Worksheet 3: Diffusion processes and atomistic water model properties

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Contents

1 Short Questions - Short Answers

What are the main differences between various atomistic water models?

- Geometry - some are planar, some tetrahedral, also the location and size of partial charges can differ
- Polarizability - some models take it into account some don't
- Rigidness - some have fixed atom positions, others model atoms connected by "springs"

What is the difference between the SPC and the SPC/E water model?

The SPC/E model takes the averaged polarization effects into account, SPC doesn't.

What are the typical terms in an atomistic classical force field?

Typical terms for the potential are: $E_{bond}, E_{torsion}, E_{angular}, E_{van-der-Waals}$, E_{LJ} and $E_{coulomb}$

How is the Pauli exclusion principle incorporated into a classical force field?

It is incorporated into the energy expression of the Lennard-Jones interactions E_{LJ}. If two (non-bonded) atoms get too close to each other their electron clouds overlap which results due to Pauli repulsion in a very strong repulsive force between these atoms. In the Lennard-Jones potential the r^{-12}- term describes this strong (Pauli -) repulsion.

2 Theoretical Task: Langevin equation - Calculation of particle positions and velocities

In this theoretical task, the Langevin equation describing the Brownian motion has to be solved:

$$\mathrm{d}v = -\gamma v \ \mathrm{d}t + \frac{\Gamma}{m} \ \mathrm{d}W \tag{1}$$

The first term on the right hand side describes the dissipative force, the second the stochastic force.

2.1 Velocities of the particle

Since the average force in the Langevin equation is already included in the first force term, the stochastic second one has to be zero on average:

$$\langle \mathrm{d}W(t) \rangle = 0 \tag{2}$$

Therefore the second term can be neglected if one is only interested in computing the average force (force term one):

$$\mathrm{d}v = -\gamma v \; \mathrm{d}t \tag{3}$$

This differential equation can be easily solved by separation of variables, which leads to to following solution (with $v_0 = v(t=0)$):

$$v(t) = v_0 \cdot \mathrm{e}^{(-\gamma t)} \tag{4}$$

The stochastic fluctuations of the second term also fulfill the following relation:

$$\langle \mathrm{d}W(t_1)\mathrm{d}W(t_2) \rangle = \delta_{t_1,t_2} \; \mathrm{d}t_1 \tag{5}$$

An explicit formal solution can be obtained as

$$v(t) = v_0 \cdot \mathrm{e}^{-\gamma t} + \frac{\Gamma}{m} \int_0^t \mathrm{e}^{-\gamma(t-s)} \; \mathrm{d}W(s) \tag{6}$$

Now one can calculate:

$$\langle v(t_1)v(t_2) \rangle = \langle v_0 \cdot v_0 \rangle \cdot \mathrm{e}^{-\gamma(t_1+t_2)} + \left(\frac{\Gamma}{m}\right)^2 \int_0^{t_1} \int_0^{t_2} \mathrm{e}^{-\gamma \cdot (t_1+t_2-(s_1+s_2))} \; \langle \mathrm{d}W(s_2)\mathrm{d}W(s_1) \rangle \tag{7}$$

$$= \langle v_0^2 \rangle \cdot \mathrm{e}^{-\gamma \cdot (t_1+t_2)} + \left(\frac{\Gamma}{m}\right)^2 \int_0^{\min t_1,t_2} \mathrm{e}^{-\gamma \cdot (t_1+t_2-2s)} \; \mathrm{d}s \tag{8}$$

$$= \langle v_0^2 \rangle \cdot \mathrm{e}^{-\gamma \cdot (t_1+t_2)} + \left(\frac{\Gamma}{m}\right)^2 \frac{1}{2\gamma} \mathrm{e}^{-\gamma \cdot (t_1+t_2)} \left(\mathrm{e}^{2\gamma \min t_1,t_2} - 1\right) \tag{9}$$

