Worksheet 4: Properties of Coarse-grained Polymers

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Contents

General Remarks

- In this worksheet, you can achieve a maximum of 20 points.
- The report should be written as though it would be read by a fellow student who attends the lecture, but doesn't do the tutorials.
- To hand in your report, send it to your tutor via email.
  - Christoph (`clohrmann@icp.uni-stuttgart.de`)
- Please attach the report to the email. For the report itself, please use the PDF format (we will *not* accept MS Word doc/docx files!). Include graphs and images into the report.
- The report should be 5–10 pages long. We recommend using LaTeX. A good template for a report is available online.
- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

The first part of the worksheet involves general questions about coarse-grained polymer models and requires you to solve a related mathematical task.
In the remainder of the worksheet, you will get to know our in-house software package ESPResSo (Extensible Simulation Package for Research on Soft matter). Using ESPResSo, you will perform several simulations involving coarse-grained polymers and analyze their properties.
All files required for this tutorial can be downloaded from the ILIAS folder.

2 Short Questions - Short Answers (3 points)

Task (3 points)
Answer the following questions:

- What are the differences between the ideal chain, the freely jointed chain, the freely rotating chain, the worm-like chain and the self-avoiding chain?
- What is the persistence length of a polymer?
- Which real polymers can be described by the worm-like chain model?

Hint

- You might want to study literature to answer these questions. A good reference would be the book:
  Polymer Physics by Rubinstein and Colby, 2003,
  Oxford University Press, ISBN: 9781613449431

3 Polymer properties, the freely rotating chain model (9 points)

The mean-square radius of gyration of a polymer with N monomers is defined as

$$\left\langle R_g^2 \right\rangle \equiv \left\langle \frac{1}{N} \sum_{i=1}^{N} \left(\vec{R}_i - \vec{R}_{\text{com}} \right)^2 \right\rangle , \tag{1}$$

where $\vec{R}_i$ denotes the position of the i-th monomer in the chain, and $\vec{R}_{\text{com}}$ the chain's center of mass.

Task (2 points)

- Show how the radius of gyration can be calculated using only difference vectors $(\vec{R}_i - \vec{R}_j)$

The freely rotating chain model fixes the angle Θ between subsequent polymer segments as well as the bond length l

$$(\vec{R}_i - \vec{R_{i-1}}) \cdot (\vec{R_{i+1}} - \vec{R}_i) = l \cos(\Theta) = const \tag{2}$$

Task (5 points)

- Calculate the maximum end-to-end distance R_{max} as a function of Θ and l.
- Show that orientation correlations decay rapidly along the chain, i.e.

$$\left\langle (\vec{R}_i - \vec{R_{i-1}}) \cdot (\vec{R}_j - \vec{R_{j-1}}) \right\rangle = l^2 \cos(\Theta)^{|i-j|} \tag{3}$$

- Rewrite eq. 3 using the exponential function and identify a persistence length
- Show that the mean squared end-to-end distance $\langle R^2 \rangle$ is given by

$$\left\langle (\vec{R}_N - \vec{R}_1)^2 \right\rangle = (N-1) l^2 \frac{1 + \cos(\Theta)}{1 - \cos(\Theta)} \tag{4}$$

The properties R_{max} and $\langle R^2 \rangle$ can be used to map this model onto the ideal chain model. The ficticious number of monomers and bond length in the corresponding ideal chain model are called Kuhn monomers K and Kuhn length b.

Task (2 points)

- Calculate K and b as a function of N, Θ and l.

Hints

- Read chapter 2 of *Polymer Physics* by Rubinstein. Sections 2.3 and 2.4 are the most important ones for this task.
- When derivating eq. 4, start by writing $\vec{R}_N - \vec{R}_1$ as a sum of difference vectors between neighbouring monomers. Then see how you can use the fact that correlations decay quickly to simplify the sums.

4 Static Properties of Coarse-grained Polymers with ESPResSo(8 points)

4.1 The Software Package ESPResSo

The software package ESPResSo is developed and maintained at the Institute for Computational Physics in Stuttgart and is mainly intended to perform coarse-grained simulations with Lattice-Boltzmann (LB), Dissipative Particle Dynamics (DPD) and Langevin Dynamics (LD). It offers a broad variety of electrostatic algorithms, analysis tools and various other features such as the support of massively parallelized hardware architectures or GPU platforms.

- The package can be obtained free of charge under `http://espressomd.org/`.
- We shall be using Python to set up the ESPResSo simulations.

In the following, you will conduct coarse-grained simulations of polymers with LD to learn how to work with ESPResSo. The simulations focus on the ideal chain model and the chain with excluded volume interactions. You can either use the computers in the ICP CIP pool or install ESPResSo on your own computer.

4.2 Installing ESPResSo

You may download and run the installation script `espresso_install.sh`, or follow the instructions below.
Download the latest ESPResSo release.

```
git clone --single-branch -b 4.1 https://github.com/espressomd/espresso.git
```

Enter the newly created ESPResSo directory, and create (and enter) a `build` directory inside

```
cd espresso
mkdir build
cd build
```

Run `cmake` inside the `build` directory

```
cmake ..
```

The computers in the CIP pool will have the needed dependencies and `cmake` should complete successfully. On your own machine you might need to install the required packages. See `http://espressomd.org/html/doc4.1.2/installation.html` for more details.
Once finished, a new file called `myconfig-sample.hpp` should have appeared. Create a copy called `myconfig.hpp`

```
cp myconfig-sample.hpp myconfig.hpp
```

and edit its contents. In order to enable the feature `LENNARD_JONES`, simply remove the comment symbol at the beginning of the line. You may now compile ESPResSo by running `make` after running `cmake` a second time

```
cmake ..
make -j8
```

Upon successful compilation, you can verify that the python-driven ESPResSo works by running

```
./pypresso
```

4.3 Setting up and Running the Simulations

Download the template Python script `espresso_polymers.py` from the ILIAS folder. Examine the template script and also have a look at the documentation (`http://espressomd.org/html/doc4.1.2/`) to understand how to set up a polymer with Langevin Dynamics. You need harmonic springs with the spring constant $k = 100$ to connect the monomers. The temperature should be set to $T = 1$ and the friction coefficient of the Langevin thermostat to $\gamma = 1$.
Once the Python script is prepared, you can run the simulation with

```
/<install_dir>/pypresso espresso_polymers.py
```

4.4 Ideal Chain

Task (4 points)

- Perform simulations of an ideal coarse-grained polymer with Langevin Dynamics for different chain lengths $N \in \{10, 20, 30, 40, 50, 100, 200\}$ and determine the average radii of gyration $\sqrt{\left\langle R_g^2 \right\rangle}(N)$.
- Determine the size exponent ν in the relation

$$\sqrt{\left\langle R_g^2 \right\rangle}(N) \propto N^{\nu}$$

.

Hint

- This task requires no modification to the simulation script

4.5 Chain with Excluded Volume Interactions

Task (4 points)

- Simulate a coarse-grained polymer with the same bonds and parameters as given above. In addition, apply Lennard-Jones interactions to the monomers with $\epsilon = 1$, $\sigma = 1$, and cutoff radius $r_c = 2^{\frac{1}{6}}$.
- Repeat the simulations for the different values of N.
- Determine ν as in the previous task.