

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

Tristan Alexander Mauck

December 23, 2024

1 Abstract

The aim of this exercise was the presentation of the effect of the different terms of the force field used in molecular dynamics simulations. For this a polymer consisting of a chain of 20 bound carbon atoms was simulated with increasing number of terms of the force field considered. For each force field configuration, the mean end-to-end distance, the radius of gyration as well the mean bond angles and mean torsion angles were recorded. The simulations were conducted with the software GROMACS.

2 Introduction and Procedure

For computational efficiency the potential energy of a molecule in MD simulations is often described by force fields. These can be split into intermolecular U_{inter} and intramolecular U_{intra} contributions. For neutral atoms, the non-bonded part of force field is given by a Lennart-Jones potential:

$$U_{inter} = \sum_m^{Atoms} \sum_{n \neq m}^{Atoms} U_{\sigma, \epsilon}^{Lennart-Jones}(r_{nm}) = 4\epsilon \left[\left(\frac{\sigma}{r_{mn}} \right)^{12} - \left(\frac{\sigma}{r_{mn}} \right)^6 \right] \quad (1)$$

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 .

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

$$\text{with } U_b = k_b(b_i - b_0)^2 \quad (3)$$

$$U_{\Theta_j} = k_\Theta(\Theta_j - \Theta_0)^2 \quad (4)$$

$$U_{\phi_k} = k_\phi(1 + \cos(n_\phi \phi_k - \phi_0)) \quad (5)$$

Here b_i , θ_j and ϕ_k are the respective equilibrium bond lengths, angles between two bonds and torsion angles of the molecule. First, the polymer was modelled as a freely joined chain. Hence, the simulation was conducted with only the first sum of the equation above was considered. The equilibrium bond length was assumed to be $b_0 = 0.1525$ nm. In a second simulation, U_θ with $\theta_0 = 120^\circ$ was added to the force field, changing the used model of the polymer to a freely rotating chain. The third simulation was run with the full intramolecular force field active (addition of U_ϕ with $\phi_0 = 180^\circ$). Finally, the full force field was used by considering the Lennart-Jones potential with following parameters: $\sigma = 0.3401$ nm and $\epsilon = 0.9786$ kJ/mol. All simulations were ran for a total time of $T = 10000$ ps with a time step of $\Delta t = 0.001$ ps.

