FYS2160, lab2: Phase transitions, numerical part
Phase coexistence by MD and in the van der Waals equation of state

In this project you will study the gas–liquid phase equilibrium of the van der Waals fluid. You will compare the heat of vaporisation of the van der Waals fluid to that of water and to Trouton's rule. To do so you will use both analytical and numerical methods. You will also do MD simulations of ice, water and water vapour and discuss the order, entropy and latent heats in relation to the experiments and Trouton's rule.

You should do the weekly exercise week 42 to prepare for this lab. Many of the concepts are introduced there and important derivations you will need are made in that exercise.

Document your work and what you learn and deliver one single, coherent "report" with the following requirements

- include both experiments, analytical and numerical work in the same report

- the report should have the following parts

  - "Introduction"
  - Main body. This includes (methods,) results and discussion, but you may subdivide the text in any way you find best.
  - "Summary" or "Conclusions"

- there should be a red thread through the report connecting the different parts. This should be established in the Introduction. The results should be discussed in relation to the red thread and in the end you should summarise the relations between the different parts of the study and how they relate to the red thread.

- the report and all figures and labels should be easily readable.

- do not copy text, lists of equipment and units and procedures and method descriptions from the lab texts.

- do include your observations of events and difficulties during your experimental and numerical work.

- the report should be delivered at the end of the day.

- the report should be a single PDF file.

You have to formulate your own red thread, but in this Lab the keywords are *latent heat, Trouton's rule, water, microscopic structure, order and entropy.*

I. MOLECULAR DYNAMICS OF ICE, WATER AND VAPOUR

In this subproject you will perform MD simulations in Lammps to get a feel for the structure and dynamics of the three phases of water, ice 1h (the common form of ice we all know), liquid water and water vapour. Do the simulation, study the output and include your observations in the report. Try to include both direct observations and what you can infer about entropy and latent heat.

One key part of this lab, is that you will not run multiple independent Lammps-simulations. Instead, the end of each simulation you run will be used as the starting point for the next. The first simulation you will run is that of ice. After this, you will run a simulation to melt the ice. Before evaporating the ice, you will first have to run a short simulation to expand the simulation cell, before you finally melt the ice.

We have borrowed starting configuration and thermalization procedures from O'Brien [1]. Go the web page and download the three files `water.in`, `forcefield.SPCE` and `restart.250K`. The first file is the input file for running the Lammps simulations. The second is a file determining the interaction between atoms in the simulations. This is read by the input file. The third file is a restart file, which contains the positions and velocities of the atoms at the end of a simulation that previously ended at 250 K. This file is also read by the input file and used as the starting point for the first simulation you will run.

- First you will run an ice simulation. Depending on your computer, the simulation will take between 5 and 10 minutes.

  - Put the input files `water.in`, `forcefield.SPCE` and `restart.250K` in your simulation directory.

- Make a copy of the input file, naming it `water_251K.in`. You will now edit `water_251K.in` to run 10 000 timesteps at 251 K, dumping the trajectory information every 10th timestep.
- Line 2: `variable T equal 251`
- Line 39: `run 10000`
- Run the simulation: `lmp -in water_251K.in`.
-

While waiting for the simulation to end, we will try to understand what the input file does. In line 7, `restart.250K` is read, and used as the starting point of our simulation. In line 26, we choose to run the simulation at a fixed volume, temperature and number of particles. That is, the temperature of the box is held at 251 K throughout the simulation (I think), making the ice increase its temperature by 1 K. The dump file created should be named `water_251K.lammpstrj`. This is automatically ensured by the temperature variable `$T`. Once the simulation is done, you should have a file named `restart.251K`, which is specified in line 40.

- Change the name of the log-file `log.lammps` to `log_water_251K.lammps` to prevent it being overwritten.
- Do *not* change the name of the `.lammpstrj` file, as the new dump files we create will get a different name automatically when we run the next simulations at different temperatures.
- Open the trajectory file in Ovito to visualise the simulation. Discuss and comment.

