FYS2160 Oblig 3

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1 Project 3

We have Helmholtz free energy for the van der Waals gas:

$$F_{wdW} = -NkT\left[\ln\left(\frac{n_Q(V-Nb)}{N}\right)+1\right] - \frac{aN^2}{V} \tag{1}$$

with $n_Q(T) = (2\pi mkT/h^2)^{3/2}$

1.1 a)

We can find the pressure from this by the thermodynamic identity

$$P(N,V,T) = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{2}$$

If we calculate the pressure for (1) we find

$$P(N,V,T) = -\left(-NkT\frac{N}{n_Q(V-Nb)}\cdot\frac{n_Q}{N} + \frac{aN^2}{V^2}\right) = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2} \tag{3}$$

1.2 b)

We now introduce

$$P_c = \frac{a}{27b^2}, \qquad V_c = 3Nb, \qquad kT_c = \frac{8a}{27b} \tag{4}$$

and

$$\hat{P} = P/P_c, \qquad \hat{V} = V/V_c \qquad \hat{T} = T/T_c \tag{5}$$

with the density

$$\hat{\rho} = 1/\hat{V} = \rho/\rho_c, \qquad \rho_c = \frac{1}{3b} \tag{6}$$

We can thus write the pressure of the van der Waals gas (3) dimensionless:

$$P = \hat{P}P_c = \frac{Nk\hat{T}T_c}{\hat{V}V_c - Nb} - \frac{aN^2}{\hat{V}^2 V_c^2}$$

$$\hat{P}\frac{a}{27b^2} = \frac{Nk\hat{T}\frac{8a}{27bk}}{\hat{V}3Nb - Nb} - \frac{aN^2}{\hat{V}^2 9N^2b^2}$$

$$\hat{P} = \frac{27b^2}{a}\left(\frac{a}{27b^2}\frac{8\hat{T}}{3\hat{V}-1} - \frac{a}{27b^2}\frac{3}{\hat{V}^2}\right) = \frac{8\hat{T}}{3\hat{V}-1} - \frac{3}{\hat{V}^2} \tag{7}$$
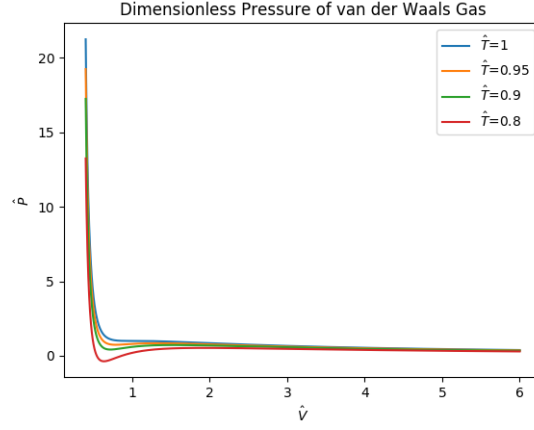
1.3   c)

If we plot the pressure (7) we get

Figur 1: We see that around $\hat{V} = 1$ we pressure as a function of $\hat{V}$ is non-injective, this means that we are unable to find an inverse $\hat{V}(\hat{P})$.

1.4   d)

We saw in (6) that we can write the density as $\hat{\rho} = 1/\hat{V}$. Using this in (7) we get

$$\hat{P} = \frac{8\hat{T}}{3/\hat{\rho} - 1} - \frac{3}{1/\hat{\rho}^2} = \frac{8\hat{\rho}\hat{T}}{3 - \hat{\rho}} - 3\hat{\rho}^2 \tag{8}$$