3 Simulation Results

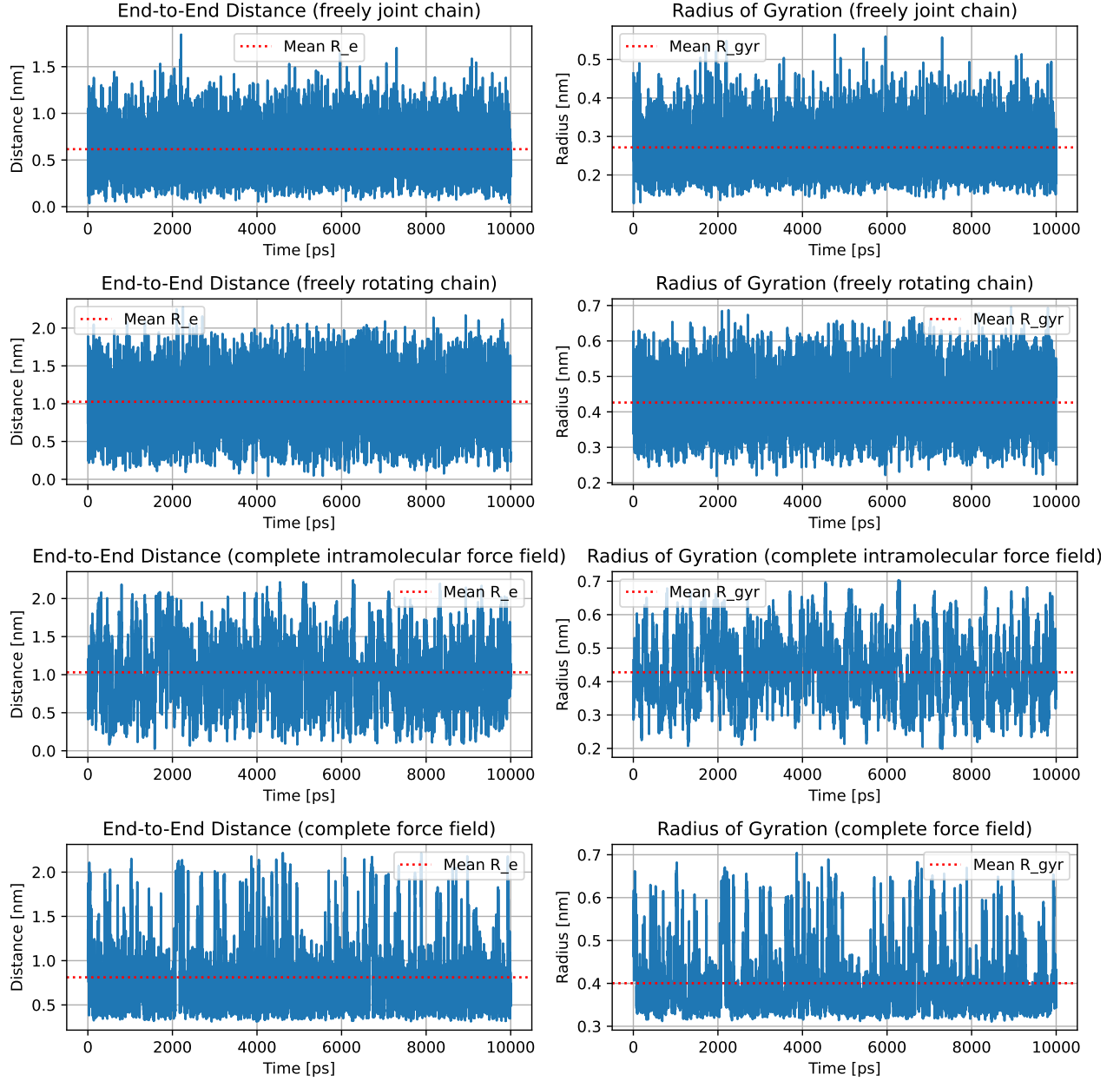


Figure 1: Mean end-to-end distance R_e and radius of gyration as a function of the simulation time. The plots in one row were created from the same model.

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

$$R_e = \sqrt{\langle (\vec{b}_1 - \vec{b}_N)^2 \rangle} \quad (6)$$

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 these quantities are shown as a function of the simulation time for each of the four models considered. 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 in the chain 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). As expected, the introduction of the angular potential has the effect of forcing the bond angles to remain close to 120 degrees. The additions of dihedral and intermolecular force field contributions only cause minor alterations of the distribution.

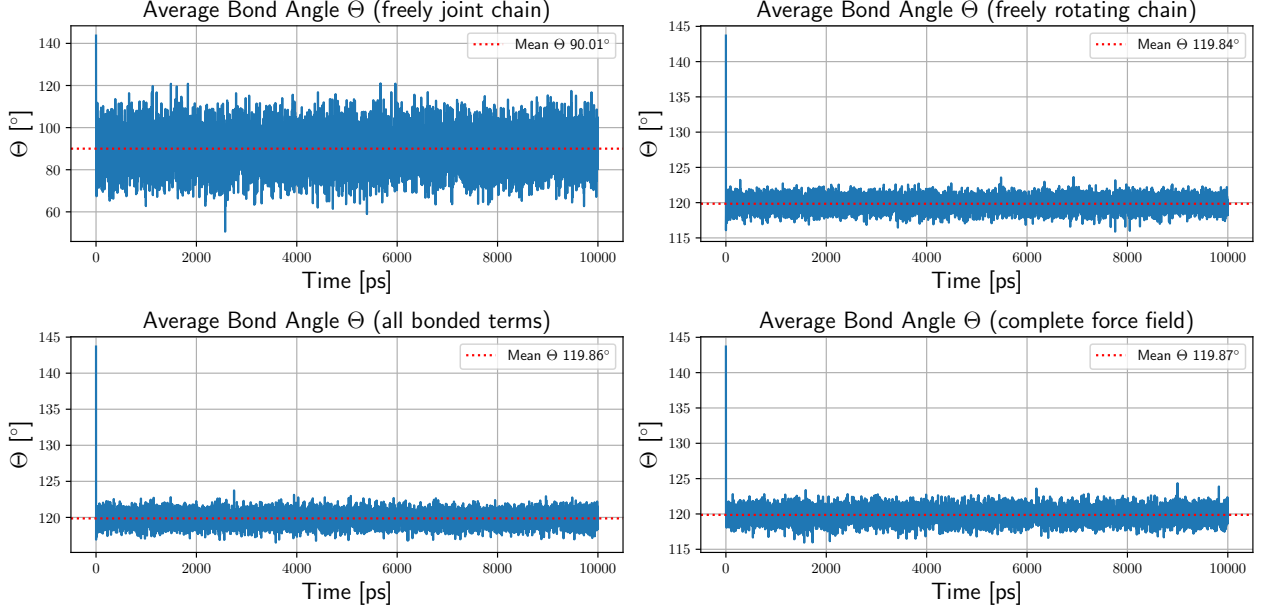


Figure 2: Chain Average of the bond angle θ for the different variation of the force field.

