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Molecular Dynamics (SS2025)
Exercise 2

Polymer Simulation with Different Forcefield Terms

Report Tasks

1. Compare your analytical solutions for R_e to the numerical ones.
2. Plot all R_e and R_{gyr} vs. the simulation time.
3. Include histograms of the θ and ϕ and plot the chain averages vs. simulation time.
4. Summarize all averages for θ , ϕ , R_{gyr} and R_e in *one* table.
5. Describe and interpret your results. Include representative snap shots generated by VMD to support your argumentation.

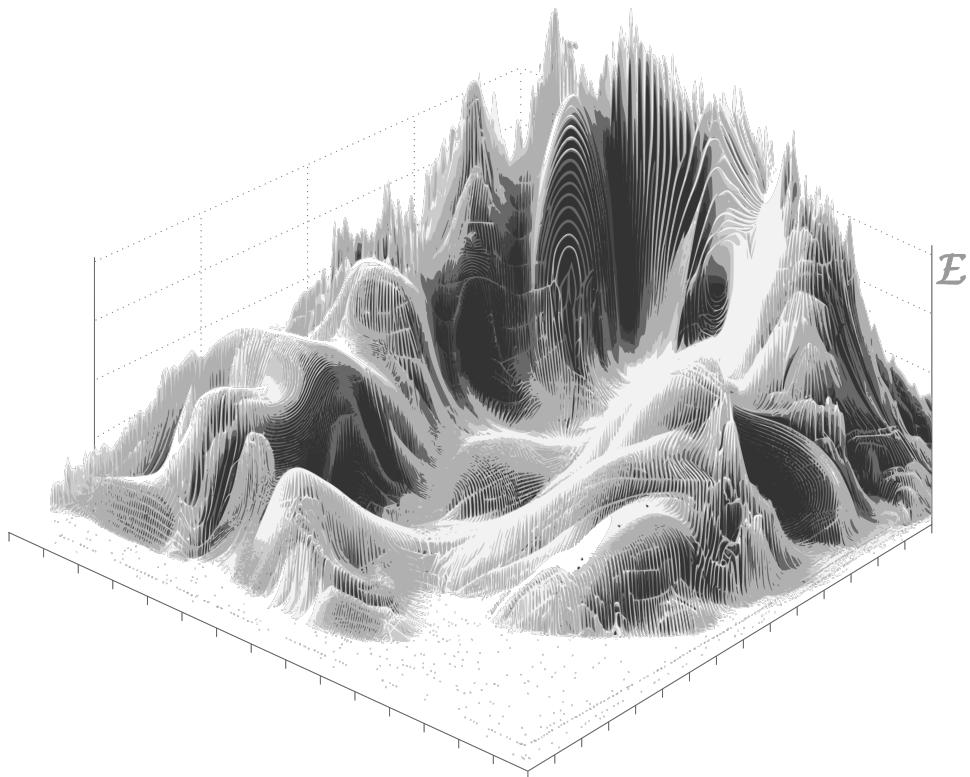


Figure 1: Conceptual depiction of the potential energy surface. Obviously, the actual potential energy surface is $6N$ -dimensional and therefore not conceivable by the human mind.

Molecular dynamics (MD) simulations are a unique method that enable the user to image time resolved processes in atomistic detail. However, the method is only approximating reality by parametrising molecular properties, e.g. charges, bond lengths etc. The complete set of these parameters, and their respective formulas, is called *forcefield* which is synonymous to the potential energy of the system. The quality of the forcefield, as well as its completeness, determines the quality of an MD simulation's predictions. In this exercise a simple polymer consisting of carbon atoms is simulated with different levels of forcefield completeness. The goal is to understand the forcefield terms and their implementation in GROMACS. Additionally, a comparison with analytical polymer models will be conducted.

