

## 9 Task Theoretical Physics VI - Statistics

### 9.1 (Paramagnetic heat engine)

Carnot engine uses paramagnetic substance, with equation of state:

$$M = \frac{nDH}{T} \Leftrightarrow H = \frac{MT}{nD} \quad (1)$$

(a)

Internal energy (wherever  $H dM$  comes from, at least it works, while  $M dH$  doesn't, in the lecture we got to know that this depends on the substance, so i guess it's  $H dM$  for all paramagnetic substances then):

$$dU(S, M) = TdS + HdM \quad (2)$$

with free energy:

$$F = U - TS$$

we get:

$$dF(M, T) = HdM - SdT$$

with

$$\begin{aligned} S &= -\left.\frac{\partial F}{\partial T}\right|_M \\ H &= \left.\frac{\partial F}{\partial M}\right|_T \end{aligned}$$

while free energy is exact, the following relation holds:

$$\frac{\partial S}{\partial M} = -\frac{\partial H}{\partial T}$$

inserting  $H$  from (1):

$$\frac{\partial S}{\partial M} = -\frac{\partial H}{\partial T} = -\frac{M}{nD}$$

entropy:

$$dS(T, M) = \left.\frac{\partial S}{\partial T}\right|_M dT + \left.\frac{\partial S}{\partial M}\right|_T dM = \frac{C_M}{T} dT - \frac{M}{nD} dM$$

inserting in (2):

$$\begin{aligned} dU(S, M) &= T \left( \frac{C_M}{T} dT - \frac{M}{nD} dM \right) + \frac{MT}{nD} dM \\ dU &= C_M dT \end{aligned}$$

Integration yields ( $C_M = C = \text{const.}$ ):

$$U = C_M(T - T_0) + U_0$$

□

Therefore the internal energy can only depend on the temperature and not on the magnetization.

(b)

The typical carnot cycle consists of two adiabatic and two isothermic parts. Absorbed heat:

$$\delta Q = dU - \delta W$$

this is:

$$TdS = \delta Q = C_M dT - \frac{MT}{nD} dM$$

The condition for the adiabatic parts is  $\delta Q = 0$ , therefore:

$$C_M dT = \frac{MT}{nD} dM$$

while using separation of variables leads to:

$$\begin{aligned} \frac{dT}{T} &= \frac{1}{C_M n D} M dM \\ \ln \frac{T}{T_0} &= \frac{M^2 - M_0^2}{2C_M n D} \\ T \Big|_{\delta Q=0} &= T_0 \exp\left(\frac{M^2 - M_0^2}{2C_M n D}\right) \end{aligned} \quad (3)$$

inserting  $T$  in (1) gives us the equation for the adiabates:

$$H \Big|_{\delta Q=0} = \frac{MT_0}{nD} \exp\left(\frac{M^2}{2C_M n D}\right) \exp\left(-\frac{M_0^2}{2C_M n D}\right) \propto M \cdot \exp(M^2) \quad (4)$$

Now we have a look at the isotherms  $T = \text{const.} \Rightarrow dT = 0$ , therefore:

$$\delta Q \Big|_T = -H dM = -\frac{MT}{nD} dM$$

while there is a minus sign in front of the  $H$  the carnot cycle has to be counterclockwise. this means for the  $H - M$ -diagram ( $T' = \text{const.}$ ):

$$H \Big|_{T=T'} = \frac{T'}{nD} \cdot M \quad (5)$$

With the help of the equations (4) and (5) we can receive fig. 1.

