FYS2160 Lab 2

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Abstract

We simulate phase transition using molecular dynamics. By combining analytical and numerical methods we model Gibbs free energy and plot the phase coexistence line. Using the Clausius-Clapeyron relation we found the latent heat to be $H_v = 4.01J$. We build on experiences from simulation to perform actual experiments in phase transitioning from solid to liquid and to gas. From our experiment we estimated the value of Trouton's rule (≈ 11) to be (13.69 ± 0.06).

I. INTRODUCTION

The experiments conducted in the lab session where focused on the molecular dynamics of phase transitions.

In the first part we rely on simulations. We start of by making simulations in the Lammps program for the three different phases of water. Then we develop a more comprehensive model using van der Waals equation of state and combine analytical methods and numerical methods to plot Gibbs reduced free energy as well as attempting to determine the latent heat.

In the second part we got hands on experiments in melting ice and vapourizing water. In these simple experiments we explore latent heat of melting and vapourizing as well as discuss van der Waals interactions and how it could have affected our measurements. Furthermore, we explore in both parts whether gas transitions follow Troutons rule.

II. METHODS

A. Molecular Dynamics

Using molecular dynamics we simulate the melting of ice and vapourization of water. First we simulate ice using Lammps. For this simulation we set the parameters such as the volume, temperature (251K) and number of particles is fixed. For the next step we start a new simualation that starts where the previous simulation ended - and we simulate the melting of ice. For the last part we use an already finished simulation given because of time contraints. The last simulation is of water vapourization.

B. van der Waals equation of state

B1. Numerical methods

In order to determine the heat of vaporization for the van der Waals fluid we utilize the numerical approximation of $\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$, which is:

$$\frac{dP}{dT} = \frac{P[1:] - P[:-1]}{T[1:] - T[:-1]} \quad (1)$$

We then reduce the number of points in T and dV by one and use the average between two neighbour points.

We use then the following relation to determine the latent heat:

$$L = T\Delta V \frac{dP}{dT} \quad (2)$$

C. Vapourization experiment

In the experiment we are connected to the Pasco Capstone program monitoring the pressure in the bowl. When we can visually see the water start boiling we open the venting valve to let in pressure into the chamber. We start at 41kPa and repeat the venting every 5kPa untill 100kPa. For each venting we sample the temperature and pressure. From the program we obtain the linear fit to the sample points, the b value and r value.

We find the heat using the reformulated Clausius-Clapeyron relation:

$$ln\frac{P_1}{P_2} = -\frac{H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Where P is pressure, H_v is latent heat for vapourization, T is temperature in Kelvin and R is the gas constant given at 8.3145 $J/molK$.

From the Capstone program we find a value for the Troutons rule $\frac{H_v}{R}$ - we then divide this by T_{vap} which is the boiling temperature at atmospheric pressure. Trouton found that for many liquids the following relation holds:

$$\frac{H_{vap}}{RT_{vap}} = \frac{\Delta S_{vap}}{R} = 11 \pm 1 \quad (4)$$

This is the value we will be comparing our experimental values against.

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D. Melting experiment

In this experiment we will melt ice in a thermally insulated cylinder filled with water. We heat up the water to 30° C and then place a ice block with mass 282.95 g into the water. We record the temperature change across time using the Pasco Capstone program. In order to find the latent heat in the process of melting the ice we use the following relation:

$$m\left[H_m + C_v(T_2 - T_0)\right] = C_0(T_1 - T_2) \qquad (5)$$

Where H_m is the latent heat C_v is the specific heat capacity of water at 10° given as $4200\ J/(kgK)$. For this equation we need the starting heat capacity at 30C° C_0 which we find through the relation:

$$C_0 \frac{dT}{dt} = UI \qquad (6)$$

$$C_0 = \frac{UI}{dT/dt} \qquad (7)$$

Where U is the voltage, I is the current and the time derivative of the temperature $\frac{dT}{dt}$.

III. RESULTS

A. Vapourization experiment

From the Capstone program we obtained the slope:

$$\frac{H_v}{R} = -5110 \pm 21. \qquad (8)$$

Plotting the experimental data as such in figure 1: which gives using absolute values:

$$\frac{H_v}{RT_v} = 13.69 \pm 0.06 \qquad (9)$$

using water's boiling/vaporization temperature at ambient pressure $T_v = 100 \circ C = 373.15\ K$.

