Fys2160 Lab2

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Abstract

In this assignment we looked into the phase transitions of water, trying to gain a greater understanding of the processes taking place during these transitions. We estimate values for the enthalpy involved in these transitions, and managed to show that the gas-liquid phase transition of water somewhat adheres to Trouton's Rule. We found the relation $H_v/(RT_b)$ to be $13.8kJ/mol$ numerically, while the relation was theoretically expected to be $11 \pm 1kJ/mol$. We explained this deviation to the theory by dipole-dipole interaction between water molecules. The numerical simulations showed a linear relationship between the energy and enthalpy of the system, no matter the phase.

1 Introduction

In this report we wish to study and gather a better understanding of important properties of water, as well as phase transitions. Firstly, we will be conducting experiments on various phases of water to better understand calorimetry principles, gain insights into phase transitions, and understand fascinating water properties. Secondly, we're performing MD simulations using Lammps software to study the gas-liquid phase equilibrium of the van der Waals fluid. This involves simulating ice, water, and water vapor, with aim to match our findings with Trouton's rule.

2 Theory

We can study the heat needed for water to change phases from solid to liquid, and liquid to gas, in two different ways. We can explain the phase transitions of water, by theory presented in the course FYS2160.

2.1 Transition from liquid to vapor

We can use the formula

$$m[H_m + C_v(T_2 - T_0)] = C_0(T_1 - T_2)$$

to describe a system in which ice is melting. Here, m is the mass of ice, and our value C_0 can be found by the formula $C_0 dT/dt = UI$, and $C_v = 4200J(kgK)$ $T_0 = 0^oC$, and T_1 and T_2 are start and end time.
The value H_m, is the latent heat, or the heat it takes to melt the ice into liquid form, which we will try to find experimentally.

2.2 The transition for liquid-vapor

When a liquid turns from a phase of liquid into vapor, one would expect it to act according til Trouton's rule. Trouton's rule is a rule for gas vaporization, that implies

$$\frac{H_v}{RT_b} = 11 \pm 1$$

where H_v is the enthalpy of vaporisation and T_b is the boiling temperature, which we set to $T_b = 100$. This is a result of the assumption that there is an equilibrium between the vapor-gas and liquid within our system, and Gibbs free energy therefore is set to 0 for said system - The Clausius-Claperyon relation. This leaves us with said expression for Trouton's rule. We can further deduce the expression

$$ln\frac{P_1}{P_2} = -\frac{H_v}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

2.3 Numerical part: phase coexistence

The van der Waals fluid model imporves the ideal gas theory, accounting for attractive and repulsive interactions. This alters the Helmholtz free energy equation by introducing an effective volume $(V - Nb)$ and an average binding energy $(-a(N/V)^2)$. Helmholtz free energy for the van der Waals fluid is:

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

We have to do some analytical work, before we start exploring water properties numerically. We want to study the relations between Gibbs free energy, pressure and volume.

$$P = -\frac{dF}{dV} \quad G = F + PV$$

We will use the critical parameters:

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

to express the reduced parameters:

$$\hat{V} = V/V_c \quad \hat{P} = P/P_c \quad \hat{T} = T/T_c$$

We start with $\hat{P}$:

$$P = -\frac{dF}{dV} = NkT\frac{1}{V - Nb} - \frac{aN}{V^2}$$

$$\hat{P} = P/P_c = \frac{8\hat{T}}{3\hat{V}-1} - \frac{3}{\hat{V}}$$

We can use this to express the reduced Gibbs free energy:

$$\hat{G} = \frac{8G}{3NkT_c} = \frac{8(F+PV)}{3NkT_c}$$

I will split this expression in two for simplicity:

$$\frac{8F}{2NkT_c}$$

$$= -\frac{8\hat{T}}{3}\left(\ln\frac{n_Q}{b} + \ln(V/(Nb)-1)+1\right) - \frac{8aN}{3kT_cV}$$

$$= -\frac{8\hat{T}}{3}\ln(3\hat{V}-1) + f(\hat{T}) - \frac{27bN}{V}$$

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

Where $f(\hat{T}) = -\frac{8}{3}\hat{T}(\ln\frac{n_Q}{b}+1)$. Now for the second part:

$$\frac{8PV}{3NkT_c} = \frac{8NkTV}{3NkT_c(V-Nb)} - \frac{8aN}{3kT_cV}$$

$$= \frac{8V\hat{T}}{3V-Nb} - \frac{8aN27b}{3(8a)V}$$

$$= \frac{8\hat{T}\hat{V}}{3\hat{V}-1} - \frac{3\hat{V}}{\hat{V}^2} = \hat{P}\hat{V}$$

Combine these and get:

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

3 Method

As explained, we wish to study the physics behind phase changes in water and the energy needed to do so, which we do in two different ways in this report. The first way is by running simulations in lammps, which visualizes these changes for us.