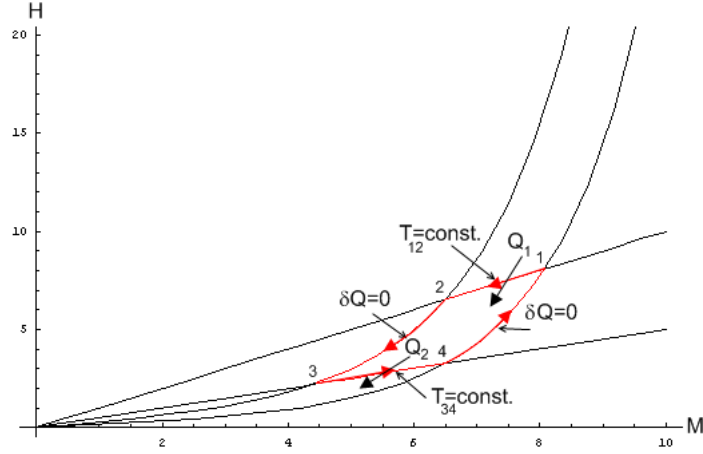


Figure 1:  $M - H$  diagram of a typical Carnot cycle

(c)

The total heat adsorbed is meant to be calculated. While the adiabatic parts won't change the heat, we just have to consider  $Q_1$  and  $Q_2$  (fig. 1) on the isotherms ( $T_{12} > T_{34}$ ). For the isotherms we can use:

$$\delta Q|_T = -H dM$$

Therefore we receive

$$W_{12} = Q_1 = - \int_1^2 H dM = - \frac{T_{12}}{nD} \int_1^2 M dM = \frac{T_{12}}{2nD} (M_1^2 - M_2^2)$$

and

$$W_{34} = Q_2 = - \int_3^4 H dM = \frac{T_{34}}{2nD} (M_3^2 - M_4^2)$$

This leads to the total heat absorbed of:

$$Q_{tot} = Q_1 + Q_2 = \frac{1}{2nD} (T_{12} (M_1^2 - M_2^2) + T_{34} (M_3^2 - M_4^2))$$

The work done on the adiabates is:

$$\delta W = dU = C_M dT$$

which leads to:

$$W_{23} = C_M (T_{34} - T_{12})$$

and

$$W_{41} = C_M (T_{12} - T_{34})$$

therefore  $W_{23} + W_{41} = 0$  and the total work done is:

$$W = Q_{tot} = \frac{1}{2nD} (T_{12} (M_1^2 - M_2^2) + T_{34} (M_3^2 - M_4^2))$$

(d)

The efficiency of the carnot cycle is known to be:

$$\eta = 1 - \frac{T_{cold}}{T_{hot}}$$

which we are going to show for this case too, while  $T_{12} = T_{hot}$  and  $T_{34} = T_{cold}$ .  
Definition of efficiency:

$$\eta = \frac{\Delta W}{\Delta Q_{abs}} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

we just have to insert  $Q_1$  and  $Q_2$  know:

$$\begin{aligned}\eta &= 1 + \frac{Q_2}{Q_1} \\ &= 1 + \frac{T_{34}(M_3^2 - M_4^2)}{T_{12}(M_1^2 - M_2^2)} \\ &= 1 - \frac{T_{34}(M_4^2 - M_3^2)}{T_{12}(M_1^2 - M_2^2)}\end{aligned}\tag{6}$$

while we now have to show, that  $(M_4^2 - M_3^2) = (M_1^2 - M_2^2)$  we start from (3)

$$T_{12} = T_{34} \exp\left(\frac{M_1^2 - M_4^2}{2C_M n D}\right)$$

and

$$T_{34} = T_{12} \exp\left(\frac{M_3^2 - M_2^2}{2C_M n D}\right)$$

rewritten:

$$\begin{aligned}\frac{T_{12}}{T_{34}} &= \exp\left(\frac{M_1^2 - M_4^2}{2C_M n D}\right) \\ \frac{T_{12}}{T_{34}} &= \exp\left(\frac{M_2^2 - M_3^2}{2C_M n D}\right)\end{aligned}$$

this means:

$$\begin{aligned}\exp\left(\frac{M_1^2 - M_4^2}{2C_M n D}\right) &= \exp\left(\frac{M_2^2 - M_3^2}{2C_M n D}\right) \\ M_1^2 - M_4^2 &= M_2^2 - M_3^2 \\ M_1^2 - M_2^2 &= M_4^2 - M_3^2\end{aligned}$$

this is exactly what we wanted to show. Inserting the result in (6) leads to the final result:

$$\eta = 1 - \frac{T_{34}}{T_{12}} = 1 - \frac{T_{cold}}{T_{hot}}$$

□

## 9.2 (Phase transition in a van der Waals gas)

Van der Waals gas:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (7)$$

(a)

