

# Worksheet 3: Charge Distribution Around a Charged Rod

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## General Remarks

- Deadline for the report is **Wednesday, 4th of July 2018, 12:00 noon**
- 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.
  - David ([david.sean@icp.uni-stuttgart.de](mailto:david.sean@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 L<sup>A</sup>T<sub>E</sub>X. A good template for a report is available online.
- The worksheets are to be solved in **groups of two or three** people.

## 1 Introduction

This tutorial is based on an article by Deserno et al. [1]. Throughout the tutorial, you will try to reproduce some plots from the article. As further reading, you can refer to [2], which is probably a bit more comprehensive.

<b>Task</b>	(3 points)
<ul style="list-style-type: none"> <li>• Read the article [1]. You can access it online: <a href="http://pubs.acs.org/doi/abs/10.1021/ma990897o">http://pubs.acs.org/doi/abs/10.1021/ma990897o</a> If you have trouble accessing the article, write an email to your tutor!</li> </ul>	

## 2 Short Questions - Short Answers

<b>Task</b>	(4 points)
Answer the following questions:	
<ul style="list-style-type: none"> <li>• What is counterion condensation?</li> <li>• What does the Bjerrum length describe?</li> <li>• Describe the concept of a mean field theory. (2 points)</li> </ul>	

### Solution

- Counterion condensation describes the phenomenon of counterions condensing onto a strongly charged polymer in solution, effectively reducing its line charge density. According to Manning theory, this happens whenever the Bjerrum length  $l_B$  in the solvent is larger than the distance of charges  $l_c$  within the polymer. In water, where the Bjerrum length is  $l_B \approx 7.1 \text{ \AA}$ , this implies that counterion condensation is important for many standard polyelectrolytes, where  $l_c$  typically lies between 2 and 3  $\text{\AA}$ .
- The Bjerrum length is the distance between two elementary charges at which their electrostatic interaction energy equals the thermal energy:

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{\epsilon_r l_B} = k_B T \quad \Rightarrow \quad l_B = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\epsilon_r k_B T} \quad (\text{SI units})$$

- The concept of a mean field theory is to reduce the complexity of a statistical many-body problem by describing the interactions of single components (*e.g.* particles) with the rest of the system as an interaction with a mean field. This effectively reduces the many-body problem to a one-body problem. In statistical physics, this means to decouple an  $N$ -particle system's Hamiltonian into a sum of  $N$  one-body Hamiltonians with an effective mean field.

Note that usually, the application of a mean field theory means that effects arising from correlations between individual components or non-uniformity of the system will not be represented properly.

### 3 The Simulated System

The system under consideration is a so-called *cell model* of a polyelectrolyte, i.e. a polymer that dissociates charges in solution (cf. lecture). In the cell model, a polyelectrolyte is modelled as a single, charged, infinite rod with its counterions and maybe some additional salt that is confined to a cylindrical cell. The observable of interest is the distribution of ions  $P(r)$  around the rod.

To obtain the charge distribution, we will introduce two methods that can be used to tackle the problem. The first method is the Poisson-Boltzmann theory, an analytical mean-field theory, the second method is to carry out computer simulations. We will learn about the strength and weaknesses of both methods.

The cell model is defined by the following parameters:

**Bjerrum length**  $l_B$  In water, the Bjerrum length is 7.1 Å under normal conditions.

**Line charge density**  $\lambda$  The line charge density of the rod is the number of charges per length unit. It is closely coupled to the *Manning parameter*  $\xi = \frac{\lambda l_B}{e_0}$ .

**Rod radius**  $r_0$  The radius of the charged rod defines the minimal distance between an ion center and the rod center.

**Cell radius**  $R$  The radius of the cylindrical cell defines the maximal distance between an ion center and the rod center.