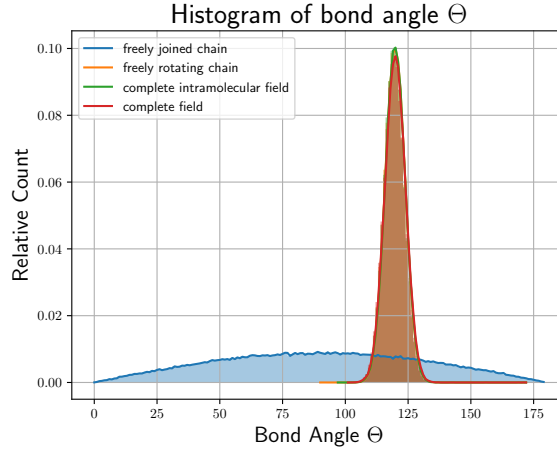


Figure 3: Histogram of the chain average of the bond angle Θ

Similarly, the effect of the force field variations on the torsion angles ϕ were 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 behaviour of the dihedral angles 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.

Without intermolecular forces, it seems that the states close $\phi = 180^\circ$ and $\phi = 0^\circ$ are populated roughly equal. This however is changed once the Lennart-Jones potential is activated causing an overweight of the states close to $\phi = 180^\circ$.

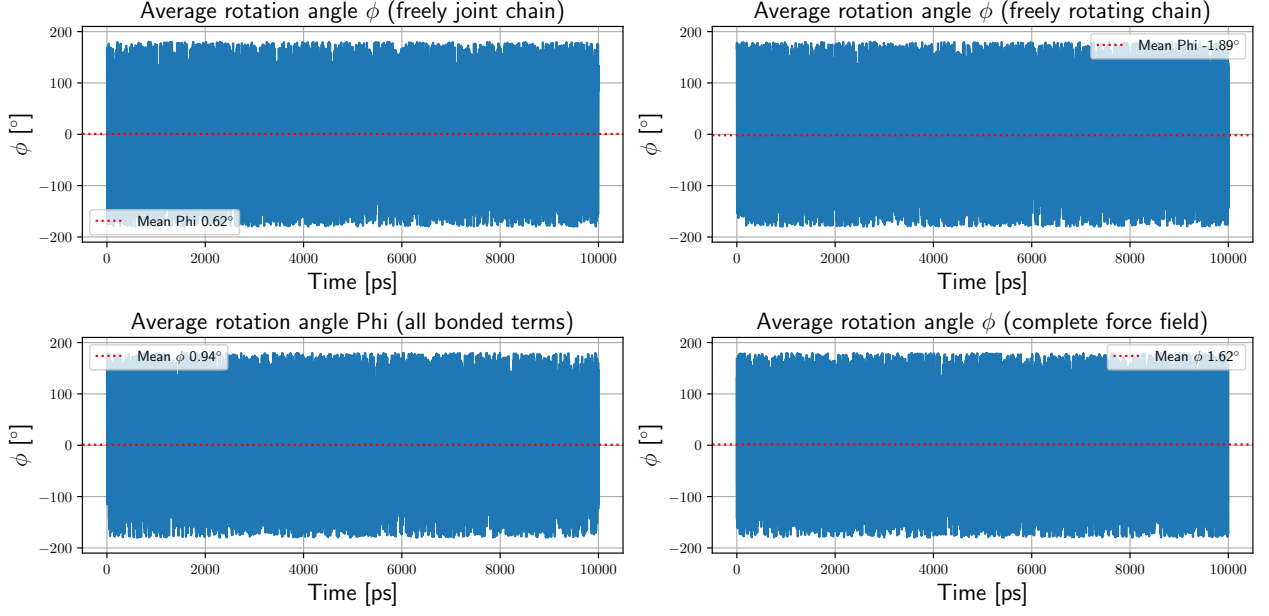


Figure 4: Average chain torsion angle ϕ as a function of the simulation time for different variations of the force field.

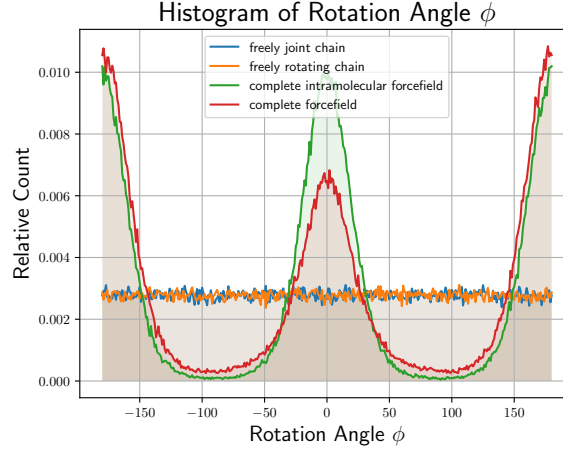


Figure 5: Histogram of the chain average of the bond angle ϕ

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	all bonded terms	full force field
Analytic R_e	0.68 nm	1.18 nm	—	—
Result R_e	0.62 nm	1.03 nm	1.03 nm	0.81 nm
Result R_{gyr}	0.27 nm	0.43 nm	0.43 nm	0.40 nm
Result $\langle\theta\rangle$	90.01°	119.84°	119.86°	119.87°
Result $\langle\phi\rangle$	0.62°	−1.89°	0.94°	1.62°

