Worksheet 3: Properties of Coarse-grained Polymers

Solutions

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Contents

Remarks

The Solutions provided here show possible approaches to solve the tasks from the corresponding worksheet and may not be exhaustive.

1 Introduction

In the first part of this worksheet, you will have to answer a few general questions about coarse-grained polymer models and 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 lecture's homepage.

2 Short Questions - Short Answers (6 points)

Task (6 points)

Answer the following questions:

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

Hint

- You might want to study literature to answer these questions. A good reference would be the book *Polymer Physics* by Rubinstein.

Solution

- The persistence length of a polymer chain is a measure for its stiffness. It is the expected value of the distance l along the polymer's contour at which correlations between its tangential vectors $\vec{e}(l)$ vanish:

$$l_p = \int_0^\infty \left(\int \vec{e}(l)\vec{e}(l+\Delta l)dl \right) d\Delta l \tag{1}$$

- The worm-like chain model can be used to describe very stiff polymers such as double-stranded DNA, RNA, or proteins.
- The ideal chain is a synonym for the freely jointed chain, where the bond angles between single monomers are uncorrelated, rendering the model to behave like a 3d random walk with fixed step size.
  In contrast to the ideal chain, the self-avoiding chain incorporates a repulsive potential between monomers, effectively incorporating an excluded volume.
  The worm-like chain model describes a continuosly flexible isotropic rod. It is a special case of the freely rotating chain model with vanishing length of the Kuhn monomers restricted to small bond angles and constant persistence length.

3 Polymer Properties (6 points)

Consider an ideal linear chain with N Kuhn monomers of length b and fixed end-to-end vector $\boldsymbol{R}$ directed along the x-axis.

Task (6 points)

- Demonstrate that the mean square projection of the radius of gyration onto the direction of its end-to-end vector is

$$\frac{1}{N}\sum_{i=1}^{N}\langle((\boldsymbol{r}_i-\boldsymbol{r}_{\mathrm{com}})_x)^2\rangle=\frac{1}{36}Nb^2\left(1+\frac{3\boldsymbol{R}^2}{Nb^2}\right)\ , \tag{2}$$

  where $\boldsymbol{r}_i$ is the position of the i-th monomer and $\boldsymbol{r}_{\mathrm{com}}$ is the position of the polymer's center of mass.

- Show that the mean square projection of the radius of gyration onto the perpendicular direction is independent of the magnitude $|\boldsymbol{R}|$ of the end-to-end vector:

$$\frac{1}{N}\sum_{i=1}^{N}\langle\Big((\boldsymbol{r}_i-\boldsymbol{r}_{\mathrm{com}})_y\Big)^2\rangle=\frac{1}{N}\sum_{i=1}^{N}\langle((\boldsymbol{r}_i-\boldsymbol{r}_{\mathrm{com}})_z)^2\rangle=\frac{1}{36}Nb^2 \tag{3}$$

Remarks

Note that

- for $|\boldsymbol{R}|=0$, the mean square radius of gyration of a ring polymer $\langle R_g^2\rangle=\frac{Nb^2}{12}$ is recovered,
- for $|\boldsymbol{R}|=b\sqrt{N}$, the mean square radius of gyration of an ideal linear chain $\langle R_g^2\rangle=\frac{Nb^2}{6}$ is recovered,
- and for $|\boldsymbol{R}|=bN$, the mean square radius of gyration $\langle R_g^2\rangle=\frac{1}{12}N^2b^2$ is recovered in the limit of large N.

It is interesting to point out that the asymmetry of the ideal linear chain $\left(1+\frac{3\boldsymbol{R}^2}{Nb^2}\right)$ is quite large and a typical shape is better represented by an elongated ellipsoid than by a sphere.

Solution

- to do
- to do

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

4.1 The Software Packege ESPResSo

The software package ESPResSo is developed and maintained at the Institute for Computational Physics 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/wordpress/download/`.
- Be advised to also have a look at the ESPResSo manual to understand how it operates: `http://espressomd.org/jenkins/job/master-doc/lastSuccessfulBuild/artifact/doc/ug/ug.pdf`

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

Download and unpack the ESPResSo package version 3.2.0 (`espresso-3.2.0.tar.gz`). Follow the build procedure as given in the manual on pp. 23ff.

The `configure` script should be run with the option `--without-cuda` in order to avoid problems during compilation. After using `./configure` but *before* compiling with `make`, please uncomment the macros in `myconfig-sample.h` for `LENNARD_JONES` and rename it to `myconfig.h`.

4.3 Setting up and Running the Simulations

Download the template Tcl script `template.tcl` from the lecture website.

Examine the template script and also have a look at the manual (and perhaps on the test cases, too) to understand how to set up a polymer with Langevin Dynamics. You need harmonic springs with the spring constant $k = 10$ 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 Tcl script is prepared, you can run the simulation with

```
$> /<install_dir>/Espresso template.tcl
```

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 $R_g(N)$.
- Determine the parameter ν in the relation $R_g(N) \propto N^{\nu}$.