3.1 Numerical part: the Phase Coexistence by MD

We begin our mission in lammps by simulating an icecube. This simulation runs over 10000 timesteps at 251K. The simulation stores important data in a file 'log-water-251K.lammps'. This information can be further studied by opening it in the program 'Ovito', or imported into python and further processed there.

Then, we run a simulation in lammps which will melt this icecube, with a number of 20000 timesteps at a T equal to 300. As a result, we get a file containing both energies and the enthalpy at each of these timesteps in a file 'log-water-300K.lammps', which we can plot and discuss further if we so wish.

We run another simulation at 301K go expand the volume of our box, to make it less crowded for the particles within our simulation. We log the data in a file called 'log-water-301K.lammps'.

To finally visualize evaporation of water, we make use of data from a log-file from the course web page, to avoid having to run a simulation that would've taken roughly 1.5 hours with 5000 timesteps. The data is stored within a file named 'log400K.lammps'

3.2 Experimental part: Melting and Vaporization

We want to study energy needed to transform water between its different phases, which means it is needed to divide this experiment into two different parts. First, we will study ice melting, and then we will study water evaporating.

The experiment for melting ice is performed by using a system consisting of a stainless steel container with a plastic lid and insulating material, a heating element, a stirrer, and a thermometer. The calorimeter is filled with 1.25l water at room temperature, and both the stirrer and data logger gets turned on. The heater set to 0.75A. Logging takes place until the water inside of the calorimeter hits 30 degrees Celsius, and then an ice-cube is inserted into the system, and we log the temperature until it stabilizes.

The experiment for vaporizing water is done by connecting a flask containing water, by rubber tube to a buffer volume, and by using a water aspirator pumping the pressure inside the flasks to a pressure 10^2 Pa, which is below the atmospheric pressure. The system is connected to a set of valves used to control the pressure. Data is then accumulated by allowing the water within the flask to boil until there is a stable temperature and pressure within the system, and then logging these values. Then, the pressure within the system is increased a little by opening one of the valves, and when the water within the flask is boiling, the values for temperature and pressure is again noted. This cycle is repeated until the pressure within the system reaches atmospheric pressure 10^5 Pa.

4 Results

4.1 Numerical part: the Phase Coexistence by MD

To visualize the results of our simulations with lammps, we make a set of plots from our data sets. For each of the data sets, we plot the enthalpy H against the total energy E_n, as well as a plot of both the enthalpy and total energy at each step n in time. This can be seen in figure 1, 2, 3 & 4

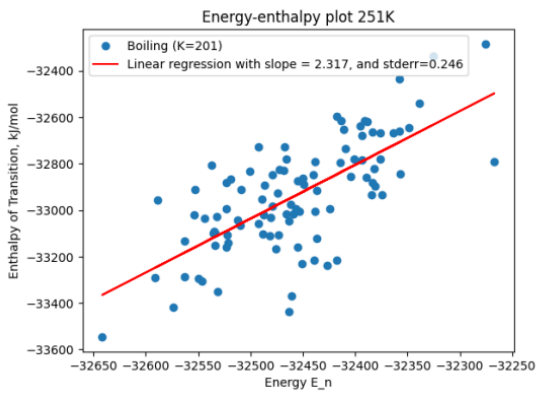

Figure 1:

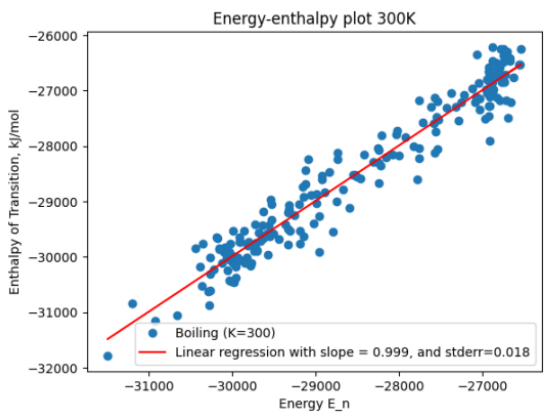

Figure 2:

One can use the numerical work we presented in our theory to analyse whether these simulations and the latent heat was realistic. Figure 5 shows how we chose a value for $0.4 \leq T_b \leq 0.9$ to determine the coexistence line numerically.We found at what pressure we found the self interaction point in the

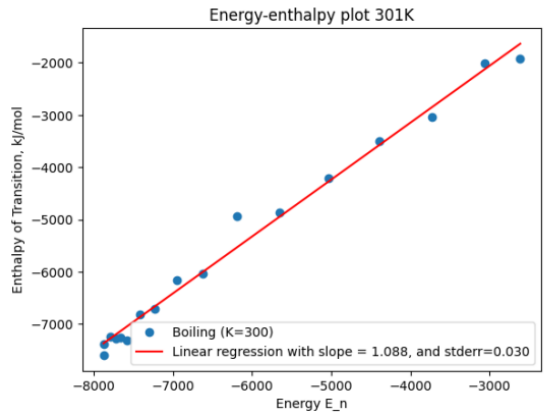

Figure 3:

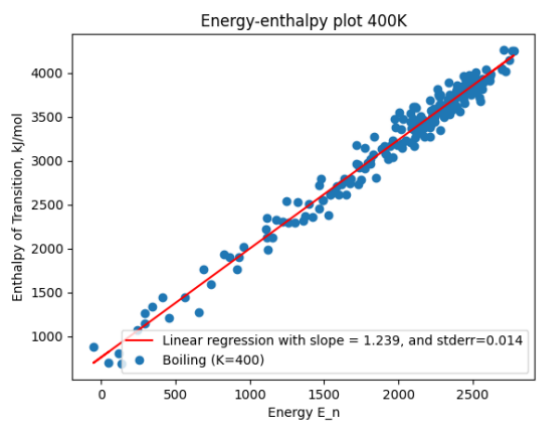

Figure 4:

$G(P)$ plot. Then, we used this and looked a the $P(V)$ plot below to determine the coexistence pressure. By taking the change in volume we found in he $P(V)$ plot and solving for L/T, we used the information gathered from our previous plots, we created the plot in Figure6.

$$L/T = \Delta V \frac{dP}{dT}$$

We then used the information we gathered to compare it with Trouton's rule, and got $H_v/(RT_b) = \frac{43.2 \cdot 10^3}{8.314 \cdot 373} 13.8 kJ/mol$, which is a bit off from the expected $H_v/(RT_b) = 11 \pm 1 kJ/mol$.

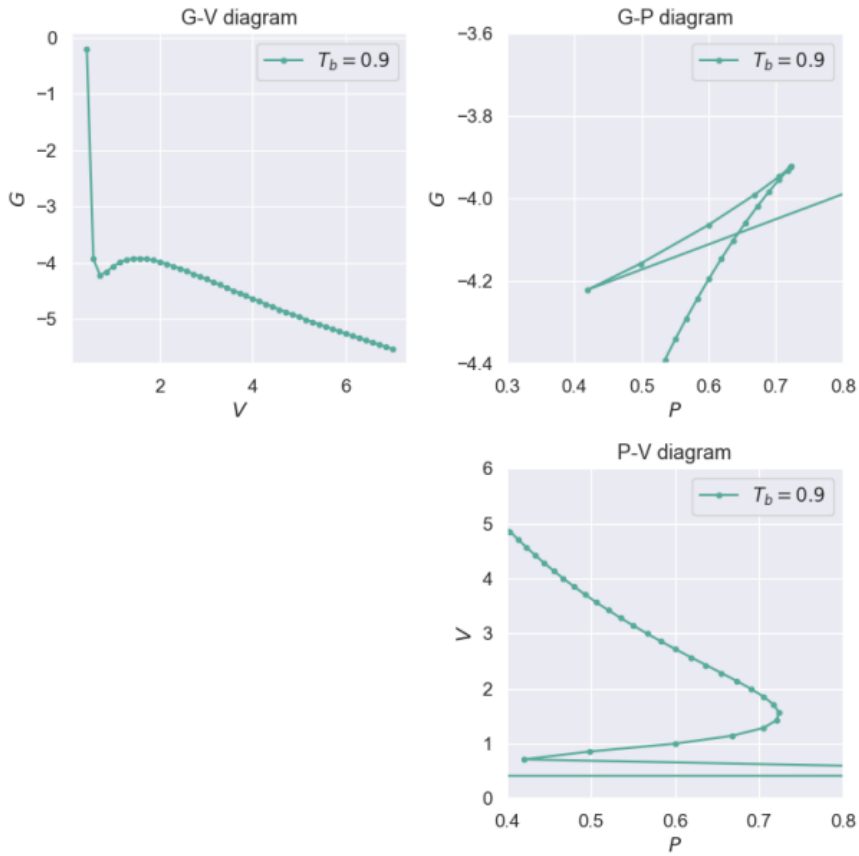

Figure 5: Plots of reduced Gibbs free energy at $\hat{T} = 0.9$ and pressure for the same reduced volumes.