For $t_1 = t_2 = t$ this results in

$$\langle v(t)^2 \rangle = \langle v_0(t)^2 \rangle \cdot \mathrm{e}^{-2\gamma t} + \left(\frac{\Gamma}{m}\right)^2 \frac{1}{2\gamma} \mathrm{e}^{-2\gamma t} \left(\mathrm{e}^{2\gamma t} - 1\right) \tag{10}$$

$$= \langle v_0(t)^2 \rangle \cdot \mathrm{e}^{-2\gamma t} - \frac{\Gamma}{2m\gamma} \mathrm{e}^{-2\gamma t} + \left(\frac{\Gamma}{m}\right)^2 \frac{1}{2\gamma} \tag{11}$$

$$= \left(\langle v_0(t)^2 \rangle - \frac{\Gamma}{2m\gamma}\right) \mathrm{e}^{-2\gamma t} + \left(\frac{\Gamma}{m}\right)^2 \frac{1}{2\gamma} \tag{12}$$

Since in equilibrium we must have the equipartition theorem for one dimension ($\langle v(t)^2 \rangle_{\mathrm{eq}} = k_{\mathrm{B}} \cdot T/m$, in three dimensions the right hand side would have to be multiplied by three) Γ can be calculated (for $t \to \infty$ the first part of equation 12 vanishes):

$$\Gamma = \sqrt{2\gamma k_{\mathrm{B}} T m} \tag{13}$$

2.2 Position of the particle

By integrating equation 6 we get an expression for the position.

$$x(t) = x_0 + \int_0^t \left[v_0 \cdot e^{-\gamma u} + \frac{\Gamma}{m} \int_0^u e^{-\gamma(u-s)} \, dW(s) \right] du \tag{14}$$

$$= x_0 + \frac{v_0}{\gamma} \left(1 - e^{-\gamma t}\right) + \frac{\Gamma}{m} \int_0^t dW(s) \int_s^t e^{-\gamma(u-s)} du \tag{15}$$

$$= x_0 + \frac{v_0}{\gamma} \left(1 - e^{-\gamma t}\right) + \frac{\Gamma}{m\gamma} \int_0^t \left(1 - e^{-\gamma(t-s)}\right) \, dW(s) \tag{16}$$

For the mean position, the last term gets zero because of it dependents on $dW(s)$. So the result is:

$$\langle x(t) \rangle = x_0 + \frac{v_0}{\gamma} \left(1 - e^{-\gamma t}\right) \tag{17}$$

This gives us in the limit of ...

- short time scales $(\gamma t << 1)$: $\langle x(t) \rangle \approx x_0 + v_0 \cdot t$
- long time scales $(\frac{1}{\gamma t} << 1)$: $\langle x(t) \rangle \approx x_0 + \frac{v_0}{\gamma}$

In addition, equation 16 results in the following mean-square displacement:

$$\langle \Delta x(t)^2 \rangle = \langle (x(t) - \langle x(t) \rangle)^2 \rangle = \langle x(t)^2 \rangle - (\langle x(t) \rangle)^2 \tag{18}$$

$$= \left(\frac{\Gamma}{m\gamma}\right)^2 \int_0^t \int_0^t \left(1 - e^{-\gamma(t-s_1)}\right) \left(1 - e^{-\gamma(t-s_2)}\right) \langle \, dW(s_1) \, dW(s_2) \rangle \tag{19}$$

$$= \left(\frac{\Gamma}{m\gamma}\right)^2 \int_0^t \left(1 - e^{-\gamma(t-s)}\right)^2 \, ds \tag{20}$$

$$= \frac{2k_B T}{m\gamma} \int_0^t 1 + e^{-2\gamma(t-s)} - 2e^{-\gamma(t-s)} \, ds \tag{21}$$

$$= \frac{2k_B T}{m\gamma} \left(t + \frac{4e^{-\gamma t} - e^{-2\gamma t}}{2\gamma} - \frac{3}{2g} \right) \tag{22}$$

