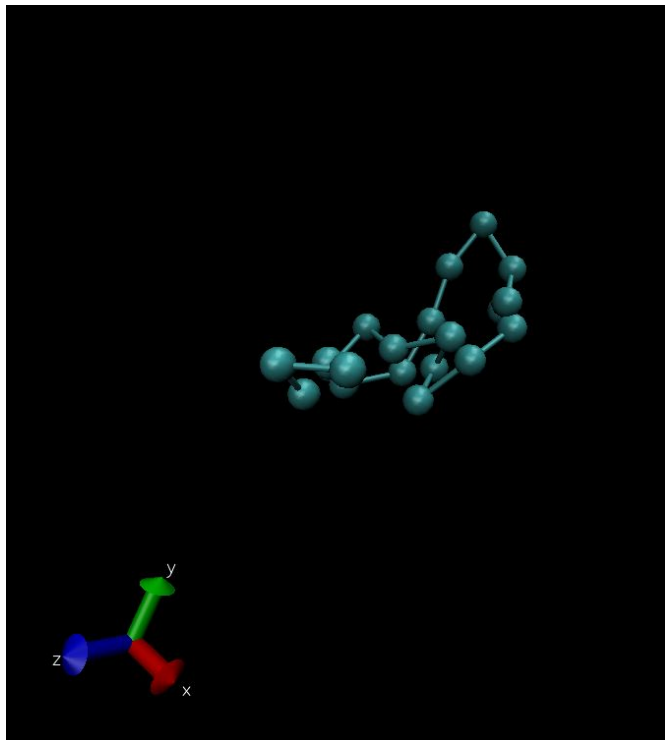


Figure 6: The polymer as a freely joint chain. Notice how the absence of the angular potential allows for varying bond angles.

U_θ activated, more extended states are favoured and the bond angles remain close to $\theta_0 = 120^\circ$. See figure 7. This is also confirmed by the histogram of the bond angles (figure 3). Still both these force field components allow the molecule to have torsion angles from -180° to 180° . From the histogram of the torsion angles we see that there does not seem to be any preference. With the introduction of U_ϕ this changes and torsion angles of -180° , 0° and 180° are favoured. This is most likely due to the structure of the force field U_ϕ . Here all three values give the minimum possible energy. In practice the preference of these angles means that the molecule lies more or less in one plane. For this see figure 8. The addition of the Lennart-Jones potential does not seem to change the behaviour of the molecule much. Possibly a certain attraction of the intermolecular potential supports "u-shaped" rings (see figure 9) better than before leading to a smaller value of R_e .

5 Bibliography

- [1] Jensen, Peter; Polymer models; <https://www.theorie.physik.uni-muenchen.de/lsfrey/teaching/archiv/sose06/softmatter/talks/PeterJensen-Polymers.pdf>
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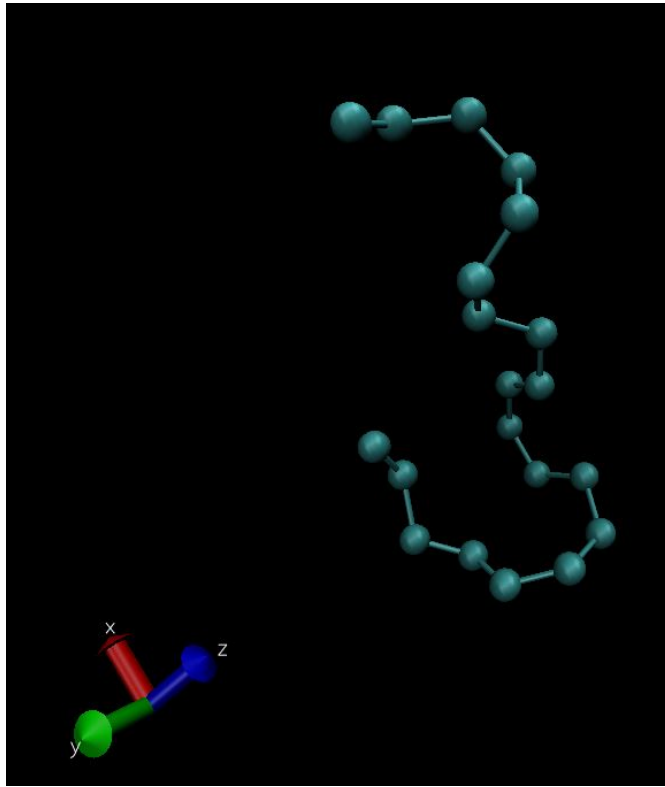


Figure 7: The polymer as a freely rotating chain. More extended states are favoured and all bonds remain close to the given θ_0 .