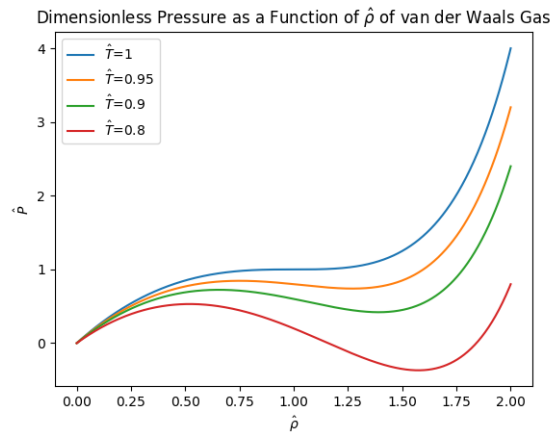## 1.5   e)

We can so plot the pressure against density:

Figur 2: The pressure of the van der Waals gas as a function of $\hat{\rho}$

1.6   f)

As seen in fig. 2, for $\hat{T} \geq 1$ does pressure become an injective function of the density. This means that we can find an inverse $\hat{\rho}(\hat{V})$. This will be unique. This means that for $\hat{T} < 1$ there will be no

such unique function.

1.7   g)

We want to see where the isothermal compressibility is negative:

$$\kappa = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right) < 0 \tag{9}$$

We see that this happens when $\partial \rho/\partial P < 0$, which is the same as saying that $\partial P/\partial \rho < 0$. We can see from figure 2 that this happens for every temperature except $\hat{T} = 1$ around $0.5 \leq \hat{\rho} \leq 1.55$ (more or less). We can also compute this numerically
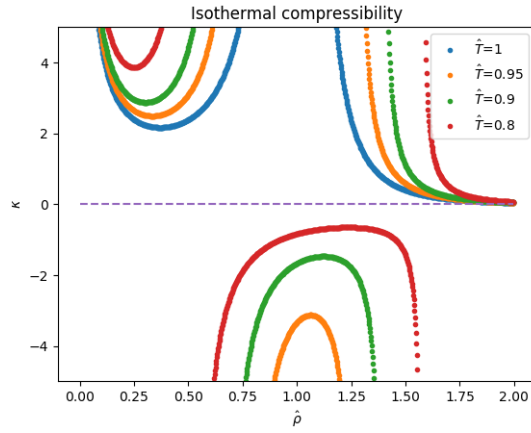

Figur 3: The isothermal compressibility as function of $\hat{\rho}$.

We can see that our approximation of the range of $\hat{\rho}$ was pretty good for $\hat{T} = 0.8$, and as the temperature raises this interval becomes narrower, until for $\hat{T} = 1$ κ is positive for all $\hat{rho}$.

1.8   h)

We are going to look at the PV isotherms of N_2. To do this use (7) and (1.2) to find

$$P = P_c\left[\frac{8\hat{T}/T_c}{3\hat{V}/V_c - 1} - \frac{3V_c^2}{\hat{V}^2}\right] \tag{10}$$

Where

$$P_c = 33.6 \text{ atm}, \qquad V_c = 0.089 \text{ l/mol}, \qquad T_c = 126 \text{ K} \tag{11}$$

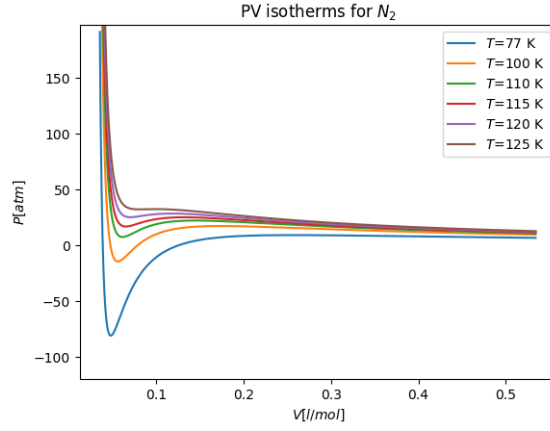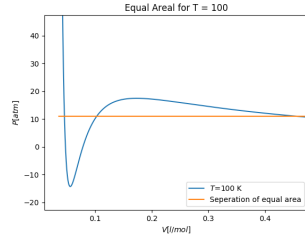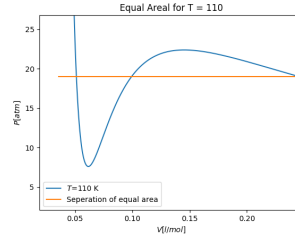If we plot this for $T = 77, 100, 110, 115, 120, 125$ K we get