We divide by the boiling of water at atmospheric temperature and solve for H_v:

$$H_v = 5110R$$
$$= (42.5 \pm 0.2)\ kJ/mol \qquad (10)$$

B. Melting experiment

As measured in the Capstone program we obtained slope:

$$\frac{dT}{dt} = 0.0115 \pm 1.1 \cdot 10^{-6} \qquad (11)$$

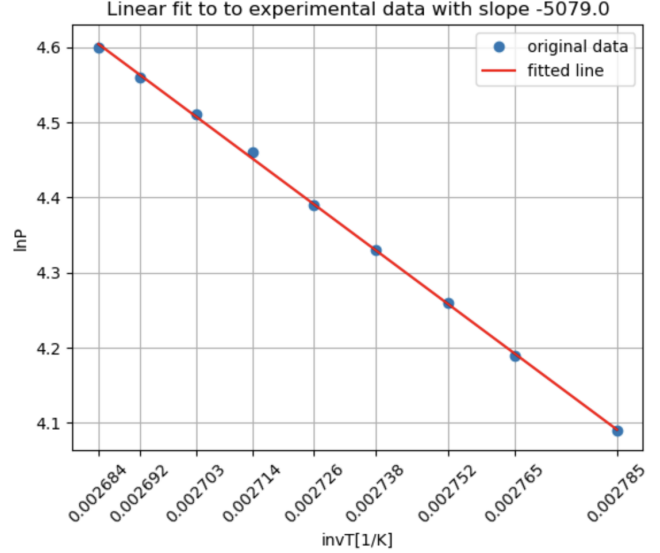We used this value to calculate the heat capacity:

Figure 1: Experimental data from the vapourzation experiment.

$$C_0 = UI \cdot \left(\frac{dT}{dt}\right)^{-1}$$
$$= 85V \cdot 0.75A \cdot (0.0115)^{-1}$$
$$= 5543.478\ J/K \qquad (12)$$

The temperature recordings were: $T_0 = 0°$ C, $T_1 = 30.1°$ C, $T_2 = 11.41°$ C. The mass of the ice block as $m = 282.95$ g. We the use the relation 5 to calculate the enthalpy in the melting process:

$$m\left[H_m + C_v(T_2 - T_0)\right] = C_0(T_1 - T_2)$$
$$H_m + C_v(T_2 - T_0) = \frac{C_0(T_1 - T_2)}{m}$$
$$H_m = \frac{C_0(T_1 - T_2)}{m} - C_v(T_2 - T_0)$$
$$H_m = \frac{5543.478\ J/K\ (30.1 \circ C - 11.41 \circ C)}{282.95\ g}$$
$$-4200\ J/(kg\ K)\ (11.41 \circ C - 0)$$
$$H_m = 318\ 247.3014\ J/kg$$

where $C_v = 4200$ J/(kg K) is the specific heat capacity of water at 10∘ C.

We then convert H_m from $1/kg$ to $1/mol$ by multiplying with $18.02 g/mol$ which results in:

$$H_m = 5734\ J/mol \qquad (13)$$

For the uncertainity we use the general uncertainity relations. We calculated the uncertainity of heat capacity as follows:

$$\delta C_0 = C_0 \frac{\delta(dT/dt)}{(dT/dt)} = \underline{0.5} \tag{14}$$

We also calculated the uncertainity of enthalpy as:

$$\delta H_m = H_m \sqrt{(\frac{\delta C_0}{C_0})^2 + (\frac{\delta m}{m})^2 + (\frac{\delta T_1}{T1})^2 + (\frac{\delta T_2}{T_2})^2}$$
$$\approx \underline{10} \tag{15}$$

Including the uncertainities for the calculated heat capacity C_0 and enthalpy H_m, and also converting the H_m from per kg to per mol - which results in:

$$C_0 = (5543.5 \pm 0.5) J/K \tag{16}$$
$$H_m = (5.8 \pm 10) kJ/mol \tag{17}$$

C. Numerical work

See the attached jupyter notebook file `numerical_work.ipynb`.

