Worksheet 3: Diffusion processes and atomistic water model properties

April Cooper, Patrick Kreissl und Sebastian Weber

June 17, 2013

University of Stuttgart

Contents

1 Short Questions - Short Answers **2**

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

2.1 Velocities of the particle 2

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: $\langle \mathrm{d}W(t) \rangle = 0$. Therefore the second term can be neglected if one is only interested in computing the average force (force term one):

$$\mathrm{d}v = -\gamma v \ \mathrm{d}t \tag{2}$$

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

$$v(t) = v_0 \cdot \mathrm{e}^{(-\gamma t)} \tag{3}$$

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

$$\langle \mathrm{d}W(t)\mathrm{d}W(t')\rangle = \mathrm{d}t' \tag{4}$$

An explicit formal solution can be obtained as

$$v(t) = v_0 \cdot \mathrm{e}^{-\gamma t} + \frac{\Gamma}{m}\int_0^t \mathrm{e}^{-\gamma(t-s)} \ \mathrm{d}W(s) \tag{5}$$

Now one can calculate:

$$\langle v(t_1)v(t_2)\rangle = \langle v_0(t_1)v_0(t_2)\rangle \cdot \mathrm{e}^{(-\gamma(t_1+t_2))} + \frac{\Gamma}{m}\int_0^{t_1}\int_0^{t_2} \mathrm{e}^{-\gamma\cdot(t_1+t_2-(s_1+s_2))} \ \mathrm{d}W(s_2)\mathrm{d}W(s_1) \tag{6}$$

$$= \langle v_0(t)^2\rangle \cdot \mathrm{e}^{-\gamma\cdot(t_1+t_2)} + \frac{\Gamma}{m}\int_0^{\min t_1,t_2} \mathrm{e}^{-\gamma\cdot(t_1+t_2-2s)} \ \mathrm{d}W(s) \tag{7}$$

$$= \langle v_0(t)^2\rangle \cdot \mathrm{e}^{-\gamma\cdot(t_1+t_2)} + \frac{\Gamma}{2m\gamma}\mathrm{e}^{-\gamma\cdot(t_1+t_2)}\left(\mathrm{e}^{2\gamma\min t_1,t_2} - 1\right) \tag{8}$$

For $t_1 = t_2 = t$ this results in

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

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

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

Since in equilibrium we must have the equipartition theorem for one dimension ($\langle v(t)^2\rangle_{\mathrm{eq}} = k_{\mathrm{B}} \cdot T$, 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 11 vanishes):

$$\Gamma = 2m\gamma k_{\mathrm{B}}T \tag{12}$$

Therefore the velocity of one particle can is given by

$$v(t) = v_0 \cdot \mathrm{e}^{-\gamma t} + 2\gamma k_{\mathrm{B}}T\int_0^t \mathrm{e}^{-\gamma(t-s)} \ \mathrm{d}W(s) \tag{13}$$