

Worksheet 2: Diffusion Processes and Properties of Atomistic Water Models

Frank Uhlig Johannes Zeman Christian Holm

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Institute for Computational Physics, University of Stuttgart

Contents

1	Introduction	2
2	Short Questions - Short Answers (5 points)	2
3	Diffusion Processes - Ballistic and Diffusional Regime (7 points)	3
4	Atomistic Water Simulations with GROMACS (8 points)	6
4.1	Visualizing the System	6
4.2	Running the Simulations	6
4.3	Analysis	7

General Remarks

- Deadline for the report is **Monday, 9th of May 2016, 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.
 - Frank (fuhlig@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^AT_EX. A good template for a report is available online.
- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

In this worksheet, you will first tackle several theoretical tasks related to Brownian motion in implicit solvent simulations. In the second part, you will perform explicit solvent simulations with different water models (SPC, SPC/E, and TIP3P) using the open-source Molecular Dynamics software package GROMACS. In the remainder of the worksheet, you will run various analyses on the simulation data and investigate the properties of the different water models.

All files required for this tutorial can be found in the archive `templates_sm2_ws2.tar.gz` which can be downloaded from the lecture's homepage.

2 Short Questions - Short Answers (5 points)

Have a look at http://www.edinformatics.com/interactive_molecules/water.htm.

Task	(5 points)
Answer the following questions:	
<ul style="list-style-type: none"> • Why is a water molecule polar? • What is a hydrogen bond? • What are the values for the H-O-H angle in water and the typical distance of a hydrogen bond? • What are the main differences between various atomistic water models? • What is the difference between the SPC and the SPC/E water model? 	

Hints

- The above website provides some nice applets to play with. Anyway: Don't trust the results of the measurements you can make there!

3 Diffusion Processes - Ballistic and Diffusional Regime (7 points)

The Langevin equation is an effective description of particle diffusion in an *implicit* solvent. The interaction of particles with the surrounding solvent is replaced by their coupling to a virtual heat bath in the form of a dissipative and a stochastic force. The corresponding one-dimensional differential equation is given by

$$m \frac{dv(t)}{dt} = -\gamma v + \eta \quad (1)$$

with $\gamma = m\zeta$ and $\eta dt = \Gamma dW(t)$. The first term on the right hand side of the Langevin equation describes the dissipative force whereas the second term incorporates the stochastic force in terms of Gaussian white noise generated by a Wiener process.

Task (3 points)
Solve the Langevin equation to obtain $\langle v^2(t) \rangle$. Have a look at the hints below!

Hints

- First, obtain a general solution $v(t)$ of equation (1). The general solution of an equation of the form $\frac{dy(x)}{dx} + p(x)y(x) = q(x)$ is given by $y(x) = \frac{1}{u(x)} (\int_0^x u(x')q(x')dx' + C)$ with $u(x) = \exp(\int p(x)dx)$.
- Subsequently, obtain a particular solution: Determine the value of C by requiring $v(0) = v_0$ as an initial condition.
- The first and second moments of a Wiener process are given by $\langle dW(t) \rangle = 0$ and $\langle dW(t')dW(t'') \rangle = dt'$. This means that an integral $\int \langle dW(t) \rangle$ will vanish and a double integral of the form $\int_0^t \int_0^t f(t')f(t'')\langle dW(t')dW(t'') \rangle$ will simplify to $\int_0^t f^2(t')dt'$. Use this to obtain an expression for $\langle v^2(t) \rangle = \langle v(t)v(t) \rangle$.

In a canonical ensemble, particle velocities are Maxwell-Boltzmann distributed:

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{m}{2k_B T} v^2} \quad (2)$$

Thus, it follows for the expectation value of the kinetic energy per particle that

$$\langle E_{\text{kin}} \rangle = \frac{1}{2} m \langle v^2 \rangle = \int_0^\infty \frac{1}{2} m v^2 P(v) dv = \frac{1}{2} k_B T, \quad (3)$$

which is nothing but the equipartition theorem for one dimension.

Task (1 point)
Give an expression for Γ as a function of temperature in the limit of long time scales ($t \rightarrow \infty$).

Hints

- Use equation (3) together with the previously calculated expectation value $\langle v^2(t) \rangle$. Think about which terms vanish for $t \rightarrow \infty$!

Solving the Langevin equation (1) for the displacement $x(t) = \frac{dv(t)}{dt}$ assuming $x(0) = x_0 = 0$ allows to obtain the following expression for the mean square displacement:

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

For very short time scales, the displacement $x(t)$ can be approximated by the free particle term

$$\lim_{t \rightarrow 0} (x(t)) = v_0 t \quad (5)$$

Task (2 points)

- Use equation (5) together with the result of the equipartition theorem (3) to obtain an expression of $\langle x^2(t) \rangle$ for $t \rightarrow 0$ (ballistic regime).
- Use equation (4) in the limit of long time scales ($t \rightarrow \infty$) together with your result for Γ from the previous task to obtain an expression of $\langle x^2(t) \rangle$ for $t \rightarrow \infty$ (diffusional regime).
- How does $\langle x^2(t) \rangle$ scale with t in the respective cases?