C1. Lammps simulations

The simulations' log files could not be attached on canvas. The energy graphs are plotted for $\hat{T} = 300$ K in figure 2 and for $\hat{T} = 400$ K in figure 3.
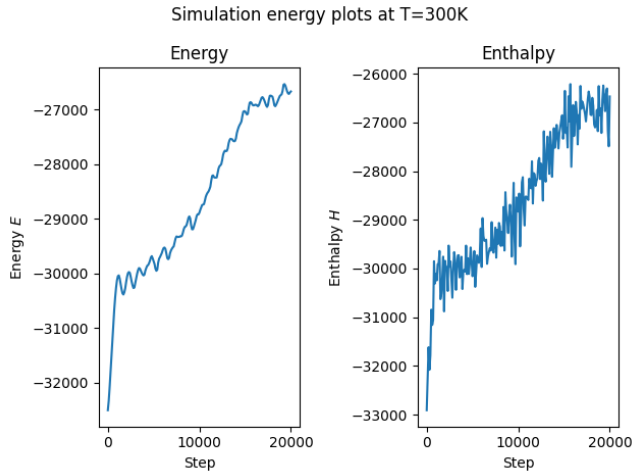

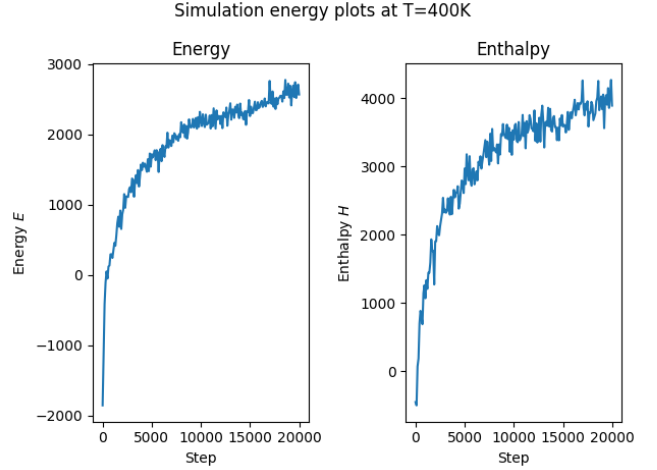Figure 2: Total energy and enthalpy plotted over time for the lammps simulation with $\hat{T} = 300$ K.

Figure 3: Total energy and enthalpy plotted over time for the lammps simulation with $\hat{T} = 400$ K.

D. Analytical work

See Appendix A for the Analytical work.

E. Numerical work

In the numerical part the reduced functions $\hat{G}(\hat{V})$, $\hat{G}(\hat{P})$ and $\hat{P}(\hat{V})$ resulted in the plots presented in figure 4.
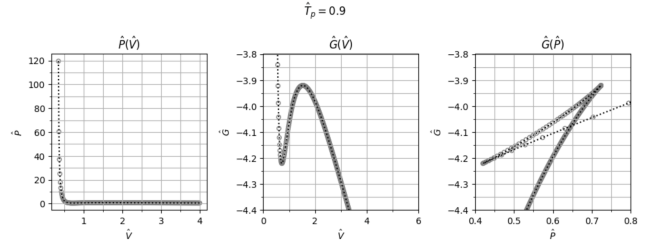

Figure 4: Plot of the reduced Gibbs free energy and reduced volumes, reproduced as figure 1 in lab notes. Temperature used for all three plots $\hat{T}_p = 0.9$

By eye search method we found the for each value of $\hat{T}_p$ and the corresponding pressures $\hat{P}$ and volume change $\hat{V}$. The values are summed up in figure 5:

Next values from figure 5 were used to plot the coexistence line in figure 6:

We determined the latent heat using the numerical method explained in methods and is done in file `numerical_work`. Taking the mean of the numerical estimation we found $H_v = 4.01 J$.

Next we found $\hat{H}/\hat{V}$ for the van der Waals fluid plotted in figure 7:

$\hat{T}_p$	$\hat{P}$	$\Delta\hat{V}$
0.4	0.025	37.3
0.5	0.065	16.4
0.6	0.146	7.23
0.7	0.272	3.54
0.8	0.452	1.62
0.9	0.692	0.4

Figure 5: Table noting the coexistence pressure $\hat{P}(\hat{T})$ together with the corresponding volume change.
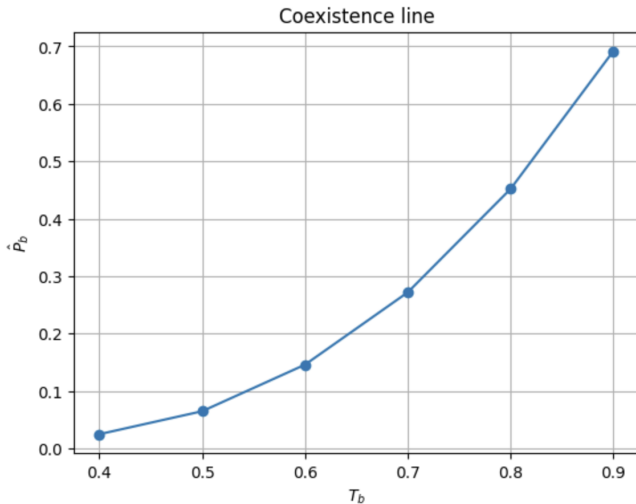

