

## CHEM-E4115 Monte Carlo Exercise: Ion condensation around a macroion

In the exercise, you study microion condensation around a spherical macroion using a Metropolis Monte Carlo simulation. The simulated macroion is a relatively large, charged particle (ion) in a water solution containing small ions (microions). The system could, for example, describe a vesicle functionalized with some charged ligands or some other charged colloidal particle in solution.

The model used in this exercise is a coarse-grained, implicit solvent model. It encompasses only Coulombic interactions between the ions (both the macroion and the microions) and their hard sphere interactions. The hard sphere interactions mean that the ions have a finite radius and cannot overlap in the simulation. Implicit solvent means that the solvent (here water) is described by representing it by a continuum dielectric constant which screens the Coulombic

interactions. The model uses Bjerrum length  $\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$ , as the unit of length and the elementary charge  $e$  as the unit of charge.

### The aims of the exercise are to learn and practice

- Setting up a study with which one can examine a macroion system using Monte Carlo simulations and performing the study
- Convergence, error estimation, and analysis of Monte Carlo simulations
- Critical assessment of the performed simulations and the data produced by them

*Note that the software used for this exercise outputs >200 files for each 100 000 MCsteps run with the provided parameter file. **Use a separate folder for these simulations!***

***In the exercise, first put running a simulation corresponding to the macroionMCtest.parameters file. This is for the purpose of examining MC simulation convergence. The system is larger than your parameter variation study and takes about 1h to run for 100000 steps. When the convergence test is running, select one of these for your topic of study. To make feasible ending the exercise in 2h, use the system size specified in the macroion.parameter file. Most of the systems specified below will run ~10 min or less with that. See tips below for what to analyze.***

1. *How does microion size influence their condensation around the macroion? Ion size can be, for example,  $0.0 \lambda_B$  (point ions),  $0.5 \lambda_B$ ,  $1.0 \lambda_B$ , or  $2.0 \lambda_B$ . Use a macroion with  $3 \lambda_B$  diameter for a good visibility of differences.*
2. *How does microion valency influence their condensation around the macroion? Ion valency can be, for example  $-1e$ ,  $-2e$ , or  $-3e$ . Note that your macroion charge needs to be dividable by 6 so that you can examine all these valencies. Here, the macroion diameter should be  $\sim 5 \lambda_B$  diameter with the proposed setup. Ion diameter can be  $0.5\lambda_B$  (or  $0.0\lambda_B$ , different effects visible)*
3. *How does macroion size influence the ion condensation when the ions have finite size, for example  $1.0 \lambda_B$  diameter? Macroion diameter can be, for example  $5 \lambda_B$ ,  $2 \lambda_B$  and  $1 \lambda_B$ .*

## Practical tips

- The software used to run the Monte Carlo simulation is run in Mylly2 by
- `jsub cmd ewaldMC_courseversion [PARAMETERFILE NAME] [OUTPUT FILE] [MCSTEPS]`
- A model parameter file `macroion.parameters` is available for the software in the course MyCourses folder.
- 100000 MC steps using the provided parameter file take <10 min.
  
- If your simulation does not progress, check that all the particles you are trying to insert into the box volume fit into it easily – the code may be stuck trying to insert the requested ions in a too full box. If that happens, “`qdel [jobID number]`” will remove the job from Mylly2 queue. Queue status and `[jobID numbers]` can be checked by “`qstat`”
  
- The program outputs `.gro` –files.
  - Individual `.gro` files can be viewed with VMD (files need to be transferred to local computer). For example, loading into VMD `[OUTPUT FILE]0.gro` shows your initial configuration. See the end of the file for how to use vmd to visualize macroion systems.
  - In the exercise folder, a unix shell script called `combine_grofiles.sh` is provided. This shell script 1) combines your `.gro` outputs to a Gromacs `.xtc` trajectory 2) generates a Gromacs analysis tools index file with index group POL referring to your macroion and group IONS referring to your ions. With these two outputfiles you can use Gromacs analysis tools to analyze the Monte Carlo results.
  - When you have down loaded the script to Mylly2, please give command `chmod u+x combine_grofiles.sh` to make the file executable in linux environment.
  - The command `module load gromacs` is needed as the script uses Gromacs tools.
  - After this, the command format to use the shell script is
    - `./combine_grofiles.sh [MC OUTPUT FILE, NO ENDINGS] [FIRST (a number)] [STEP (a number)] [LAST (a number)]`