For long time scales the exponential functions approx zero. It results in:

$$\langle \Delta x(t)^2 \rangle \propto \frac{2k_B T}{m\gamma} t \tag{23}$$

With the equation $\langle \Delta x(t)^2 \rangle = 2Dt$ (for three dimensions $6Dt$) you get the following diffusion constant:

$$D = \frac{k_B T}{m\gamma} \tag{24}$$

3 Computational Task: Atomistic water simulations with GROMACS

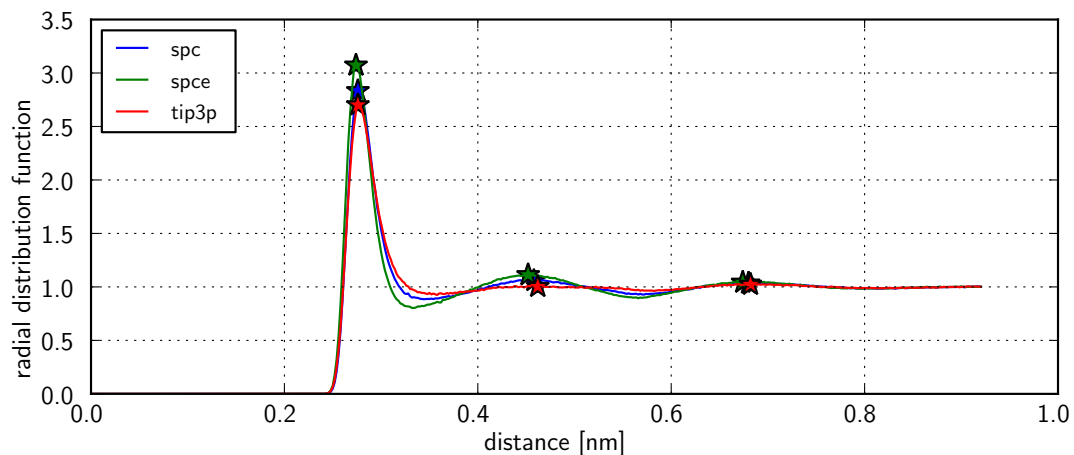## 3.1 Radial distribution function

Figure 1: Radial distribution function. The peaks are marked with stars.

All water models give similar distances for the peaks. The height and visibility of the peaks is very different, however. *SPC/E* produce the highest and *TIP3P* the lowest maxima. *SPC* is in between.
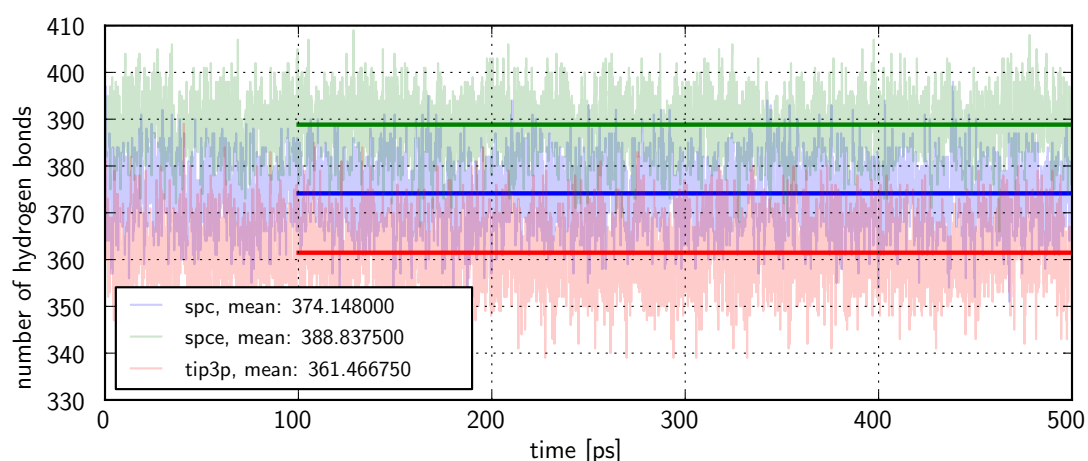
3.2 Hydrogen bond analysis

Figure 2: Fluctuation of the number of hydrogen bonds.

The water molecule works as a donor and an acceptor for hydrogen bridges due to its electronegative oxygen and electropositive hydrogen. The number of hydrogen bonds fluctuates.