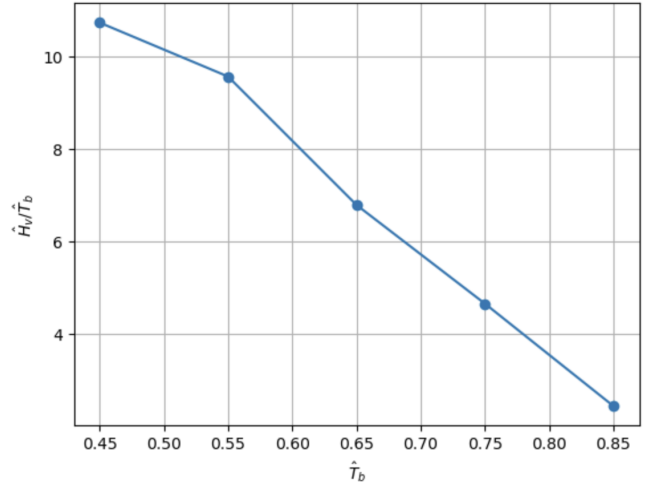Figure 6: Coexistence line using the reduced values for the function $\hat{P}(\hat{T})$.

Figure 7: $\hat{H}/\hat{V}$ for the van der Waals fluid.

IV. DISCUSSION

A. Vapourization experiment

From our experiment we estimated the value of Trouton's rule (≈ 11) to be (13.69 ± 0.06) which is a deviation of 24.5%, whereas the actual value was outside our error. This deviation is probably from inaccurate measurements and physical phenomenon. The physical phenomenon may be that water molecules attracted to each other through hydrogen bonds. Thus the experiment yielding a higher value may be caused more energy needed to break the hydrogen bonds between water molecules.

The pressure from the water gas as a result of boiling is said to be lower than the total gas pressure $P_{Tot} = P_w + P_{air}$ in the bottle. This probably does not matter for our specific measurements as our sensor is measuring the P_{air} in the other bottle. Since the bottle containing the water and water vapour is technically separated by the cooling effect, water vapour does not enter the air bottle. Thus it does not matter for our calculations that P_w is lower than the total pressure, as we are solely measuring P_{air}.

The temperature measurement on the other hand is done in the bottle containing the water. The sensor is not inside the water, but in the vapour. A reason for this is to obtain stable temperature measurements. If the sensor was dipped in the water the tempereature readings could be off as the water is constantly heating from the heat element and there are processes such as convection occuring in the water. By having the sensor in the gas we avoid this and the condensation formed around the sensor would probably contribute to stable readings. We also observed the the enthalpy calculation for for vaporization to be much higher than melting, approximately 7 times bigger. Water molecules in ice form crystalline structure with hydrogen bonds - however, in liquid form

there is many more ways the molecules can arrange themselves. This allows for many ways the molecules can interacts through van der Waals bonds, thus the molecules are intearcting through both hydrogen bonds and van der Waals bonds. The significant difference in enthalpy for melting and vapourization could reflect that a lot more energy is needed to break the bonds between water molecules in liquid form.

B. Lammps simulations

Viewing the simulation outputs in Ovito we clearly see the H2O-shapes of the molecules. In the first simulation with $\hat{T} = 251$ K we observe the water crystallizing: the molecules get denser and denser and the total volume decreases somewhat. However, for the next simulation with $\hat{T} = 300$ K we don't see the melting that we were supposed to. We see a reset fluid again melting to ice, we suspect this maybe is because at last some steps of each simulation the atoms fly away from each other incredibly fast almost like an instant vaporization, we think this is a simulation bug. For the simulation with bigger volume the (incorrect) crystallization also takes longer as the fluid is less dense which makes sense.

For the final simulation with $\hat{T} = 400$ K we plotted the energy graphs, but they did look kind of similar except that the higher energy had higher energy. The difference between $\hat{T} = 300$ K and $\hat{T} = 400$ K were the slightly different way the energies increase, however they both increase. It seems like the higher temperature system reaches equilibrium slightly faster. For $\hat{T} = 400$ K both the energies rise with an exponential drop-off. In comparison the former starts with a more gradual increase and then drops off in the same fashion as the latter. The former has very high (to the 10^4 order of magnitude) negative values, compared to the latter which has some negative and some positive values on the order of magnitude of 10^3. This makes sense as the higher temperature system will have more energy.