Analytical Calculation of Polymer Properties

Consider a polymer consisting of N beads at positions \vec{b}_1 to \vec{b}_N . The first task is to calculate the mean end-to-end distance R_e .

$$R_e = \sqrt{\left\langle \left(\vec{b}_1 - \vec{b}_N \right)^2 \right\rangle} \quad (1)$$

R_e shall be calculated analytically for the freely jointed chain and the freely rotating chain. The former is defined only by a fixed bond length L , whilst the latter additionally features a fixed angle θ between adjacent beads.

Simulation of a Polymer

The complete polymer forcefield U_{tot} can be split into an intramolecular term U_{intra} and an intermolecular term U_{inter} .

$$U_{\text{tot}} = U_{\text{inter}} + U_{\text{intra}} \quad (2)$$

On the one hand, U_{inter} only consists of the Lennard-Jones potential $U_{\varepsilon,\sigma}$, depending on the parameters ε and σ and the interatomic distance r_{mn} . Since the nonbonded interactions are applied pairwise to all atoms in the system their calculation is computationally expensive. Mathematically, this becomes apparent from the double sum in the equation.

$$U_{\text{inter}} = \sum_m^{\text{Atoms}} \sum_{n \neq m}^{\text{Atoms}} U_{\varepsilon,\sigma}(r_{mn}) \quad (3)$$

The Lennard-Jones potential is one of many standard potentials implemented in GROMACS and the interpretation of its parameters is quite intuitive. ε corresponds to the potential well depth and σ is indicative of the particle radius which could be shown from its mathematical expression.

$$U_{\varepsilon,\sigma}(r_{mn}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{mn}} \right)^{12} - \left(\frac{\sigma}{r_{mn}} \right)^6 \right] \quad (4)$$

Another important potential that is herein omitted is the Coulomb potential which describes charge-charge interactions. On the other hand, U_{intra} consists of bond, angular and dihedral contributions. The bonded potential U_b and the angular potential U_θ are harmonic potentials and therefore defined by an equilibrium distance b_0 and angle θ_0 as well as a force constant k_b or k_θ . Usually, the dihedral term is a cosine potential defined by the force constant k_ϕ , phase

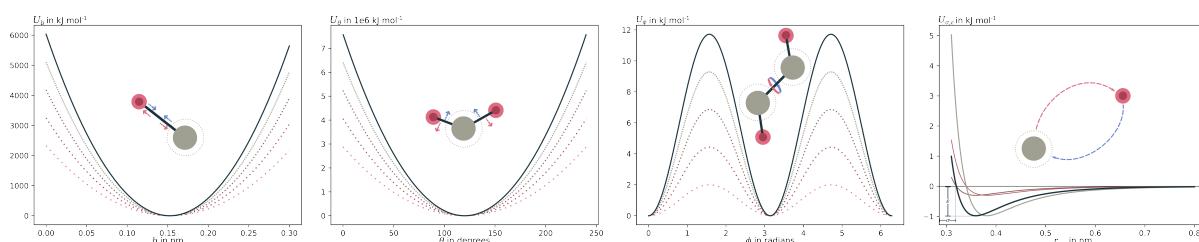


Figure 2: Exemplary plots of each force field term. On the very left the bonded potential is plotted, followed by angular, torsional and non-bonded potential. The colored, dotted lines in each panel depict the same force field term of decreasing strength (force constant). In case of the non-bonded potential this trend is visualised via the line width for aesthetic reasons. Furthermore, the epsilon and sigma value of the strongest potential are annotated close to the origin. Notice the differences in the energy scale of each contribution.

ϕ_0 and periodicity n_ϕ .

$$U_{\text{intra}} = \sum_i^{\text{bonds}} U_b(b_i) + \sum_j^{\text{angles}} U_\theta(\theta_j) + \sum_k^{\text{dihedrals}} U_\phi(\phi_k) \quad (5)$$

$$U_b(b_i) = k_b (b_i - b_0)^2 \quad (6)$$

$$U_\theta(\theta_j) = k_\theta (\theta_j - \theta_0)^2 \quad (7)$$

$$U_\phi(\phi_k) = k_\phi (1 + \cos(n_\phi \phi_k - \phi_0)) \quad (8)$$

Your task is to perform an NVT simulation of a polymer consisting of 20 atoms for the following cases:

1. freely jointed chain; only U_b is active.
2. freely rotating chain; U_b and U_θ are active.
3. complete intramolecular forcefield; U_{intra} is active.
4. complete forcefield; U is active with $\varepsilon = 0.9786 \text{ kJ mol}^{-1}$ and $\sigma = 0.3401 \text{ nm}$.

