Worksheet 3
Diffusion processes and properties of atomistic water models

Jens Smiatek*and Christian Holm†

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ICP, Uni Stuttgart

Important remarks

- Due date: **Tuesday, May 20th, 2014, 10:00**
- You can send a PDF file to Anand Narayanan Krishnamoorthy (anand@icp.uni-stuttgart.de) or submit a hand-written copy.
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart.de) or Anand Narayanan Krishnamoorthy (anand@icp.uni-stuttgart.de).

Short Questions - Short Answers (5 points)

Have a look at

`www.edinformatics.com/interactive_molecules/water.htm`

1. Q1: Why is water a polar molecule?
2. Q2: What is a hydrogen bond?
3. Q3: What are the values for the H-O-H angle in water and the typical distance of a hydrogen bond?
4. Q4: What are the main differences between various atomistic water models?
5. Q5: What is the difference between the SPC and the SPC/E water model?

*smiatek@icp.uni-stuttgart.de
†holm@icp.uni-stuttgart.de

Theoretical Task: Diffusion processes - Ballistic and diffusional regime

The Langevin equation is an effective description for particle diffusion in an implicit solvent. The force on a particle is given by a dissipative and a stochastic force. The corresponding differential equation in one dimension is given by

$$m\dot{v} = -\gamma v + \eta \tag{1}$$

with $\gamma = m\zeta$ and $\eta dt = \Gamma dW$. The first term on the r.h.s. of the Langevin equation describes the dissipative force whereas the second term incorporates the stochastic force in terms of Gaussian white noise. It has to be noted that the corresponding moments of the random force in terms of a Wiener process are given by

$$< dW(t) >= 0 \tag{2}$$

and

$$< dW(t)dW(t') >= dt'. \tag{3}$$

T1: Determination of Γ (4 points)

The squared velocity of the particle as a solution of the Langevin equation is given by

$$\langle v^2(t)\rangle = \langle v_0^2\rangle e^{-\zeta t} + \frac{\Gamma^2}{2\zeta m^2} + \frac{\Gamma^2}{2\zeta m^2} e^{-2\zeta t} \tag{4}$$

where Γ has to be determined. Please find an expression for Γ by using the equipartition theorem in the limit of a diffusion process.

T2: Diffusion coefficient (1 points)

The result for the squared particle position is given by

$$\langle x^2(t)\rangle = \frac{\langle v_0^2\rangle}{\zeta^2}(1 - e^{-\zeta t})^2 + \frac{\Gamma^2}{m^2\zeta^2} - \frac{\Gamma^2}{2m^2\zeta^3}(3 - 4e^{-\zeta t} + e^{-2\zeta t}). \tag{5}$$

Please determine the diffusion coefficient in the limit of long time scales.

Computational Task: Atomistic water simulations with GROMACS (10 points)

In this exercise we will simulate the properties for different water models with GROMACS which is a freely available Molecular Dynamics software package (www.gromacs.org). We will focus on the SPC, SPC/E and TIP3P water models. In this task, GROMACS will serve as a simulation engine. In the next worksheet we will learn how to set up a simulation with GROMACS.

C1: Running the simulation (4 points)

Please download the corresponding zip-archive from the webpage. After unpacking, you will find different files in the directory.
The files are:

- spc216.gro: pre-equilibrated water structure with 216 solvent molecules
- grompp.mdp: Parameters for the simulation
- topol.top: Topology file for the water simulation which includes a link to the force field parameters
- index.ndx: File which is needed for the analysis

Open the water configuration (spc216.gro) with vmd.

```
vmd spc216.gro
```

The file shows a pre-equilibrated water structure with 216 solvent molecules. Have also a look at the other files in the zip-archive. Copy the files into three different directories with the names spc, spce and tip3p. First we will start the simulation of the SPC water. You can either download your own copy of GROMACS or use the CIP computers. In the following, the usage of GROMACS with the CIP computers will be described.
Type the command

```
/group/allatom/gromacs-4.6.1-plumed-1.3/bin/grompp_mpi_d -v
```

The command grompp prepares the input files for the simulation. After this, the simulation can be conducted via

```
/group/allatom/gromacs-4.6.1-plumed-1.3/bin/mdrun_mpi_d -v
```

The system is simulated for 500 ps with a time step of 2 fs at 300 K.
After the simulation is finished, change into the spce or tip3p directory. Change the line

```
#include "spc.itp"
```

into

```
#include "spce.itp"
```

or

```
#include "tip3p.itp".
```

in the corresponding topol.top - file. Use the commands grompp and mdrun to perform the simulations for all three water models.

C2: Analysis of the simulation - Radial distribution function (2 points)

GROMACS also offers a broad variety of analysis tools. The radial distribution function between water molecules gives a first hint towards the local water structure. To investigate the radial distribution function, use the command

```
/group/allatom/gromacs-4.6.1-plumed-1.3/bin/g_rdf_mpi_d -n index
```

and have a look at the output file with xmgrace or gnuplot. Compare the radial distribution function for all three water models and interpret the results (peaks, distance between peaks, differences between the water models ...).

C3: Analysis of the simulation - Hydrogen bond analysis (2 points)

A crucial feature of water is the pronounced effect of hydrogen bonds between the oxygen and hydrogen atoms. The occurrence of these bonds is mainly reliable for many important properties of water. We can determine the number of hydrogen bonds within the simulated system via

```
/usr/local64/gromacs4.0.4-gcc4.3-static/bin/g_hbond_mpi_d -n index
```

where the results can be compared between the different water models. Please calculate the average number of hydrogen bonds for a water molecule. What is the meaning of donors and acceptors?

C3: Analysis of the simulation - Mean-square displacement (2 points)

The diffusion coefficient D can be calculated via the mean-square displacement function

$$< \Delta r(t)^2 >= 6Dt \tag{6}$$

after a time t. You can calculate the mean-square displacement in GROMACS via

```
/usr/local64/gromacs4.0.4-gcc4.3-static/bin/g_msd_mpi_d -n index
```

Have a look at the output files for the different water models and compare them. What are the differences? Can you identify the linear $< \Delta r(t)^2 >\sim t$) and the ballistic regime (*c.f. Theoretical task 1)?*