Stability condition:

$$\left.\frac{\partial p}{\partial v}\right|_T \leq 0$$

isn't fulfilled for all  $v$  and  $T$  for (7). Using (7):

$$\begin{aligned} p &= \frac{RT}{(v - b)} - \frac{a}{v^2} \\ \left.\frac{\partial p}{\partial v}\right|_T &= 2\frac{a}{v^3} - \frac{RT}{(v - b)^2} \end{aligned} \quad (8)$$

We now have to consider the different cases in dependance of  $v$  and  $T$  for:

$$2\frac{a}{v^3} - \frac{RT}{(v - b)^2} \leq 0$$

- 1)  $T$  is large, therefore the 2nd term will always dominate and the equation will be fulfilled.
- 2) If  $T$  is small, the second term will only be bigger than the first one for  $v \approx b$  and for large  $v$ ,  $v \rightarrow \infty$ . For intermediate  $v$  the system is instable.
- 3) The third case occurs for  $\left.\frac{\partial p}{\partial v}\right|_T = 0$ , where we will be on an isotherm.

We now want to plot it, therefore we can get the isotherms for different  $T$  using (8) and for the critical case  $\left.\frac{\partial p}{\partial v}\right|_T = 0$  we get (compare to task (b)):

$$p = \frac{a}{v^2} - \frac{2ab}{v^3}$$

The  $p - V$  diagram in fig. (2) (data from wikipedia.de<sup>1</sup>) shows the instability region, while in fig (3) we can see a larger interval for  $V$ , which shows, that the instability region isn't that large.

(b)

Critical isotherm condition:

$$\begin{aligned} \left.\frac{\partial p}{\partial v}\right|_T &= 0 \\ 0 &= 2\frac{a}{v^3} - \frac{RT}{(v - b)^2} \end{aligned}$$

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<sup>1</sup><http://de.wikipedia.org/wiki/Van-der-Waals-Gleichung>

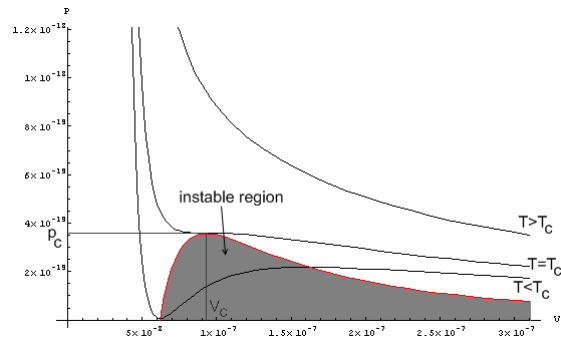


Figure 2:  $p - V$  diagram of Van der Waals gas indicating the instability region ( $a$  and  $b$  are taken for water ( $\text{H}_2\text{O}$ ), with data from wikipedia.de:  $a = 557.29 \text{ kPa dm}^6/\text{mol}^2$  and  $b = 0.031 \text{ dm}^3/\text{mol}$ )