4.2 Experimental part: Melting and Vaporization

4.2.1 Melting ice

We measure the ice to weigh about 258.2g. The experiment gave us a curve for the temperature within the system as a function of time.

We can compare the curve of the temperature as a function of time within our system from our experiment, with the shape one would expect, visualized in the assignment text figure 6.

One can clearly see that the temperature is steadily increasing, until it hits 30 degrees Celcius, and we add the icecube into the system. Then, the temperature declines abruptly, until it hits 12 degrees and stabilizes. This can be seen in figure 7.

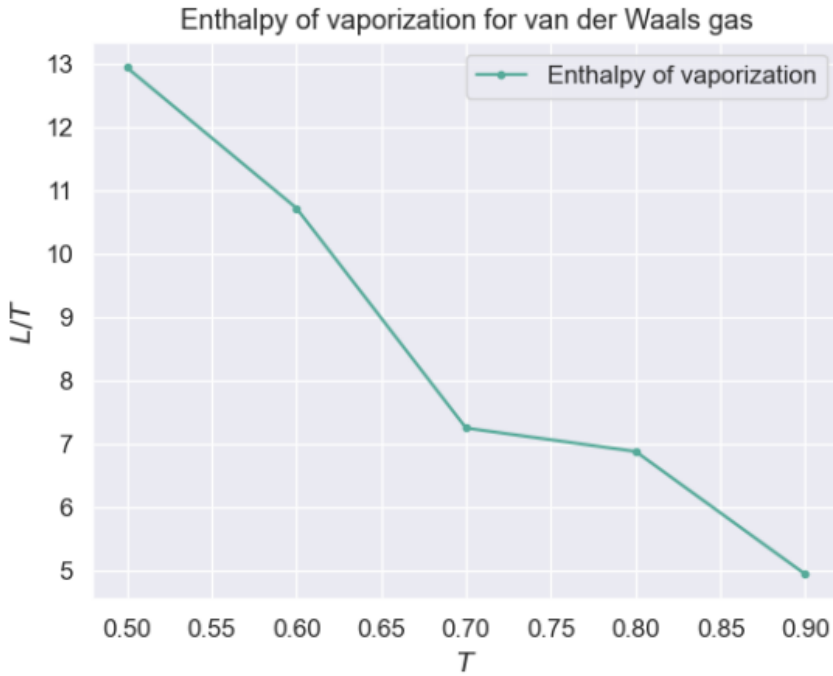

Figure 6: Latent heat as function of temperature, based on the Van der Waals method.

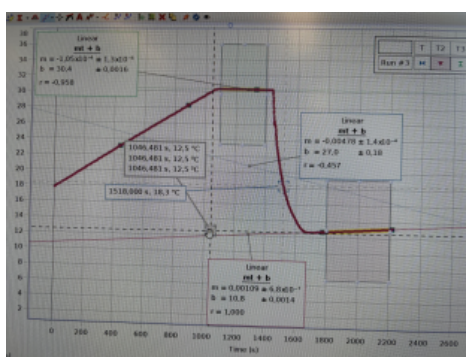

Figure 7: Plot as result of our experiment, shows the temperature within our system as a function of time

4.2.2 Evaporating water

We visualize our pressure and temperature-data by plotting lnP against $1/T$ in python:

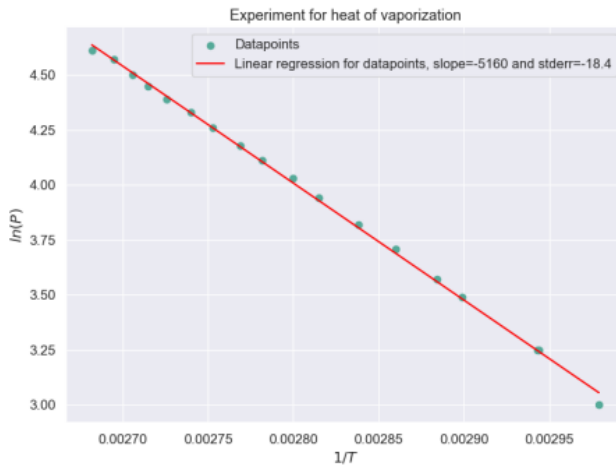

Figure 8: Experiment for heat of vaporization. Plot shows logarithm of pressure as a function of 1/T

