

# FYS2160 Oblig 3

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6. november 2017

## 1 Project 3

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

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

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

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

If we calculate the pressure for (1) we find

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

### 1.2 b)

We now introduce

$$P_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad kT_c = \frac{8a}{27b} \quad (4)$$

and

$$\hat{P} = P/P_c, \quad \hat{V} = V/V_c, \quad \hat{T} = T/T_c \quad (5)$$

with the density

$$\hat{\rho} = 1/\hat{V} = \rho/\rho_c, \quad \rho_c = \frac{1}{3b} \quad (6)$$

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

$$\begin{aligned} P &= \hat{P}P_c = \frac{Nk\hat{T}T_c}{\hat{V}V_c - Nb} - \frac{aN^2}{\hat{V}^2V_c^2} \\ \hat{P} \frac{a}{27b^2} &= \frac{Nk\hat{T} \frac{8a}{27bk}}{\hat{V}3Nb - Nb} - \frac{aN^2}{\hat{V}^2 9N^2b^2} \\ \hat{P} &= \frac{27b^2}{a} \left( \frac{a}{27b^2} \frac{8\hat{T}}{3\hat{V} - 1} - \frac{a}{27b^2} \frac{3}{\hat{V}^2} \right) = \frac{8\hat{T}}{3\hat{V} - 1} - \frac{3}{\hat{V}^2} \end{aligned} \quad (7)$$

### 1.3 c)

If we plot the pressure (7) we get

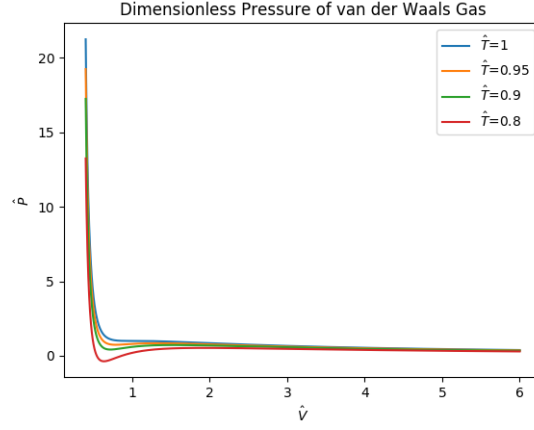


Figure 1: We see that around  $\hat{V} = 1$  we pressure as a function of  $\hat{V}$  is non-injective, this means that we are unable to find an inverse  $\hat{V}(\hat{P})$ .

### 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

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

### 1.5 e)

We can so plot the pressure against density:

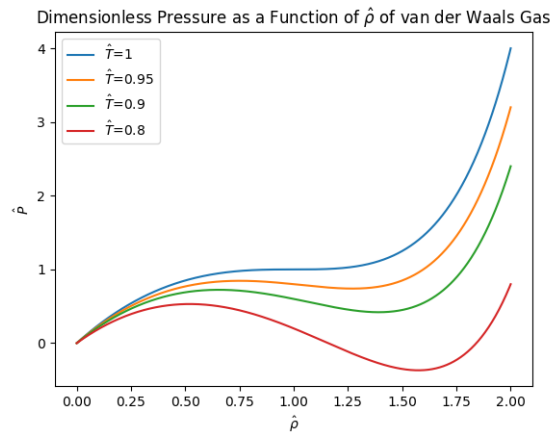


Figure 2: The pressure of the van der Waals gas as a function of  $\hat{\rho}$

### 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.

(Dette virker bare rart, sjekk dette før du leverer!!!!)

### 1.7 g)

We want to see where the isothermal compressibility is negative:

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

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

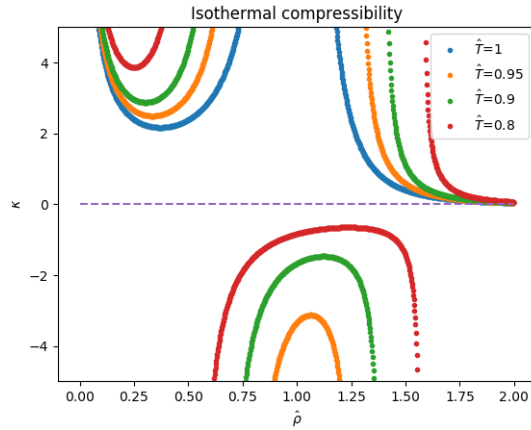


Figure 3: The isothermal compressibility as function of  $\hat{\rho}$ .