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 maintaining bond angles close to 120° prevent the molecule from easily forming a closed shape. Without the bond potential states such as the one presented in figure 6 are possible. Here one spots various bond angles allowing the molecule to assume a very dense configuration. Furthermore, looking at the trajectory, one can observe the effect of the absence of the Lennart-Jones potential as some atoms are allowed to overlap.

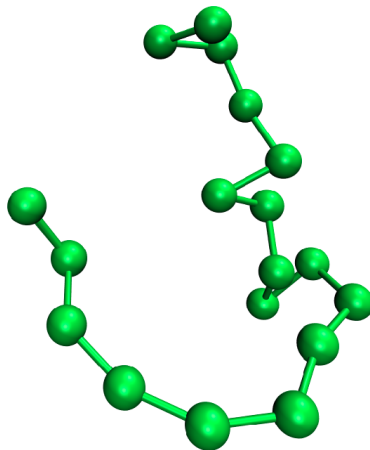


Figure 6: The polymer as a freely joint chain. Notice how the absence of the angular potential allows for uniform distribution of bond angles.

With U_θ activated, more extended states are favoured and the bond angles remain close to $\theta_0 = 120^\circ$. For an example, see figure 7. This behaviour is also confirmed by the histogram of the bond angles (figure 3). Still both these force field components allow the molecule to have a uniform distribution of torsion angles from -180° to 180° . With the introduction of U_ϕ this changes and torsion angles of -180° , 0° and 180° are favoured. This is due to the structure of the force field U_ϕ in which these three values give the minimal energy. In practice the preference of these angles means that the molecule lies more or less in one plane. For an example of such a conformation see figure 8. The addition of the Lennart-Jones potential does not seem to change the behaviour of the molecule much. Likely, the new attraction of the intermolecular potential stabilizes "u-shaped" conformations (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/sose_06/softmatter/talks/Peter_Jensen-Polymers.pdf
[accessed 05.05.2023, 22:12]

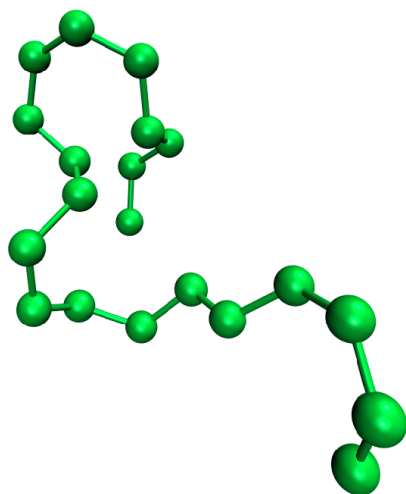


Figure 7: The polymer as a freely rotating chain. More extended states are favoured and all bonds remain close to the given θ_0 .

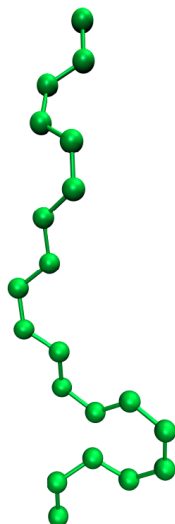


Figure 8: The polymer with fully modelled intramolecular force field. The fact that -180° , 0° and 180° are favoured means that the molecule largely lies in one plane.

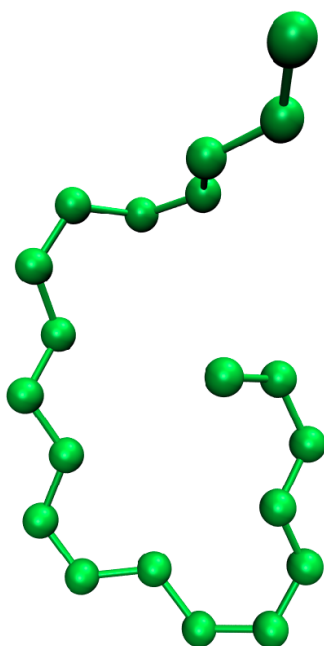


Figure 9: The polymer with fully force field.