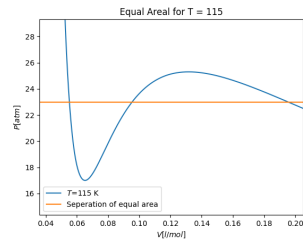Figur 4: The PV isotherms for N_2.

1.9   i)

We can find the equal area under these curves for the different temperatures. This was done by hand, then plotted:
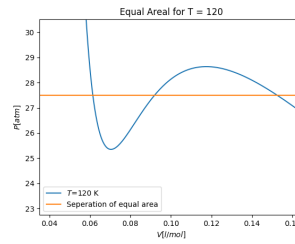

(a) Equal area for $T = 100$

(b) Equal area for $T = 110$

(a) Equal area for $T = 115$
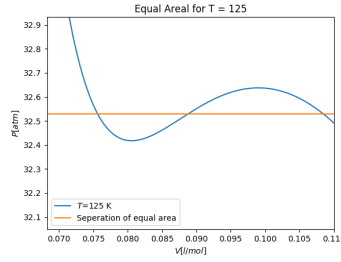

(b) Equal area for $T = 120$

Figur 7: Equal area for $T = 125$

From this we can find the liquid phase volume V_L and the gas phase volume V_g, and the difference between them:

T	V_L	V_g	$V_g - V_L$
100	0.046	0.456	0.41
110	0.051	0.246	0.195
115	0.055	0.195	0.14
120	0.062	0.152	0.091
125	0.076	0.108	0.033

Tabell 1

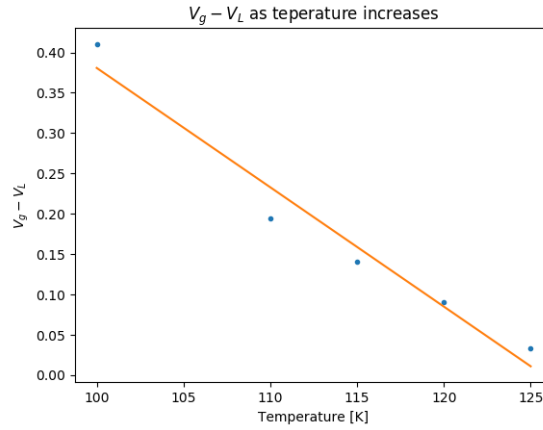If we plot $V_g - V_L$ and fit a linear polynomial to it we get

Figur 8: We can see that $V_g - V_L$ vs looks linear, we therefore fit a line to it.

The fitted line has the form

$$V_g - V_L = -0.0148 * T + 1.8598 \tag{12}$$

We know that the critical temperature is when the gas- and liquid states are indistinguishable, thus when

$$V_g - V_L = 0 \Rightarrow T = T_c = \frac{1.8598}{0.0148} = 125.75\text{K} \tag{13}$$

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2 Project 4

2.1 a)

We start with expanding dS and dV

$$ds = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{14}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{15}$$

If we insert the expression for dV into that of dS, we get

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right] \tag{16}$$

If we sort the expression we get:

$$dS = \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP \tag{17}$$

We are looking at the heating with constant pressure, so $dP = 0$ and

$$dS = \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT \Leftrightarrow \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{18}$$

We can no use the identities for the heat capacities:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{19}$$

and

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{20}$$

Which gives us the relation

$$\frac{C_V}{T} = \frac{C_P}{T} + V\alpha\left(\frac{\partial S}{\partial V}\right)_T \tag{21}$$