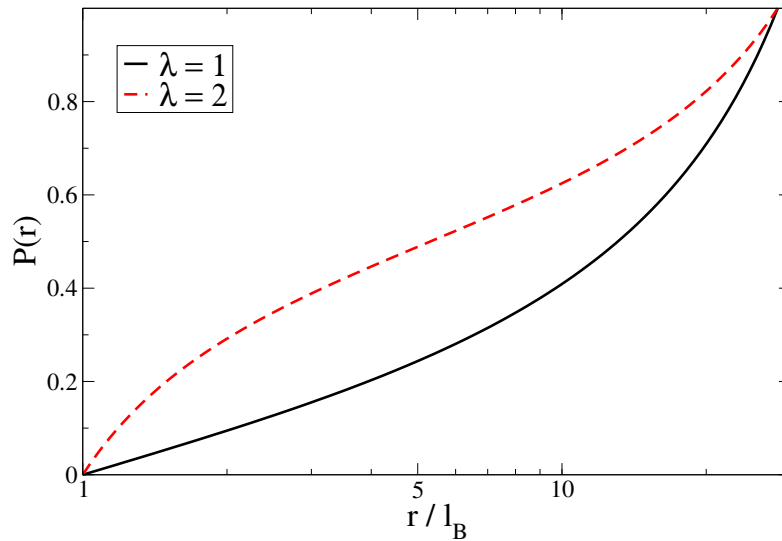
**Valency of the counterions**  $v$  The valency of the counter ions.

The default values we are going to use are:

$$l_B = 1.0, \quad \lambda \in \{1.0, 2.0\}, \quad r_0 = 1.0, \quad R = 28.2, \quad v = 1$$

Note that you should do the following tasks for both values of  $\lambda$ .

## 4 Analytical Solution: Poisson-Boltzmann Theory



**Figure 1:** Poisson-Boltzmann solution for the charge distribution  $P(r)$  over radius  $r$  for the default parameters.

On the one hand, the cell model for infinite charged rods can be solved within the *nonlinear Poisson-Boltzmann theory* (PB).

Figure 1 shows a plot of the analytical solution of the Poisson-Boltzmann equation for the default parameters. Note that the  $x$ -axis of the plot of the distribution  $P(r)$  is in logarithmic scale to stress the structure close to the rod.

For the salt-free case, an analytical solution of the charge distribution  $P(r)$  exists. It is given by equations (8) and (9) in the article. The equation contains two free parameters  $\gamma$  and  $R_M$ , which are defined by the equations (6) and (7) in the article.

<b>Task</b>	(3 points)
<ul style="list-style-type: none"><li>• Reproduce the plot in figure 1. To complete this task, you can use whatever program suits you best.</li></ul>	

### Hints

- First, solve equations (6) and (7) numerically and obtain values for  $R_M$  and  $\gamma$ .
- Then, substitute the values into equations (8) and (9) to obtain a solution for the distribution.
- If you use Mathematica, the function `FindRoot[]` might be useful. In Python, look for `scipy.optimize.fsolve()`.

## 5 Computer simulations

Alternatively, the charge distribution can be obtained from computer simulations.

### 5.1 Mapping the Cell Model onto a Simulation

It is not possible to simulate the full cell model, as it requires an infinite rod. However, we can simulate a quasi-infinite system by exploitation of periodic boundary conditions: we create a rod that spans the whole simulation box size and use periodic boundary conditions in that direction. We will model the rod by a number of fixed charged particles on a line parallel to the  $z$ -axis in the center of the simulation box. For this worksheet, you will need to enable new features for ESPResSo. It is easiest to follow the installation steps from the previous worksheet, but this time when editing `myconfig.hpp`, enable the three following features:

```
EXTERNAL_FORCES
ELECTROSTATICS
LENNARD_JONES
```

by removing the comment symbols `///. You may alternatively use the installation script provided on the course webpage.`

We would like to be able to use the fast P3M method for computing the electrostatics. Therefore, our system has to be cubic (i.e.  $L = L_x = L_y = L_z$ ) and it has to employ periodic boundary conditions in all three dimensions.

How can we map the cylindrical cell with a radius  $R$  onto a cubic simulation box with a box length  $L$  while still retaining the correct charge distribution? The trick is to use the same *ion density* in both systems. When the total ion density is the same in the cell model and in the simulation, we expect them to show the same charge distribution.

Note that the box length  $L$  defines the length of the simulated segment of the rod, and consequently the charge of this segment. Since the whole system should be neutral, this also predefines the number of counterions in the system.