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  $\hat{T} = 1$   $\kappa$  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

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

Where

$$P_c = 33.6 \text{ atm}, \quad V_c = 0.089 \text{ l/mol}, \quad T_c = 126 \text{ K} \quad (11)$$

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

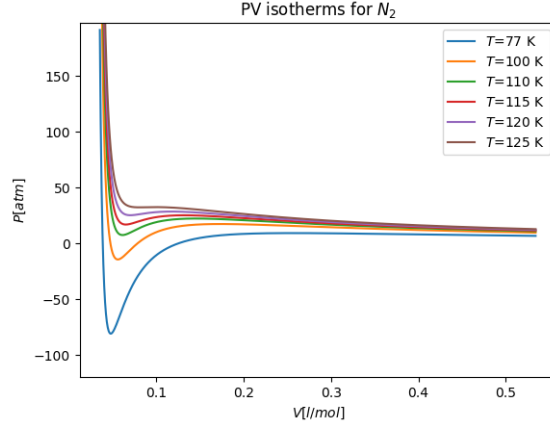


Figure 4: The PV isotherms for  $N_2$ .

1.9 i)

1.10 j)

## 2 Project 4

2.1 a)

We start with expanding  $dS$  and  $dV$

$$ds = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \quad (12)$$

$$dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \quad (13)$$

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

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T \left[ \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \right] \quad (14)$$

If we sort the expression we get:

$$dS = \left[ \left( \frac{\partial S}{\partial T} \right)_V + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T dP \quad (15)$$

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

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

We can now use the identities for the heat capacities:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V, \quad C_P = T \left( \frac{\partial S}{\partial T} \right)_P \quad (17)$$

and

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad (18)$$

Which gives us the relation

$$\frac{C_V}{T} = \frac{C_P}{T} + V\alpha \left( \frac{\partial S}{\partial V} \right)_T \quad (19)$$

We now need an expression for the last partial differentiation. We start with a constant volume  $dV = 0$ , which gives from (13)

$$0 = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \quad (20)$$

$$\Rightarrow \left( \frac{\partial P}{\partial T} \right)_V = - \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial V}{\partial P} \right)_T} \quad (21)$$

we now use that

$$\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (22)$$

and get that

$$\Rightarrow \left( \frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\beta_T} \quad (23)$$

Inserting this into (19) we get the relation for the heat capacities:

$$C_V = C_P + VT \frac{\alpha^2}{\beta_T} \quad (24)$$

## 2.2 b)

From eq. (17) we get that

$$\frac{C_P}{C_V} = \frac{\left( \frac{\partial S}{\partial T} \right)_P}{\left( \frac{\partial S}{\partial T} \right)_V} \quad (25)$$

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  $dP(S, T) = 0$

$$dP = 0 = \left( \frac{\partial P}{\partial T} \right)_S dT + \left( \frac{\partial P}{\partial S} \right)_T dS \quad (26)$$

From this we get

$$\left( \frac{\partial S}{\partial T} \right)_P = - \frac{\left( \frac{\partial P}{\partial T} \right)_S}{\left( \frac{\partial P}{\partial S} \right)_T} \quad (27)$$

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

$$dV(S, T) = 0 = \left( \frac{\partial V}{\partial T} \right)_S dT + \left( \frac{\partial V}{\partial S} \right)_T dS \quad (28)$$

$$\Rightarrow \left( \frac{\partial S}{\partial T} \right)_V = - \frac{\left( \frac{\partial V}{\partial T} \right)_S}{\left( \frac{\partial V}{\partial S} \right)_T} \quad (29)$$

We can now insert this into (25)

$$\frac{C_P}{C_V} = \frac{\left( \frac{\partial P}{\partial T} \right)_S \left( \frac{\partial V}{\partial S} \right)_T}{\left( \frac{\partial V}{\partial T} \right)_S \left( \frac{\partial P}{\partial S} \right)_T} = \left( \frac{\partial P}{\partial V} \right)_S \left( \frac{\partial V}{\partial P} \right)_T \quad (30)$$

We can then use that

$$\beta_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S, \quad \beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (31)$$

And we then get

$$\frac{C_P}{C_V} = \left( \frac{\partial P}{\partial V} \right)_S \left( \frac{\partial V}{\partial P} \right)_T = \frac{\beta_T}{\beta_S} \quad (32)$$

### 2.3 c)

We start with the first law for pressure-volume work

$$dU = dQ - dW = dQ - PdV \quad (33)$$

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

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP \quad (34)$$

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

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT \quad (35)$$

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

$$dH = dU + PdV \quad (36)$$

Inserting this for  $dU$  in (33) we get

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

and since we have constant pressure, we get

$$\left( \frac{\partial Q}{\partial T} \right)_P = C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad (38)$$