The individual contributions to the forcefield can be found in `polymer.top`. Download, open and familiarise yourself with its content. Activation of the demanded forcefield terms requires deletion of the `;` in the TOP file in front of the respective lines. `;` preceeds *comments* that are not interpreted by GROMACS. The parameters for U_{inter} can be set in the `[atomtypes]` section.

As a reminder, GROMACS requires you to execute `gmx grompp` and `gmx mdrun` to perform a simulation. The GROMACS command line reference¹ contains further information on how these commands work and which options they offer. Furthermore, to keep your directories neat, use consistent names for your simulation files. E.g., a command prompt for the freely jointed simulation could look like this:

```
gmx grompp -f polymer.mdp -c polymer.gro -p polymer_fj.top -o polymer_fj.tpr
gmx mdrun -deffnm polymer_fj -v
```

¹<https://manual.gromacs.org/documentation/2018/user-guide/cmdline.html>

Analysing the Trajectory

Once all simulation runs are finished, the trajectories need to be analysed. Herein, angular properties as well as statistic polymer properties should be calculated. GROMACS offers the built-in tools `gmx polystat` and `gmx angle` for this purpose. Since the angular potentials U_θ and U_ϕ are not included per default, their impact on the carbon chain should be investigated. Therefore, the average angle should be plotted vs. the simulation time. Additionally, an angle histogram should be generated. Both plots can be done by GROMACS via `gmx angle`. However, this command needs information about the triplets involved in one angle provided in a custom NDX file. This file plainly lists the atom numbers, making up each angle in the simulation, therefore it can be repurposed once it is generated. Luckily, GROMACS has a separate command, `gmx mk_angndx`, that outputs such a file automatically if angular information is present in the input TPR file. E.g. for the freely jointed simulation the necessary plots can be generated using the following commands.

```
gmx mk_angndx -s polymer_full.tpr -n angle.ndx -type angle
gmx angle -f polymer_fj.xtc -n angle.ndx -od fj_angle_hist.xvg -type angle -ov fj_angle.xvg
```

For the dihedrals, the same steps must be taken to plot them for the report. Thus, `gmx mk_angndx` must be executed but with the correct `-type` option, followed by the command `gmx angle`. The procedure is analogous to the one showcased above. It is recommended to plot the histograms of the individual forcefield cases into one plot so the differences become more clearly visible.

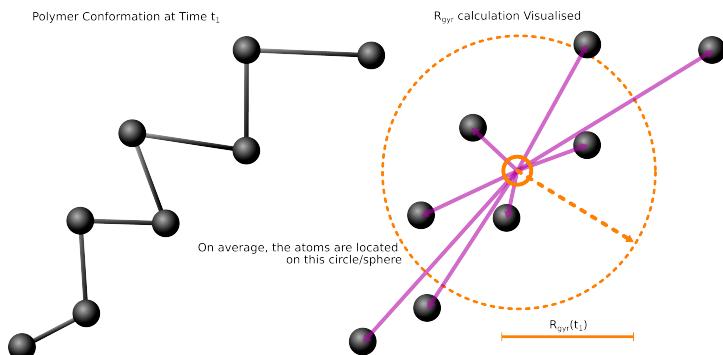


Figure 3: Visualisation of the calculation for R_{gyr} : only the atomic distances to the center of geometry of a given conformation are measured and then averaged. For extended conformations, R_{gyr} is larger than for collapsed polymer chains. However, for an equilibrated ensemble, a static time average emerges $\langle R_{\text{gyr}} \rangle_t$.