We now need an expression for the last partial differentiation. We start with a constant volume $dV = 0$, which gives from (15)

$$0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{22}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{23}$$

we now use that

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{24}$$

and get that

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta_T} \tag{25}$$

Inserting this into (21) we get the relation for the heat capacities:

$$C_V = C_P + VT\frac{\alpha^2}{\beta_T} \tag{26}$$

2.2 b)

From eq. (19) we get that

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V} \tag{27}$$

We now need to look at these expressions. We start with $\left(\frac{\partial S}{\partial T}\right)_P$. We know from this that $dP = 0$. Since the expression involves S and T we are going to look at $dP(S,T) = 0$

$$dP = 0 = \left(\frac{\partial P}{\partial T}\right)_S dT + \left(\frac{\partial P}{\partial S}\right)_T dS \tag{28}$$

From this we get

$$\left(\frac{\partial S}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T} \tag{29}$$

We use the same logic with $\left(\frac{\partial S}{\partial T}\right)_V$:

$$dV(S,T) = 0 = \left(\frac{\partial V}{\partial T}\right)_S dT + \left(\frac{\partial V}{\partial S}\right)_T dS \tag{30}$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial S}\right)_T} \tag{31}$$

We can now insert this into (27)

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial P}{\partial S}\right)_T} = \left(\frac{\partial P}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_T \tag{32}$$

We can then use that

$$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \qquad \beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{33}$$

And we then get

$$\frac{C_P}{C_V} = \left(\frac{\partial P}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_T = \frac{\beta_T}{\beta_S} \tag{34}$$

2.3 c)

We start with the first law for pressure-volume work

$$dU = dQ - dW = dQ - PdV \tag{35}$$

We then, as the exercise hinted, expand dH. We do this for $H(T,P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{36}$$

But in this system $dP = 0$, so this reduces to

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT \tag{37}$$

We also know that for this pressure-volume system the change enthalpy is given as

$$dH = dU + PdV \tag{38}$$

Inserting this for dU in (35) we get

$$dQ = \left(\frac{\partial H}{\partial T}\right)_P dT \tag{39}$$

and since we have constant pressure, we get

$$\left(\frac{\partial Q}{\partial T}\right)_P = C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{40}$$

2.4   d)
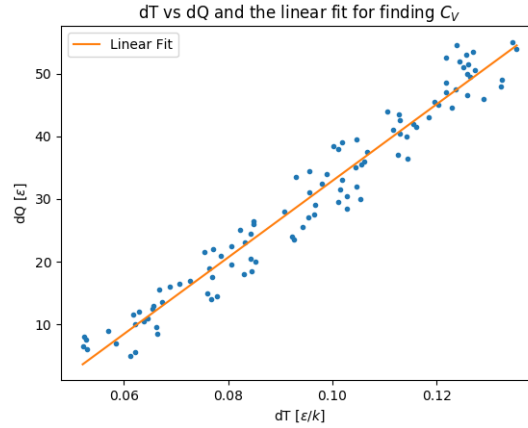
Running the lammps script we get the following data:

Figur 9: dQ versus dT for a Lennard-Jones system with constant volume. A linear fit used to find the slope, which corresponds to the heat capacity C_V

We know that

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \Rightarrow dQ = C_V dT \tag{41}$$

So the fitted slope is the C_V. So we get the result

$$C_V = (611.34 \pm 13.38)k \tag{42}$$

2.5   e)

For an ideal gas the heat capacity is given as

$$C_V = \frac{1}{2}NR \tag{43}$$

Where R is the gas constant, f the degree of freedom and N the number of particles. In LJ-units $R = 1$. All the particles are point particles and therefore have $f = 3$. And there are $N = 540$ particles. We thus get

$$C_V = 750k \tag{44}$$

This is a bit above the heat capacity we got. This may both due to an error due to a low number of particles. It may also be due to the Lennard-Jones potential not being a perfect model for an ideal gas.