## Things to analyze

- By VMD, examine how the ions behave in the different systems
- Find out how many MC steps does it take for your system to equilibrate in energy. Only data after equilibration should be used for analysis. Note that for the default file, you may need to alter the data “`printoutinterval`” in the parameter file.

- The MC output data file is [OUTPUT FILE].dat . It contains the system energy as the 4<sup>th</sup> column. How do you determine whether your system has equilibrated in energy or not?
    - Tip: if you delete the first line of [OUTPUT FILE].dat, xmgrace can plot it. The energy column is plotted `xmgrace -block [OUTPUT FILE WITHOUT 1st ROW].dat -bxy 1:4`
  - Does the equilibration time (number of MC steps) vary between the different systems you examine? How?
  - “gmx rdf ...” calculates the radial distribution function from the .xtc file generated by the `combine_grofiles.sh` shell script. This provides information on how the ions are distributed. You can use the generated index file in calculating the rdf of the microions around the macroion. If the rdf data has too many peaks, the bin size can be tuned.
  - The gromacs tools `gmx densmap` and `gmx density` can also be used for analyzing the ion distribution. This is a bit more work as they need a tpr file and this is not needed for exercise completion but mentioned here to demonstrate that a wider variety of analysis tools is available.
- Return into the /home/maria/coursefiles/ folder the convergence test .dat-file of your simulations and a file where you have written how many MC steps it took for it to equilibrate in energy. Additionally, return from the actual examination one other .dat output file that does not correspond to the input file given by Maria (modified input file) + write what that dat file corresponds to.**
- The error analysis below will make the exercise exceed the time estimated for this and is thus not required but left on this instruction sheet because it demonstrated the use of block averaging and data correlations significance

### Error analysis in molecular dynamics and Monte Carlo simulations

- Compare the error estimates by direct standard deviation calculation and method of block averages. This is done via
  - Calculate standard deviation for the data after equilibration has taken place.
    - This would be a standard means of estimating error for **uncorrelated data** points. In MD and MC, depending on the data saving interval, the consecutive data points are, however, likely to be correlated and this leads to underestimation of the data deviation (too small error estimate)
  - Calculate standard deviation for the data using the method of block averages. This is a method of defining the correlation time / number of steps in the data and circumventing the correlation via using blocks exceeding the correlation length in calculating the measurable quantities and their error estimates.
    - The method of block averages works so that you divide the equilibrated simulation run to blocks of N MC steps in length. For each block, calculate average and then calculate the standard deviation of the averages. With increasing N (decreasing number of blocks), the standard deviation is supposed to reach a plateau assuming the simulation is long enough to cover truly uncorrelated data.

- The standard deviation calculation, as well as, the averaging can be done at least with xmgrace (calculates running averages).
  - -> Data -> transformations -> running averages
  - Define first running averages with different averaging length, then calculate standard deviation over each running average (entire data set length)
  - The standard deviation values are going to be much smaller than the energy values so the plotting axes need to be scaled for the stdev values to be visible

The images show how to visualize a macroion of diameter  $5 \lambda_B$  and microions of diameter  $0.5 \lambda_B$  using VMD.

"pbx box" brings out the blue box

Create Rep to create another Representation

Select atoms in one representation as "name POC" and in another as "name AN1"

Both representations by VDW

Sphere scale 1.0 corresponds to  $0.25 \lambda_B$  diameter. Sphere scale 2.0 to  $0.5 \lambda_B$  diameter and sphere scale 20.0 to  $5.0 \lambda_B$  diameter