The diffusion coefficient D is connected to the mean square displacement $\langle x^2(t) \rangle$ through the relation

$$\langle x^2(t) \rangle = 2n_d D t \quad (6)$$

with n_d being the number of dimensions (here $n_d = 1$).

Task

(1 point)

- Provide an expression for D using the result for $\langle x^2(t) \rangle$ at long time scales from the previous task.
- Compare your solution with the Stokes-Einstein equation. How is the drag coefficient γ related to solvent viscosity?

4 Atomistic Water Simulations with GROMACS (8 points)

In this exercise, you will perform several simulations with different water models using GROMACS to learn about their properties. GROMACS is a freely available Molecular Dynamics software package (www.gromacs.org). You can either use the computers in the ICP CIP pool or install GROMACS on your own computer. The simulations focus on the SPC, SPC/E and TIP3P water models.

4.1 Visualizing the System

Download the archive `templates.tar.gz` from the lecture website. After unpacking, you will find different files in the included directory:

- `conf.gro`: pre-equilibrated water structure with 216 solvent molecules
- `grompp.mpd`: parameters for the simulation
- `topol.top`: topology file for the water simulations including a link to the force field parameters
- `index.ndx`: file needed for the analyses

You can visualize the system using `vmd` (Visual Molecular Dynamics):

```
$> vmd conf.gro
```

In the `vmd` console, you can use the following command to show the simulation box:

```
> pbc box
```

Hint

- By default, all molecules are represented by lines only. To get a nicer looking visualization, use the menu in the “VMD Main” window and click on *Graphics > Representations...*. In the "Graphical Representations" dialog that will pop up, use the *Drawing Method* drop-down menu and select *CPK*.

4.2 Running the Simulations

For the different simulations, it is a good idea to run them in separate directories. Create three new directories named `spc`, `spce`, and `tip3p`. Copy the files from the archive into each of these directories.

First, we will start a simulation using the SPC water model. In order to have the required GROMACS commands available in your terminal, execute the following command:

```
$> source /group/sm/2016/tutorial_02/gromacs-4.6.7/bin/GMXRC
```

In order to prepare the first simulation, change to the `spc` directory and call the GROMACS preprocessor `grompp`:

```
$> cd spc
$> grompp
```

If `grompp` completed without errors, the simulation can be started with

```
$> mdrun -v
```

The system will then be simulated for 500 ps with a time step of 2 fs at 300 K.

Task	(3 points)
Perform one simulation for each of the water models.	

Hints

- To tell GROMACS which water model to use, open the `topol.top` files in the different directories and change the line
`#include "spc.itp"`
to
`#include "spce.itp"`
or
`#include "tip3p.itp"`
respectively.
- Use the commands `grompp` and `mdrun` for each simulation as described above.

4.3 Analysis

In the following tasks, you will analyze the simulation data in various ways. Luckily, GROMACS already comes with a variety of easy-to-use analysis tools – how convenient!

Radial Distribution Function

The radial distribution functions (RDFs) give a first hint on the local structure of the systems. To compute the RDFs, you can use the command

```
$> g_rdf -n index
```

Task

(2 points)

- Compute the RDFs of the three systems you have simulated.
- Compare the RDFs of the different water models and interpret the results (peaks, distances between peaks, differences between water models,...)

Hint

- You can use the program `xmgrace` to plot the output `rdf.xvg` files.

Hydrogen Bond Analysis

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

```
$> echo -e "0\n0" | g_hbond
```

Task

(1 point)

- Run the hydrogen bond analysis for the different water models.
- Calculate the average number of hydrogen bonds per water molecule. What is the meaning of donors and acceptors?

Mean Square Displacement

In three-dimensional space, the diffusion coefficient D can be calculated from the mean square displacement (MSD) function

$$\langle \Delta r^2(t) \rangle = 6Dt \quad (7)$$

for large enough t . You can calculate the MSD using GROMACS with

```
$> g_msd -n index
```


Task

(2 points)

- Compute the MSD for each of the different water models.
- Have a look at the output files `msd.xvg` for the different water models and compare them. What are the differences? Can you identify the diffusional ($\langle \Delta r^2(t) \rangle \propto t$) and the ballistic regime?
- Does the form of the ballistic regime look as you would expect it from the second last task in section 3? If not, try to explain why!