- Now you will melt the ice, starting from the end of our previous simulation. We will double the steps of this simulation, to 20 000 timesteps, so the simulation will take between 15 and 25 minutes to complete.
  - Make a copy of the input file `water_251K.in`, naming the new file `water_300K.in`.
  - Line 2: `variable T equal 300` (choosing a temperature above the melting point).
  - Line 7: `read_restart restart.251K`
  - Since ice and water have different densities you have to run the simulation in the (NPT) ensemble instead of the (NVT) ensemble to allow the volume change:
    Comment out the nvt line (line 26).
    Uncomment the npt line (Line 28).
  - Line39: `run 20000`
  - Run the simulation: `lmp -in water_300K.in`.
  - Once the simulation is done, change the name of the log-file `log.lammps` to `log_water_300K.lammps`.
  - Plot the energies (E_{tot} and H) dumped in `log.lammps` and discuss.
  - Open the trajectory file in Ovito to visualise the simulation. Can you observe some of the structures mentioned in the appendices in the experiment lab text? Discuss and comment.

- Because it is unlikely to get vapour nucleation in the tiny liquid volume you must first expand the simulation cell. When looking at the previous simulations in Ovito you probably noticed that the particles have little free space to move around.
  - Make a copy of the input file `water_300K.in`, naming the new file `water_301K.in`.
  - Line 2: `variable T equal 301` (Only increasing the temperature to prevent file overwriting).
  - Line 7: `read_restart restart.300K`
  - Line 23: Uncomment the line `fix 2 all deform...`
  - Line 26: Uncomment the nvt line.
  - Line 28: Comment out the npt line.
  - Line 39: `run 2000`.
  - After the simulation is done, change the name of the log-file `log.lammps` to `log_water_301K.lammps`.
  - Visualise the simulation in Ovito. Discuss and comment.

- Now, we want to evaporate the water. However, this takes very long time. On my computer it took roughly 1.5 hours with 5 000 timesteps. Running this simulation is therefore voluntary, and should only be done **after** you have completed the next section of the lab, where you will study phase transitions of a Van der Waals system.

- The log file from an evaporation simulation can be found on the course web page.

- Download this file, named `log400K.in`.

- Plot the energies (E_{tot} and H) from this simulation, visualise and discuss.

- Proceed to section II to study the van der Waals fluid.

    - If you have *completed* the Van der Waals exercise and *want* to run the evaporation simulation, you can do so by doing the following:
    - Rename the input file `water_301K.in` to `water_400K.in`.
    - Line 2: `variable T equal 400`
    - Line 7: `read_restart restart.301K`
    - Line 23: Comment out the line `fix 2 all deform...`
    - Line 26: Comment out the nvt line.
    - Line 28: Uncomment the npt line.
    - Line 39: `run 5000` (Or lower if you want, you may get decent results with fewer steps).
    - Visualise the result in Ovito and discuss.

II. VAN DER WAALS EQUATION OF STATE

The van der Waals fluid is a mean field theory of a gas. It is a model system, just as the ideal gas, although it includes more features of realistic gases. The van der Waals gas includes two of the main effects of an attractive two-particle interaction between particles in the gas: a repulsive interaction that keeps particles apart, and an attractive long-range interaction that pulls particles together. These two effects leads to two changes in the Helmholtz free energy of the gas, as compared to an ideal gas: Instead of the volume V we introduce the effective volume, $V - Nb$, where the volume b is the excluded volume per particle, and we introduce an average binding energy, $-a(N/V)^2$. Helmholtz free energy for the van der Waals fluid is:

$$F = -NkT \left(\ln \left(\frac{n_Q \cdot (V - Nb)}{N} \right) + 1 \right) - \frac{aN^2}{V} \, , \tag{1}$$

where $n_Q(T) = \left(2\pi mkT/h^2 \right)^{3/2}$ is a function of T only.