5 Discussion

5.1 Numerical part: the phase coexistence by MD

We have visualized the data for our simulations for different temperatures in a set of different kinds of plots. The first sets of plots visualize the energy-enthalpy in the system at different temperatures. We can by reading these plots, tell that the division of enthalpy and temperature is pretty constantly equal to 1, which is what one would expect. Each of these plots, with the exception of the plot visualizing data for T=251K, also have a low deviation from this number of division.

To inspect further, we have plotted the enthalpy and temperature as a function of the steps n for each of the temperatures. From these plots, we can see that the temperature and enthalpy functions have similar shapes. For the instance when the temperature T=300K, both enthalpy and temperature has values that deviate around the same values. In the case of T=301K and T=400K, the data is not the same, but they follow the same shapes, with consistent distance in-between them. For the case of T=251K, the plot shows a cluster of data, that there's difficulty retrieving any sort of meaning from.

For the numerical work, we had to find the self-interaction point, just by looking at the graph. This would of course give us less accurate values for the coexistence pressure. This could be the reason for the drop in L/T in Figure 6. We also only had 5 points in the L/T plot, which is very little data to determine a theoretical value, because each faulty measurement has a greater impact on the result. However, our result for $H_v/(RT_b) = 13.8kJ/mol$ is a good result. We expected the value to be slightly higher than 11 ± 1, and that is what we

got.

5.2 Experimental part: Melting and Vaporization

5.2.1 Melting ice

Our value for the heat was a bit lower than the one we would expect (6000). There are uncertainties in how we conducted the experiment, especially in measuring the weight of the ice, which may explain the discrepancy. We were still quite close, as we were told by the professor that this was certainly good enough.

5.2.2 Evaporating water

We see that for our experiment, we get the value $\frac{H_v}{NkT_b} = 13.8338$, which does in fact not equate to 11. This discrepancy cannot be explained entirely by inaccuracy in measurements - this uncertainty in the Clausius-Claperyon relation that we plotted, has a value $\pm 17/373K = \pm 0.49$. Since this is such a small error, we need to explain the deviation between the values we got and the expected value by the fact that the water molecules are dipoles, and therefore acquire a larger sum of energy to be separated from one another. This results in turn, in an inflated value for Trouton's rule.

The partial pressure of water vapor is lower than the total gas pressure, which is due to the presence of air molecules. We need to keep the partial pressure of the water vapor in mind when interpreting our results, but it does not invalidate the measurements done as long as our measurements are done accurately.

We measure the temperature in the gas phase, and not the water phase, because this temperature directly affects the vapor pressure, and the phase equilibrium within the system. This data on the temperature in the gas phase can tell us a lot about the conditions that lead to phase transitions, which is what we're interested in learing more about.

The water cooling system is designed to condense the water vapor back into the liquid phase. Therefore, if we turned off the water cooling, the amount of water vapor in the system would increase, and our temperature measurements as well as the pressure would get affected.

The enthalpy of vaporisation is much higher than the enthalpy of melting, because the enthalpy is in fact directly proportional with temperature. This means, since higher temperatures are needed to make water vaporize, we're also dealing with a much higher enthalpy in this case. This, we can confirm by looking at the plotting of our simulation-data, if we want.

6 Conclusion

For the numerical part, the analytical groundwork laid the foundation for numerical exploration of water properties, focusing on Gibbs free energy, pressure, and volume relationships. Despite limited data points in the L/T plot, our

$Hv/(RT_b)$ result of $13.8kJ/mol$ aligns well with the expected range of 11 ± 1, validating our approach.

The MD simulations yielded meaningful and expected plots. It's only natural that the energy and enthalpy had a linear relationship and the fact that at 400K we saw a larger gap in between the values.

When looking at the difference of melting ice and boiling water, we could clearly see the effect of the dipol-dipol interaction which were broken when boiling the water. When melting the ice, we found the heat needed to be within an acceptable range of the expected value.

7 Appendix

https://www.uio.no/studier/emner/matnat/fys/FYS2160/h23/obligs$_l abs/lab2/lab2.pdf$