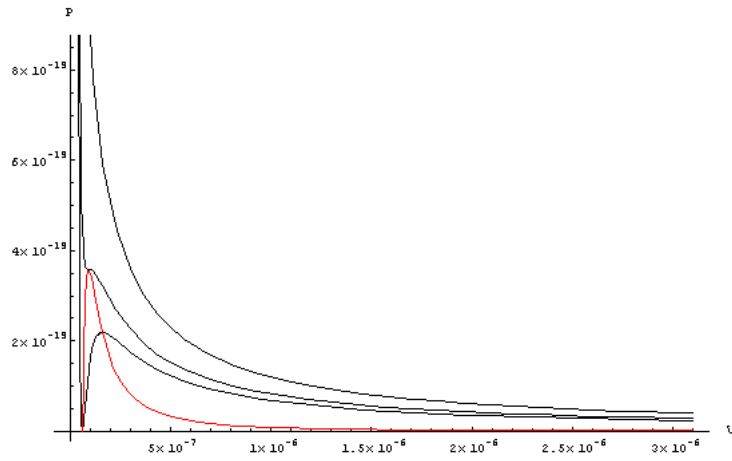


Figure 3:  $p - V$  diagram of Van der Waals gas indicating the instability region, again for  $\text{H}_2\text{O}$ , but this time for a bigger  $V$ -interval.

$$\frac{RT}{(v-b)^2} = 2\frac{a}{v^3}$$

$$T_c = 2\frac{a}{v_c^3} \frac{(v_c-b)^2}{R}$$

The second condition (change of curvature compare to (2) and/or (3)) leads to:

$$\frac{\partial^2 p}{\partial v^2} \Big|_T = 0$$

$$0 = -6\frac{a}{v^4} + 2\frac{RT}{(v-b)^3}$$

$$T_c = 3\frac{a}{Rv_c^4} (v_c-b)^3$$

using this two equations for  $T_c$ , we get:

$$2 \frac{a}{v_c^3} \frac{(v_c - b)^2}{R} = 3 \frac{a}{Rv_c^4} (v_c - b)^3$$

$$v_c = 3b$$

in (7)

$$\left(p + \frac{a}{v^2}\right)(v - b) = 2 \frac{a}{v^3} (v - b)^2$$

$$p_c = \frac{a}{v_c^2} \left(1 - 2 \frac{b}{v_c}\right)$$

$$p_c = \frac{a}{27b^2}$$

and

$$T_c = 2 \frac{a}{v_c^3} \frac{(v_c - b)^2}{R}$$

$$T_c = 2 \frac{a}{27b^3} \frac{(3b - b)^2}{R}$$

$$T_c = \frac{8a}{27bR}$$

Listing the critical terms:

$$p_c = \frac{a}{27b^2}$$

$$v_c = 3b$$

$$T_c = \frac{8a}{27bR}$$

(c)

Equation (7) in critical units:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$\left(\frac{a}{27b^2}p' + \frac{a}{9b^2v'^2}\right)(3bv' - b) = R \frac{8a}{27bR}T'$$

$$\left(p' + \frac{3}{v'^2}\right)(3v' - 1) = 8T'$$

Interestingly we got rid of the dependance of  $a, b$ . Therefore all van der Waals gases will fulfill this equation. This means they will all have the same  $p - V$ -diagram.

(d)

equilibrium condition:

$$\mu_l = \mu_g = \mu = \text{const.}$$

with  $l$ =liquid and  $g$ =gas, while  $\mu$  is the chemical potential. While we are on an isotherm  $T = \text{const.}$  Meaning  $\mu \neq \mu(T)$ . With:

$$\int_l^g d\mu = \mu_g - \mu_l = 0$$

and (from lecture 30.11.2007):

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dp$$

with  $T = \text{const.} \rightarrow dT = 0$ :

$$d\mu = v dp$$

we get:

$$\int_{p_l}^{p_g} v(p) dp = 0$$

**Intermezzo** finding  $v$ :

First we now need to get  $v$  from (7):

$$\begin{aligned} pv - pb + \frac{a}{v} - \frac{ab}{v^2} &= RT \\ v^3 - v^2 \frac{RT}{p} + \frac{1}{p}v - b \left(1 + \frac{a}{p}\right) &= 0 \end{aligned} \quad (9)$$