In this lab you are to find if the van der Waals fluid liquid – gas phase transition follows the Trouton rule $\frac{H_v}{NkT_b} \approx 11$, where H_v is the heat (enthalpy) of vaporisation and T_b is the boiling temperature. In order to do this you will need to do some analytical work and some numerical work. Here is a list of tips:

- From the Helmholtz free energy of the van der Waals fluid, calculate analytically

    - the pressure, $P = -\left(\frac{\partial F}{\partial V} \right)_{T,N}$
    - Gibbs free energy, $G = F + PV$

- Use the critical parameters

$$P_c = \frac{a}{27b^2} \, , \ V_c = 3Nb \, , \ kT_c = \frac{8a}{27b}$$

to express

    - the reduced parameters

$$\hat{V} = V/V_c, \ \hat{T} = T/T_c, \ \hat{P} = P/P_c = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2} \, ,$$

    - and the dimensionless Gibbs free energy per particle

$$\hat{G} = \frac{8G}{3NkT_c} = -\frac{8}{3}\hat{T}\ln(3\hat{V} - 1) - \frac{3}{\hat{V}} + \hat{P}\hat{V} + f(\hat{T})$$

- $f(\hat{T})$ depends only on $\hat{T}$ and not on $\hat{P}$ or $\hat{V}$. You can therefore neglect this part in the next steps where you will study how $\hat{G}$ varies with $\hat{P}$ and $\hat{V}$. See section 9.5.3 of the compendium.
- Hint: $n_Q(T)$ has dimension of inverse volume, whereas $bn_Q(T)$ is dimensionless.

- For a range of $\hat{T}_b$ between 0.4 and 1, plot $\hat{P}(\hat{V})$, $\hat{G}(\hat{V})$ and $\hat{G}(\hat{P})$, for a suitable range of volumes, $\hat{V}$ such that the self-interaction point (see Figure 1) is included. (Explain in more detail how to plot this)

- Determine the coexistence line numerically. Use the equalities of pressure and Gibbs free energy at phase coexistence, $P_l = P_g$, $G_l = G_g$ to determine the gas – liquid coexistence line $\hat{P}_b(\hat{T}_b)$. (Elobarate on eyeballing.)

- Plot the coexistence line $\hat{P}_b(\hat{T}_b)$ for $\hat{T}_b$ between 0.4 and 1. (Explain how they should loop through T-values.)

- Determine the volume change $\Delta\hat{V}$ for each temperature. (Explain what the volume change is.)

- Estimate roughly how accurately your coexistence line is (no calculation required). (Rewrite)

- Use the Clausius-Clapeyron relation to determine the latent heat (heat of vaporisation) H_v numerically for the van der Waals fluid using the coexistence line you just determined. (elaborate)

- It is found that for simple liquids the ratio $H_v/(RT_b) \sim 10$ between the enthalpy of vaporisation, H_v and the normal boiling point temperature, T_b. Over a much larger range of noble gases, organic and inorganic liquids and metals one finds $H_v/(RT_b) \sim 12$. This has been named Trouton's rule. Calculate $\hat{H}_v/\hat{T}_b$ for the van der Waals fluid and plot it versus $\hat{T}_b$.

- Use the principle of corresponding states to map the van der Waals fluid to water that has critical temperature T_c=647.096 K and pressure P_c=22.064 MPa. Which $\hat{T}$ and $\hat{P}$ does "normal water boiling point" pressure (1 atm) and temperature (373 K) correspond to?

- It has been argued that Trouton's rule follows from the principle of corresponding states. Do you agree?

- Can you find an alternative explanation for Trouton's rule using the entropy change during vaporisation?

The MD simulations will be done with input and output in "style" *real* units that are (see http://lammps.sandia.gov/doc/units.html)

- mass = grams/mole
- distance = Angstroms
- time = femtoseconds
- energy = Kcal/mole
- velocity = Angstroms/femtosecond
- force = Kcal/mole-Angstrom
- torque = Kcal/mole
- temperature = Kelvin
- pressure = atmospheres
- dynamic viscosity = Poise
- charge = multiple of electron charge (1.0 is a proton)
- dipole = charge*Angstroms
- electric field = volts/Angstrom
- density = gram/cm$^d im$
- calorie = 4.184 J