2.6 f)

The density was so kept at $\rho = 0.01$ and the temperature was varied from the triple point temperature to 10 times the critical temperature[1] in 6 steps. The resulting heat capacities was calculated for each temperature.
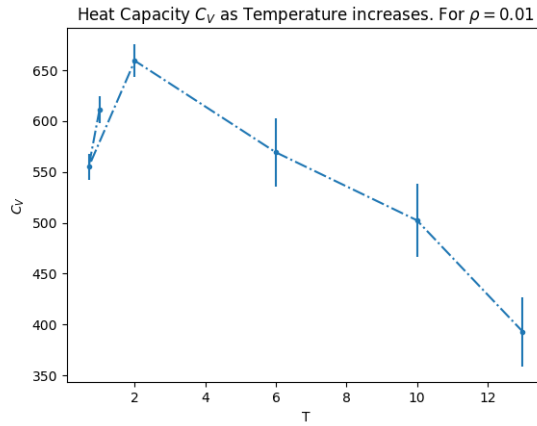

Figur 10: C_V as a function of temperature.

We can see that the heat capacity seems to decrease somewhat as temperature increases. A more constant C_V may have been expected[2], so the reason for this behaviour is not clear.

3 g)

We can now do something similar to what we did above, but we instead let the temperature be constant at $T = 2$, and vary the density from a diluted gas density of $\rho = 0.01$ to the triple point density of $\rho = 0.84$ (in practice I ended it at $\rho = 0.8$). We then get

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[1] I used $T_{tp} = 0.694$ and $T_c = 1.32$ as these was the one I found at `http://www.sklogwiki.org/SklogWiki/index.php/Lennard-Jones_model`
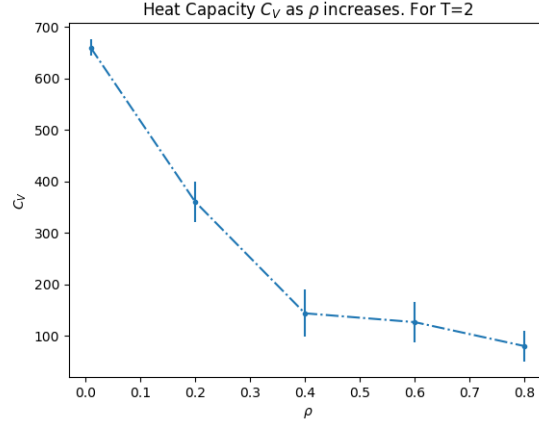
[2] We already saw that it should be constant at 750 k

Figur 11: C_V as a function of density.

Again we see a decrease in C_V as ρ increases. And again I am not sure why this is the case.

3.1   h)

If we now hold the pressure constant we can find C_P. This was done with a constant temperature $T = 2$ and at a diluted gas density $\rho = 0.01$ and at the triple point density.

	Diluted Gas	Triple Point
C_V	659.43	80.17
C_P	49.56	-208.44
$C_P - C_P$	-609.87	-288.61

Tabell 2: C_V and C_P at $T = 2$ and for diluted gas and triple point density.

We can see that both C_P and C_V have decreased alot from the diluted gas density to the triple point density. More important, C_P should not be negative! This seems to be a problem with lammps (for me at least). At the triple point density the simulation goes its own way. Even though I use $T = 2$, the simulation insist on using $T = 0.92$ in the log file. The log file also gives a negative heat capacity, so it is not my calculation. Why this is, I simply don't know.

Since we need β_T to find the theoretical value of $C_P - C_V$, which I'm not sure who to find from our simulations, since it depends on a constant temperature – the temperature in the simulation varies. So I have nothing to compare the numerical data with, unfortunately.

3.2   i)

Running the lammps script and fitting for dQ vs dT, we get a numerical value for the heat capacity for N_2

$$C_V = 3.188 \tag{45}$$

We expect that the units for C_V should be $[Q]/[T]$. In real unit this becomes $(Kcal/mole)/K = Kcal/(mole \cdot K)$. So

$$C_V = 3.188 \text{ Kcal/mole/K} \tag{46}$$