Solution

$\boldsymbol{N}$	10	20	30	40	50	100	200
$\langle \boldsymbol{R_g} \rangle$	1.308	1.857	2.272	2.598	2.913	4.248	5.627

Table 1: Radii of gyration $\langle R_g \rangle$ of an ideal (freely jointed) chain for different chain lengths N simulated with ESPResSo 3.2.0.

- The average radii of gyration are listed in table 1.
- Fitting a function $f(N) = aN^{\nu}$ to the simulation data yields an exponent $\nu \approx 0.478$, which is close to the theoretical prediction of $\nu = 0.5$:

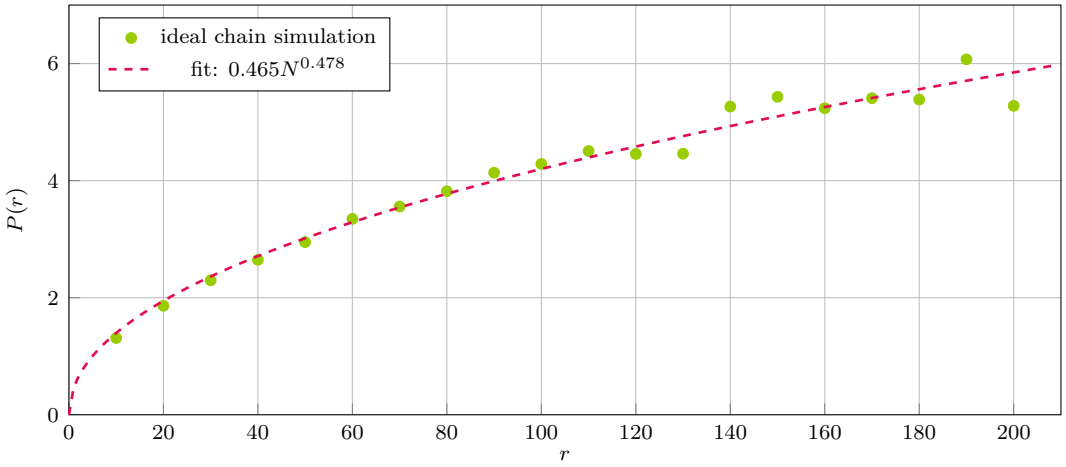

Figure 1: Radii of gyration $\langle R_g \rangle$ of an ideal (freely jointed) chain for different chain lengths N simulated with ESPResSo 3.2.0. Dots (●): Simulation data. Line (- - -): fit.

4.5 Chain with Excluded Volume Interactions

Task (4 points)

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

Solution

$\boldsymbol{N}$	10	20	30	40	50	100	200
$\langle \boldsymbol{R_g} \rangle$	1.798	2.812	3.636	4.526	5.081	8.284	11.672

Table 2: Radii of gyration $\langle R_g \rangle$ of a self-avoiding chain for different chain lengths N simulated with ESPResSo 3.2.0.

- The average radii of gyration are listed in table 2.

- Fitting a function $f(N) = aN^{\nu}$ to the simulation data yields an exponent $\nu \approx 0.646$, which is – as expected – greater than 0.5:

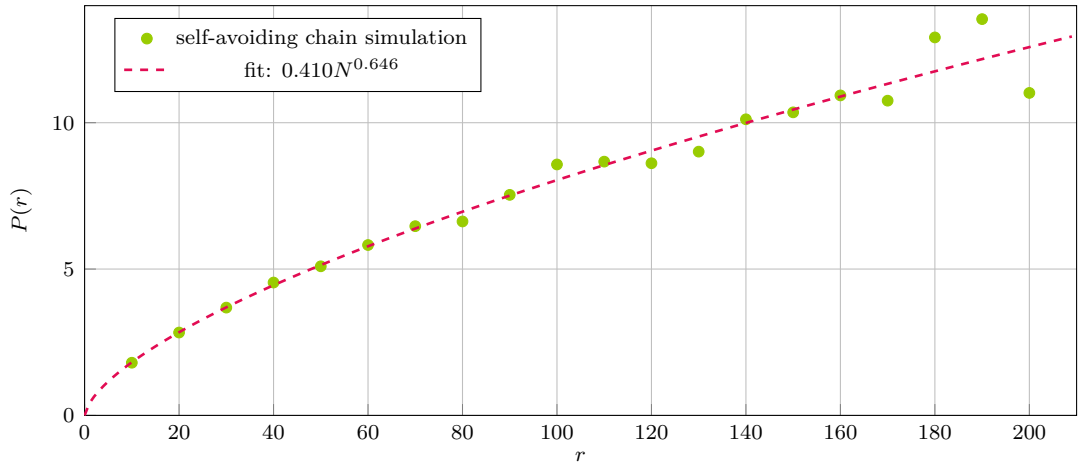

Figure 2: Radii of gyration $\langle R_g \rangle$ of a self-avoiding chain for different chain lengths N simulated with ESPResSo 3.2.0. Dots (●): Simulation data. Line (- - -): fit.