The average was calculated starting at $100\,\text{ps}$ to ensure equilibrium. *SPC/E* yields the highest and *TIP3P* the lowest value. The difference between the values is up to $9\,\%$.
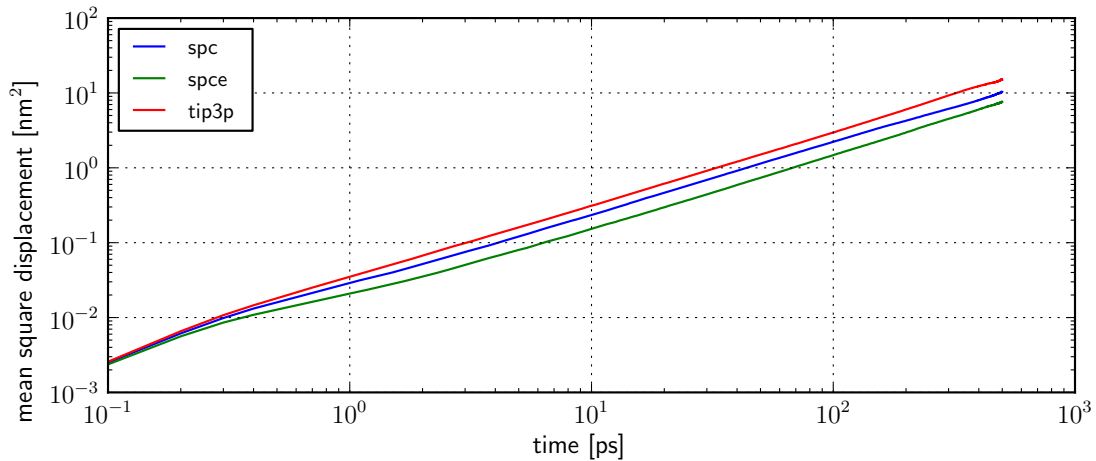
3.3 Mean-square displacement

Figure 3: Mean-square displacement.

The full-logarithmic plot of the mean-square displacement $< \Delta r(t)^2 >$ shows the existence of two regimes. Until $0.3\,\text{ps}$ the slope is higher than afterwards. In theory the slope at the beginning has to be twice as high because of the quadratic time-dependence of the means-square displacement in the ballistic regime. In the following linear regime the displacement is proportional to the time itself.
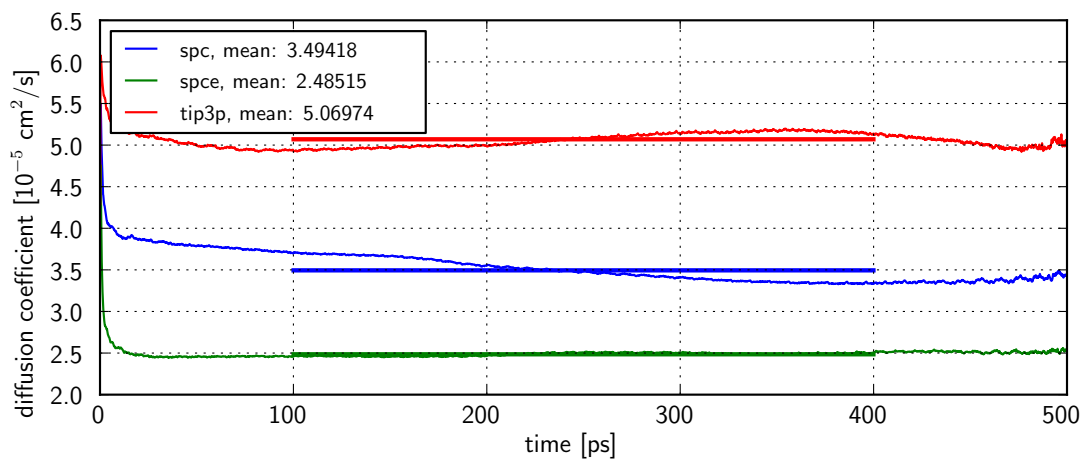

Figure 4: Diffusion coefficient.

The formula $< \Delta r(t)^2 > = 6Dt$ was used to to calculate the diffusion coefficient D. The average values were determined between $100\,\text{ps}$ and $400\,\text{ps}$.