

Molekulardynamik (SS10) Übungsblatt 5

Liquid water II

1 Hydrogen bonds in SPC/E water

A common definition for a hydrogen bond in water is that the donor-hydrogen-acceptor angle is less than 30° and that the donor-acceptor distance is less than the distance where the first minimum in the oxygen-oxygen RDF occurs. Calculate the number of hydrogen bonds on a simulation of SPC/E water at 300 K temperature and 1 bar pressure. What is the average number of hydrogen-bonds per water molecule? How does this number compare to ice, where every water molecule participates in 4 hydrogen bonds? Calculate also the distance and angle distribution of the hydrogen-bonds? What is the average distance/angle ?

The SPC/E water model is rigid (OH and HH distance kept fixed), has a partial charge of $-0.8476 e$ on the oxygen atom, and has only one Lennard-Jones interaction site on the oxygen atom ($\sigma = 0.3166 \text{ nm}$, $\epsilon = 0.65 \text{ kJ/mol}$).

Use the program g_hbond to calculate the number of hydrogen bonds and the distance/angle distributions:

```
$ g_hbond -n index.ndx -num -dist -ang
```

2 The heat of vaporization of SPC/E water

Calculate the heat of vaporization of SPC/E water at $T = 300 \text{ K}$ and $p = 1 \text{ bar}$. The gas phase is approximated as an ideal gas. Compare the result to the experimental value

$$\Delta H_{\text{vap}} = -41.5 \text{ kJ/mol.}$$

What could be the reason for the different result?

Use the program g_energy to calculate the energy of the system.

3 The heat capacity at constant volume of SPC/E water

We calculate the heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

of SPC/E water.

a) In a straightforward approach, we perform three simulations in the NVT ensemble at 290 K, 300 K, and 310 K. In every simulation, we calculate the average of the total internal energy U . C_V is obtained by numerical differentiation. Split the result into electrostatic contributions, Lennard-Jones contributions, and kinetic contributions. Which part dominates? Compare the kinetic contribution to the heat capacity of an ideal gas. Compare the oxygen oxygen radial distribution functions for the three temperatures and interpret the observed trend with regard to the results for C_V .

Start from a system, where the density is converged at a pressure of 1 bar at $T = 300$ K. Use a Nose-Hoover thermostat. The energy and it's different contributions can be calculated with the program `g_energy`. Note that the short- and long-range contributions of the electrostatic energy are listed separately, as well as the long-range correction for the Lennard-Jones energy. The radial distribution function can be calculated with the program `g_rdf`.

b) Use the relation

$$k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{N,V} = \sigma_U^2 = \langle U^2 \rangle - \langle U \rangle^2.$$

Perform simulations for a Berendsen thermostat and for a Nose-Hoover thermostat. Which method gives the correct results? Why? Can we also split these results into electrostatic contributions, Lennard-Jones contributions, and kinetic contributions?

c) Can we get results for the same temperature and particle number, but for a larger box volume? Increase the box vectors of your system by 20% and repeat the simulation. What do you observe?

4 Diffusion at high pressure

a) Perform a simulation of the Lennard-Jones fluid simulated in exercise sheet 4 for a temperature of 188K at 100 bar, 1000 bar and 5000 bar. Calculate the diffusion constant D and the radial distribution function $g(r)$. Interpret the pressure dependence of your results.

b) Perform simulations of SPC/E water for a temperature of 230 K and pressures of 1 bar and 3000 bar and for a temperature of 300 K and pressures of 1 bar, 3000 bar and 10 000 bar. Calculate the diffusion constant D and the oxygen-oxygen radial distribution function $g_{OO}(r)$. Interpret the pressure dependence of your results.

Use the programs `g_msd` and `g_rdf` to calculate the diffusion constant and the radial distribution function. See the instructions on exercise sheet 4.