this is a cubic equation, which is solvable by using CARDANO's formula. From the script "Mathematik für Physiker II - Lineare Algebra" by Lutz Heindorf:

$$x^3 + ax^2 + bx + c = 0$$

this can be reduced to the CARDANO's formula ( $p_C$  means  $p_{\text{Cardano}}$ , to better distinguish between pressure and the variable)

$$y^3 = p_C y + q$$

using the substitution  $y = x + \frac{a}{3}$ . The result is then:

$$y = u + v = \sqrt[3]{\frac{q}{2} + \sqrt{\frac{q^2}{4} - \frac{p_C^3}{27}}} + \sqrt[3]{\frac{q}{2} - \sqrt{\frac{q^2}{4} - \frac{p_C^3}{27}}}$$

We now have to substitute, while  $x = v$  and  $a = -\frac{RT}{p}$ , we therefore use:

$$y = v - \frac{RT}{3p} \Leftrightarrow v = y + \frac{1}{3} \frac{RT}{p}$$



inserting this in (9) we get:

$$\begin{aligned} & \left(y + \frac{1}{3} \frac{RT}{p}\right)^3 - \left(y + \frac{1}{3} \frac{RT}{p}\right)^2 \frac{RT}{p} + \frac{1}{p} \left(y + \frac{1}{3} \frac{RT}{p}\right) - b \left(1 + \frac{a}{p}\right) = 0 \\ y^3 + \frac{2}{3} \left(\frac{RT}{p}\right) y^2 + \frac{1}{9} \left(\frac{RT}{p}\right)^2 y + \frac{1}{3} \left(\frac{RT}{p}\right) y^2 + \frac{2}{9} \left(\frac{RT}{p}\right)^2 y + \frac{1}{27} \left(\frac{RT}{p}\right)^3 + \\ & - \left(\frac{RT}{p}\right) y^2 - \frac{2}{3} \left(\frac{RT}{p}\right)^2 y - \frac{1}{9} \left(\frac{RT}{p}\right)^3 + \frac{1}{p} y + \frac{1}{3} \frac{RT}{p^2} - b \left(1 + \frac{a}{p}\right) = 0 \end{aligned}$$

rearranged in CARDANO's formula form:

$$y^3 = \left[ \frac{1}{3} \left(\frac{RT}{p}\right)^2 - \frac{1}{p} \right] y + \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right]$$

with:

$$\begin{aligned} p_C &= \frac{1}{3} \left(\frac{RT}{p}\right)^2 - \frac{1}{p} \\ q &= \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right] \end{aligned}$$

Inserting this in CARDANO's formula:

$$\begin{aligned} y &= \sqrt[3]{\frac{q}{2} + \sqrt{\frac{q^2}{4} - \frac{p_C^3}{27}}} + \sqrt[3]{\frac{q}{2} - \sqrt{\frac{q^2}{4} - \frac{p_C^3}{27}}} \\ &= \sqrt[3]{\frac{1}{2} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right]} + \sqrt[3]{\frac{1}{4} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right] - \frac{\left(\frac{1}{3} \left(\frac{RT}{p}\right)^2 - \frac{1}{p}\right)^3}{27}} \\ &+ \sqrt[3]{\frac{1}{2} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right]} - \sqrt[3]{\frac{1}{4} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right] - \frac{\left(\frac{1}{3} \left(\frac{RT}{p}\right)^2 - \frac{1}{p}\right)^3}{27}} \end{aligned}$$