<b>Task</b>	(2 points)
<ul style="list-style-type: none"><li>• Map the default cell model parameters onto a cubic simulation box, i.e. compute <math>L</math> for the given value of <math>R</math>. How many ions need to be simulated?</li><li>• Download the ESPResSo template python script <code>template.py</code> from the lecture's website. This script sets up a system in the described way, but for a different set of parameters. Study the script and understand how it works. Adapt the script to the given default parameters.</li></ul>	

### 5.2 First Runs

Now the script is prepared for the first simulations. You can run the script with the command

```
$> /<espresso_install_path>/pypresso template.py
```

Once the simulation is finished, it will have produced output files for later analysis. It is too expensive to measure observables after each time step and results would be correlated. Instead, observables are measured only after a fixed number of timesteps `steps_per_frame` has passed (which is referred to as a *simulation frame*). The number of frames that are done in a single simulation run is defined by `max_frames`. The script will create three files:

**rod-energy.dat** contains the total coulomb energy over time.

**rod.vsf** will contain the structure header of particles for every time frame (see `vtf`, `vsf`, `vcf` format).

**rod.vcf** will contain the positions ( $x, y, z$ ) of particles for every time frame (see `vtf`, `vsf`, `vcf` format).

#### Task

(2 points)

- Run the previously adapted script `template.py` and visualize the trajectory with VMD. Do you see ions crowd near the rod?
- Analyze the trajectory file `rod-dist.vcf` and plot the average radial distance of the counterions to the rod vs time, remember what you learned from the VMD visualization. Increase the time until this value converges.

#### Hint

- You may combine the `vsf` and `vcf` files to a `vtf` or keep them separate. In which case you will need to specify both to VMD:

```
$>vmd rod.vsf rod.vcf
```

- Remember that you have to run the simulations for two different values of  $\lambda$ ! Consider running the simulations in two different subdirectories, so that they do not overwrite each others' files.
- You don't need to save the position of the rod beads, consider using `type=...` parameter in `writevsf()` and `writevcf()`
- The mean radial position should not diverge. If it increases with time try to find what is wrong.

### 5.3 Equilibration and Sampling Time

Now we can start with the real simulations. First, we need to make sure that the systems is equilibrated, and we need to get an idea how many simulation frames we will need to sample to get good statistics. To do that, you should monitor the slowest observable that you can find. In general, the energies and the different energy components are a good starting point.

During equilibration, you will notice that the observable has a trend, i.e. it grows or drops. Only after you can not observe any trend anymore, the system can be assumed to be equilibrated. Usually, the values themselves fluctuate very strongly, so that the trend might well hide within the fluctuations. Therefore, it is useful to create *running averages* of the observables over a few hundred frames that average out the fluctuations and zoom the resulting curve. The program `xmgrace` can create running averages (choose *Data > Transformations > Running Averages...* from the menu).

Now you need to find out for how many frames you need to sample your simulation. To get useful statistics, the sample should encompass at least several of the slowest fluctuations.

#### Task

(2 points)

- Run the simulation. Monitor the energies. Increase the number of frames done in the script (`max_frames`) and until the energy settles. How does this compare to the time for the average radial position to settle? When you think you do not see a trend anymore, let the simulation run again for at least the number of steps performed so far as a safety margin.
- Now analyze the fluctuations. How many timesteps do the slowest fluctuations span? If you have a number, multiply it by 10 and you have the number of frames that your sample should minimally encompass.

### 5.4 Measuring the Charge Distribution

Finally, the charge distribution can be measured. Modify the the script to make sure the system is equilibrated before taking data. Set the number of frames to be simulated (between data output) to the number of frames that you got out above. Make sure all the frames are uncorrelated using the times obtained previously.

#### Task

(4 points)

- Measure the charge distribution around the rod for both values of  $\lambda$ .
- Plot the resulting charge distribution and compare it to the distribution obtained from the both Poisson-Boltzmann solutions. Do they match? If not, try to explain what might be the reason.

## Hint

- Be careful while generating the histograms! The bins do not have the same size (they are log-spaced).
- For the histogram, use the ergodic hypothesis to stack up the frames to generate one large system.

## Bibliography

- [1] Markus Deserno, Christian Holm, and Sylvio May. The fraction of condensed counterions around a charged rod: Comparison of Poisson-Boltzmann theory and computer simulations. *Macromolecules*, 33:199–206, 2000.
- [2] M. Deserno. *Counterion condensation for rigid linear polyelectrolytes*. PhD thesis, Universität Mainz, February 2000.