V. CONCLUSION

We simulated phase transition using molecular dynamics. Using the Clausius-Clapeyron relation we found the latent heat to be $H_v = 4.01 J$. From our experiment we estimated the value of Trouton's rule (≈ 11) to be (13.69

Appendix A. Analytical work

Use the critical parameters $P_c = \frac{a}{27b^2}$, $V_c = 3Nb$, $kT_C = \frac{8a}{27b}$ to express the reduced parameters $\hat{V}, \hat{T}, \hat{P}$:

$\hat{V}$:

$$\hat{V} = \frac{V}{V_c}$$
$$= \underline{\frac{V}{3Nb}}$$

$\hat{T}$:

$$\hat{T} = \frac{T}{T_c}$$
$$= \underline{\frac{27bkT}{8a}}$$

$\hat{P}$:

$$\hat{P} = \frac{P}{P_c}$$
$$= \frac{27b^2}{a} P$$
$$= \frac{27b^2}{a} \left(\frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \right)$$
$$= \underline{27b^2 \left(\frac{NkT}{a(V - Nb)} - \frac{N^2}{V^2} \right)}$$

in addition, using the expression for $\hat{V}$, we have that

$$\hat{P}(\hat{V}, \hat{T}) = 27b^2 \left(\frac{NkT}{a((\hat{V}3Nb) - Nb)} - \frac{N^2}{(\hat{V}3Nb)^2} \right)$$
$$= 27b^2 \left(\frac{kT}{a(3\hat{V}b - b)} - \frac{1}{9\hat{V}^2b^2} \right)$$
$$= \frac{27bkT}{a(3\hat{V} - 1)} - \frac{3}{\hat{V}^2}$$
$$= \underline{\frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2}}$$

and the dimensionless gibbs free energy per particle:

$$\hat{G} = \frac{8}{3NkT_c} G$$
$$= \frac{8}{3NkT_c} \left(-NkT \left(\ln\left(\frac{n_Q(V - Nb)}{N} \right) + 1 - \frac{V}{V - Nb} \right) - \frac{2aN^2}{V} \right)$$
$$= -\frac{8T}{3T_c} \left(\ln\left(\frac{n_Q(V - Nb)}{N} \right) + 1 - \frac{V}{V - Nb} \right) - \frac{16aN}{3VkT_c}$$
$$= -\frac{8}{3}\hat{T} \left(\ln\left(\frac{n_Q(V - Nb)}{N} \right) + 1 - \frac{V}{V - Nb} \right) - \frac{16aN}{3V\frac{8a}{27b}}$$
$$= -\frac{8}{3}\hat{T} \left(\ln\left(\frac{n_Q(V - Nb)}{N} \right) + 1 - \frac{V}{V - Nb} \right) - \frac{16aN}{3(\hat{V}3Nb)\frac{8a}{27b}}$$
$$= -\frac{8}{3}\hat{T} \left(\ln\left(\frac{n_Q(V - Nb)}{N} \right) + 1 - \frac{V}{V - Nb} \right) - \frac{6}{\hat{V}}$$
$$= -\frac{8}{3}\hat{T} \ln\left(\frac{n_Q(V - Nb)}{N} \right) - \frac{8}{3}\hat{T} + \frac{8}{3}\hat{T}\frac{V}{V - Nb} - \frac{6}{\hat{V}}$$
$$= -\frac{8}{3}\hat{T} \ln\left(\frac{n_Q(V - Nb)}{N} \right) - \frac{6}{\hat{V}} + \frac{8}{3}\frac{27bkT}{8a}\frac{V}{V - Nb} - \frac{8}{3}\hat{T}$$
$$= -\frac{8}{3}\hat{T} \ln\left(\frac{n_Q(V - Nb)}{N} \right) - \frac{6}{\hat{V}} + \frac{8}{3}\frac{27bkT}{8a}\frac{(\hat{V}3Nb)}{(\hat{V}3Nb) - Nb} - \frac{8}{3}\hat{T}$$
$$= \underline{-\frac{8}{3}\hat{T} \ln\left(3\hat{V} - 1 \right) - \frac{3}{\hat{V}} + \hat{P}\hat{V} + f(\hat{T})}$$

Appendix B.   Scripts

See attached python files `G_and_V_plots.py` and `plot_energies.py`.