Now the retransformation to  $v$ :

$$\begin{aligned} v &= y + \frac{1}{3} \frac{RT}{p} \\ v &= \sqrt[3]{\frac{1}{2} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right]} + \sqrt[3]{\frac{1}{4} \left[ \frac{2}{27} \left(\frac{RT}{p}\right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left(1 + \frac{a}{p}\right) \right] - \frac{\left(\frac{1}{3} \left(\frac{RT}{p}\right)^2 - \frac{1}{p}\right)^3}{27}} \end{aligned}$$

$$\begin{aligned}
& + \sqrt[3]{\frac{1}{2} \left[ \frac{2}{27} \left( \frac{RT}{p} \right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left( 1 + \frac{a}{p} \right) \right]} - \sqrt[3]{\frac{1}{4} \left[ \frac{2}{27} \left( \frac{RT}{p} \right)^3 - \frac{1}{3} \frac{RT}{p^2} + b \left( 1 + \frac{a}{p} \right) \right]} - \frac{\left( \frac{1}{3} \left( \frac{RT}{p} \right)^2 - \frac{1}{p} \right)^3}{27} \\
& + \frac{1}{3} \frac{RT}{p}
\end{aligned}$$

Well, this result doesn't seem elegant, calculating the integral would cost a lot of time. Maybe this wouldn't even lead to the correct result, therefore we spare the time and try a hopefully more elegant way.

**Back to our problem:**

While  $v$  doesn't have a proper form, we will try another way using Gibbs free energy  $G$ :

$$G = U - TS + pV$$

while  $U = TS - pV + \mu N$  this means:

$$G = \mu N \Rightarrow g = \mu$$

while  $\mu_l(T, p_{lg}) = \mu_g(T, p_{lg}) = \text{const.}$  (we are on one of the isotherms with a fixed  $T$  and  $p_{lg}$  equilibrium pressure, with  $l, g$  points in fig. (6)) we can derive for the Gibbs free energy at  $l$  and  $g$ :

$$\begin{aligned}
G_l(T, p_{lg}) &= G_g(T, p_{lg}) \\
U_l - TS_l + p_{lg}V_l &= U_g - TS_g + p_{lg}V_g
\end{aligned}$$

using free energy definition  $F = U - TS$  we get:

$$\begin{aligned}
F_l + p_{lg}V_l &= F_g + p_{lg}V_g \\
F_l - F_g &= p_{lg}(V_g - V_l)
\end{aligned}$$

Alternatively we can use the differential of the free energy:

$$dF = dU - SdT - TdS = dG - pdV - Vdp$$

while  $p = \text{const.}$  since we are looking for the equilibrium pressure and  $G = \text{const.}$  we get:

$$dF = -pdV$$

which can be integrated:

$$F_l - F_g = - \int_{V_g}^{V_l} pdV$$

This means the equation:

$$\int_{V_l}^{V_g} pdV = p_{lg}(V_g - V_l) \tag{10}$$

holds, while we are on an isotherm ( $T = \text{const.}$ ).

Geometrical interpretation yields  $A = B$ , which is shown in fig (6). This means the integration can be done independently of the path of integration, while on the left side of (10) we integrate over the isotherm and on the right side, this is simply integration over the constant pressure  $p_{lg}$ . We can now think about what this physically could mean. We know that we have the gas phase at  $g$  and the liquid phase at  $l$ , now between those points this must be our phase transition area. While the task was about this area, we already know, that there is a mixture of both phases in this area. The graph seems to be physically correct, since the gas phase doesn't change in pressure too much, but in volume, while the liquid phase isn't changing in volume too much (incompressibility) but the pressure change is huge.

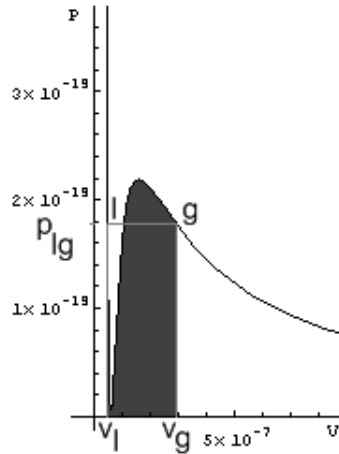


Figure 4:  $p - V$  diagram of Van der Waals gas (left side of equation (10))

