# Excercise 6

Let us study some Ar and water. For help see the end of the assignment pdf.

**Assignment 1. (1/2)** Wan der Waals equation. The van der Waals equation is a generalization of the ideal gas law and reads

$$\left(p + a\rho^2\right)(1/\rho - b) = k_B T,$$

where $\rho = N/V$. Solve your values for $a$ and $b$ by runing NVE simulations of your choice for gaseous Ar. Visualize. Monitor equilibration and after you have found a point in picoseconds, perform the analysis. (You might want to adjust box size which you can find on the last line of your starting.gro. You can use **-b** option in **g_energy** to start your analysis from that point on in ps)

**g_energy -b [t_eq] ...**

When giving your solution for $a$ and $b$, also convince the assistant with curves of your choice that you have thermalized the sample and that your simulation is numerically stable. Can you make any estimate the error of your values? Would one expect to find a relation between the parameter $b$ and $\sigma^{LJ}$? If, what would you guess it to be, and how do your simulations perform?

**Assignment 2. (1/2)** Hydrogen bonding in water. Simulate water with the TIP4P/2005 force field at points A=(22°C, 0.1Mpa), B=(200°C, 1.6 MPa), C=(400°C, 48MPa) and D=(600°C, 134MPa). Convince the assistant that you have thermalized the sample and that your simulation is numerically stable. For the simulated, systems calculate number of hydrogen bonds using **g_hbonds** and compare your results to those of Sahle *et al.* PNAS (2013).

**Assignment 3. 0 points, returned anonymous** We are committed in putting a lot of effort to improving and find your feedback invaluable. So, please spend 5 minutes giving constructive feedback
*https://elomake.helsinki.fi/lomakkeet/45626/lomake.html*
Thank you!

# Results of Sahle et al.

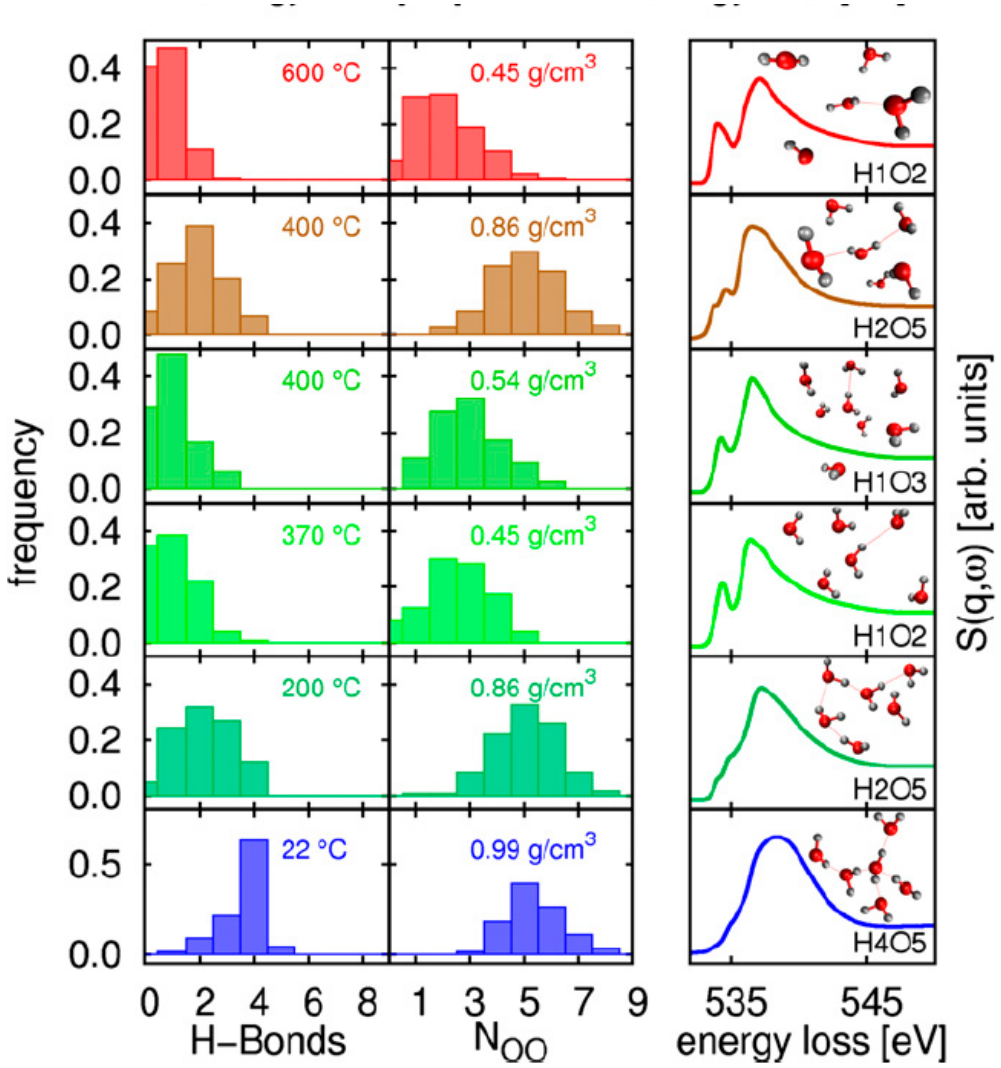


**Fig. 4.** (*Lower Left*) Distribution of the number of H-bonds of the central water molecule in the clusters extracted from the different MD snapshots for all pressure and temperature conditions estimated by geometric criteria (details are provided in main text). (*Lower Center*) Same except for the number of oxygen neighbors within 3.6 Å from the central oxygen atom. (*Lower Right*) Averages over XRS spectra calculated for snapshots resembling the most frequently occurring subset of configurations from the histograms (*Lower Left*) as well as representative stick and ball plots of these motifs. arb., arbitrary. (*Upper*) Comparison of calculated XRS spectra of similar local motifs for different *p*, *T* conditions (details are provided in main text).

# Force field for water

For Ar it was OK to give the parameters explicitly in the top file. For molecules, one naturally uses databases – like the one provided with gromacs. Now you will still get a top file **tip4p2005.top**, but please take a look at it. We seem to have everything for simulation except the starting $\mathbf{r}_0$... To generate a box of 4-point water from snapshot of thermalized 216 molecules (**WAT216.tip4p.gro**) take the following route (or code it yourself).It is instructive to start from **empty.gro**. Have a look at it and then type.

**editconf -f empty.gro -bt cubic -d 1.70 -o box.gro**

Take a look at **box.gro** and continue

**genbox -cp box.gro -cs WAT216.tip4p.gro -p tip4p2005.top -o thething.gro**

Now take a look at **thething.gro** and check it with vmd. You can of course play with the radius above. Make sure that your top file now contains the correct number of waters. Running of the stuff we know already.

# Changes in inputs

Some self-explaining changes/additions to the .mdp files for water simulations:

```
; ELECTROSTATICS
coulombtype              = pme ; particle-mesh ewald summation as water has charges.
                               ; We will learn this soon.
; OPTIONS FOR BONDS
constraints              = all-angles ; In addition to constraints defined in
                                      ;topology, convert all bonds and angles
                                      ;to bond-constraints. Now the water is rigid
; Type of constraint algorithm
constraint-algorithm     = shake    ;Optionally one can leave this out and
                                    ; apply the default algorithm LINCS
shake-tol                = 0.0001     ; The default
; Do not constrain the start configuration
continuation      = no             ; IS IT CONTINUATION OR NOT
```