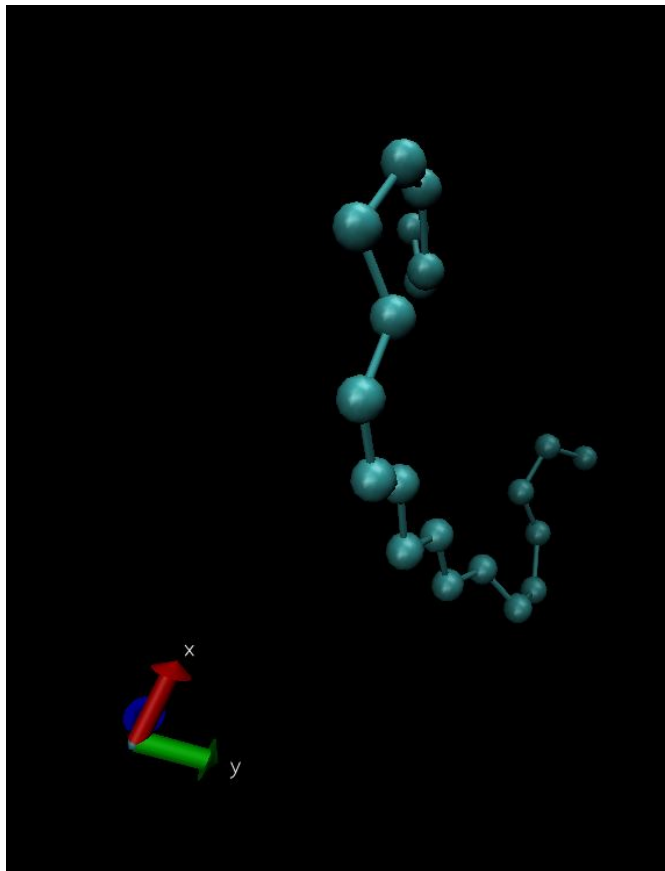


Figure 8: The polymer with fully modelled intramolecular force field. The fact that -180° , 0° and 180° are favoured means that the molecule largely lies in one plane.

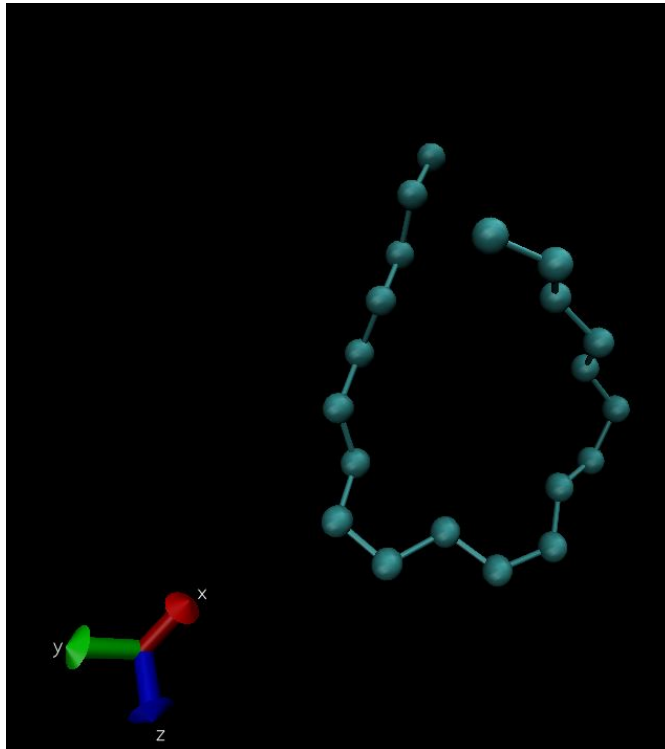


Figure 9: The polymer with fully force field.