[1] Chrstopher O'Brien. Working with water in Lammps, 2020. URL https://sites.google.com/a/ncsu.edu/cjobrien/tutorials-and-guides/working-with-water-in-lammps.
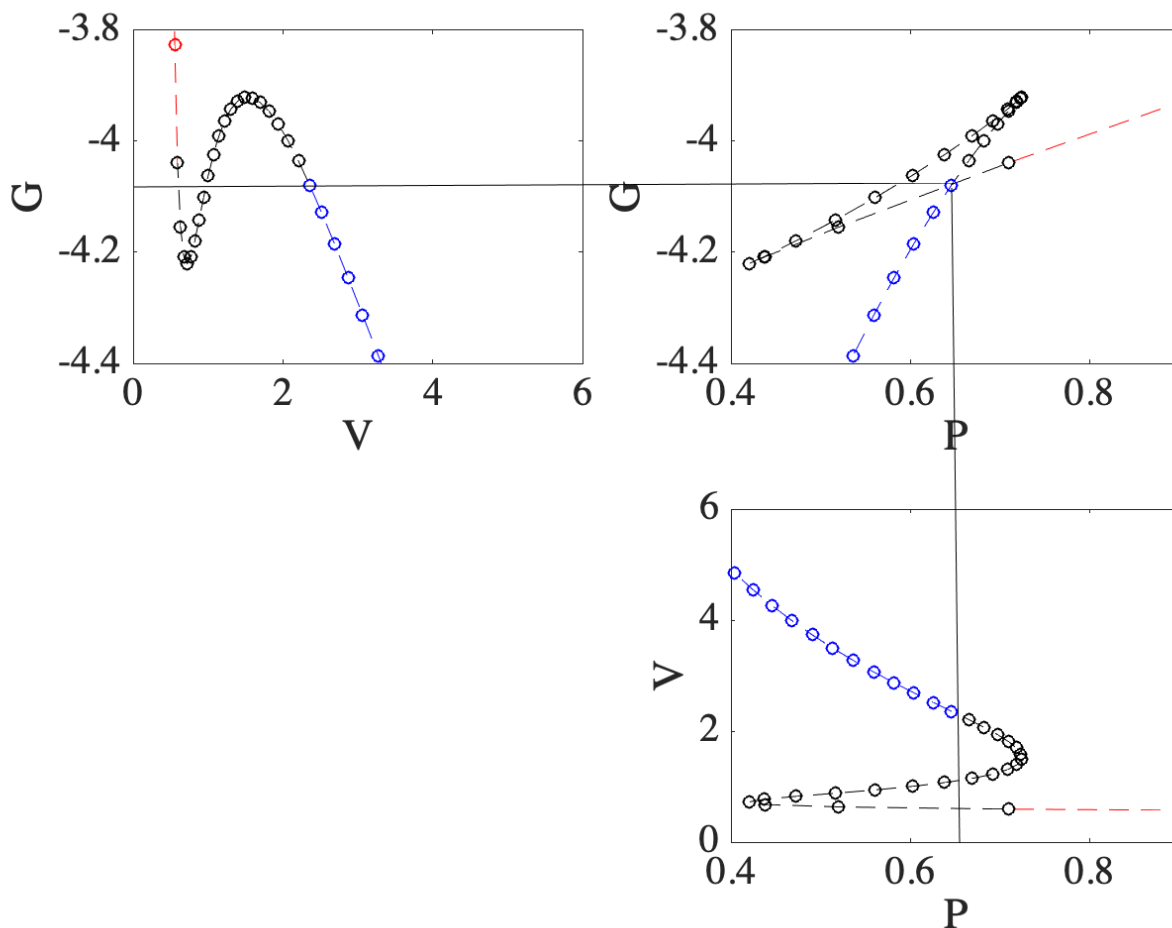
FIG. 1: Plots of reduced Gibbs free energy at $\hat{T} = 0.9$ and pressure for the same reduced volumes. The red part of the curve corresponds to the liquid phase, the blue part is the gas phase and the black part is the unstable part of the curve corresponding to the liquid-vapour coexistence. The black lines demonstrate how the equal area construction to find the coexistence pressure $\hat{P}_b(\hat{T}_b)$ corresponds to the self intersection of the $\hat{G}(\hat{P})$ curve.