In the first section you were prompted to calculate R_e analytically. These calculations should agree with the numerical result that one can obtain from a simulation. For your report, include the time averages for R_e and plots that feature its development over time. Do the same for the radius of gyration R_{gyr} . As aforementioned, GROMACS has its built-in tool to calculate these properties. In the following, you find an example code.

```
gmx polystat -s polymer_fj.tpr -f polymer_fj.xtc -o fj_polystat.xvg
```

Try to summarise all measurements in a table for a better overview of the results. Discuss the agreement of the analytical and numerical results for R_e . Also compare the results from the different simulations and try to justify the results based on the underlying forcefield terms. You may try to reinforce your arguments with visual proof drawn from VMD.

Tutorial on Visualising a Trajectory

The standard visualisation program used for molecular dynamics simulation is called VMD. For simulation output generated by GROMACS you have to input the GRO file and the XTC file to visualise your trajectory, e.g. for the freely jointed simulation output.

```
vmd polymer.gro polymer_fj.xtc
```

Since the GRO file only specifies the atom configuration, instead of `polymer_fj.gro`, you can input `polymer.gro` which is recommended. You may try matching GRO and XTC files but the bonds might be visualised incorrectly.

Since the VMD defaults, when loading a trajectory, are suboptimal from an aesthetic and a practical standpoint, follow the tutorial below for an improved trajectory appearance. Firstly, the visibility is greatly enhanced by aligning the structure (see figure 4). This means, the structure of each time frame is centered on the coordinates of a reference frame followed by rotations, that minimise the atomic distances between the two frames. This operation makes the trajectory appear much smoother.

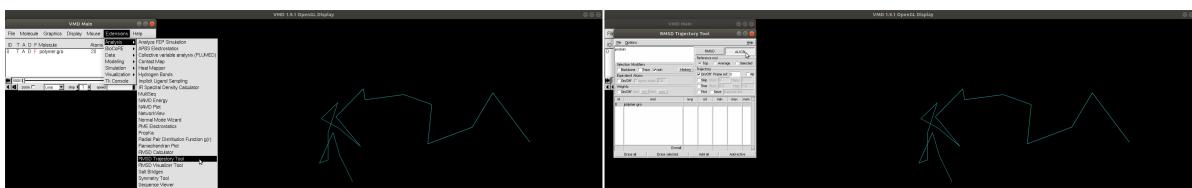


Figure 4: Extensions ⇒ Analysis ⇒ RMSD Trajectory Tool ⇒ window opens ⇒ Align ⇒ close the window

Secondly, the representation of the molecule per default is set to lines which looks a bit uncanny. Changing this to Licorice and applying gaussian smoothing to the trajectory, enhances the user experience even further (see figure 5).

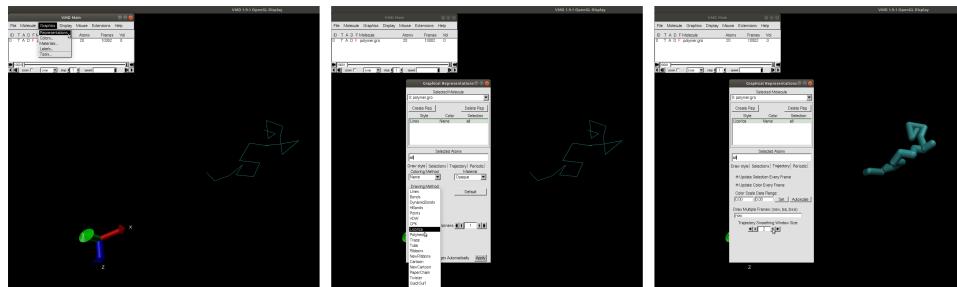


Figure 5: Graphics ⇒ Representations ⇒ window opens on Tab Draw Style
⇒ Drawing Method ⇒ Licorice (⇒ optional: adjust Bond Radius) ⇒ switch Tab to Trajectory
⇒ set Trajectory Smoothing Window Size to 3 ⇒ Close the Window

For including snap shots into your report, you have to revert `Trajectory Smoothing Window Size` back to zero since this setting manipulates the atom positions. The easiest and quickest way to generate images from VMD is to take a screenshot.