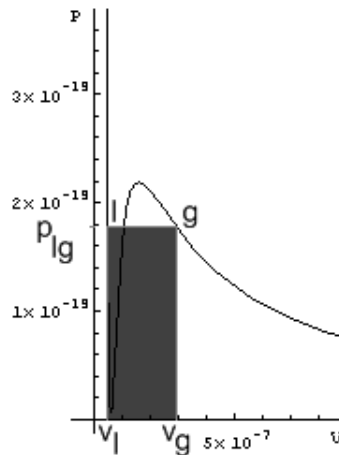


Figure 5:  $p - V$  diagram of Van der Waals gas (right side of equation (10))

We can now even calculate the pressure  $p_{lg}$ , if we insert  $p$  from (7) with

$$p = NRT \left( \frac{1}{V - bN} \right) - \frac{N^2 a}{V^2}$$

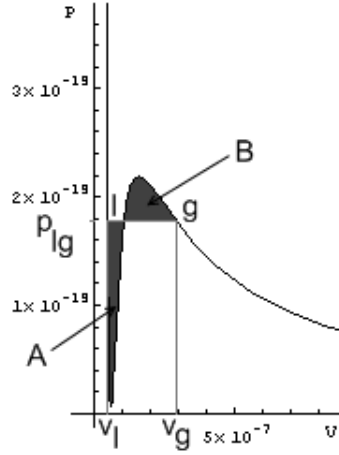


Figure 6:  $p - V$  diagram of Van der Waals gas indicating that  $A = B$ , while this comes from comparison of fig. 4 and fig. 5.

we get:

$$\begin{aligned}
 p_{lg}(V_g - V_l) &= - \int_{V_g}^{V_l} p dV \\
 p_{lg}(V_g - V_l) &= \int_{V_g}^{V_l} \left( -NRT \left( \frac{1}{V - bN} \right) + \frac{N^2 a}{V^2} \right) dV \\
 p_{lg}(V_g - V_l) &= [-NRT \cdot \ln(V - bN)]_{V_g}^{V_l} + \left[ -\frac{N^2 a}{V} \right]_{V_g}^{V_l} \\
 p_{lg}(V_g - V_l) &= NRT [\ln(V_g - bN) - \ln(V_l - bN)] + N^2 a \left[ \frac{1}{V_g} - \frac{1}{V_l} \right] \\
 p_{lg}(V_g - V_l) &= N \left[ RT \ln \frac{(v_g - b)}{(v_l - b)} + a \left( \frac{1}{v_g} - \frac{1}{v_l} \right) \right] \\
 p_{lg} &= \frac{1}{(v_g - v_l)} \left[ RT \ln \frac{(v_g - b)}{(v_l - b)} + a \frac{v_l - v_g}{v_g v_l} \right] \\
 p_{lg} &= \frac{RT}{(v_g - v_l)} \ln \frac{(v_g - b)}{(v_l - b)} - \frac{a}{v_g v_l}
 \end{aligned}$$

(e)

Using the free energy:

$$F = F_l + F_g \quad (11)$$

we will derive the relative particle numbers

$$n_l = \frac{N_l}{N}$$

$$n_g = \frac{N_g}{N}$$

$$n_l + n_g = \frac{N_l + N_g}{N} = 1$$

with (11)

$$\frac{F}{N} = \frac{F_l}{N} \frac{N_l}{N_l} + \frac{F_g}{N} \frac{N_g}{N_g}$$

$$f = \frac{F_l}{N_l} n_l + \frac{F_g}{N_g} n_g$$

$$f = f_l n_l + f_g n_g$$

now we use  $g = \mu$  and  $g = f + pv$  meaning  $f = \mu - pv$ ,  $\mu = \mu_g = \mu_l$ ,  $p_l = p_l = p_g$  and  $n_l + n_g = 1 \Leftrightarrow n_l = 1 - n_g$ :

$$\mu - p_l v = (\mu_l - p_l v_l) n_l + (\mu_g - p_g v_g) n_g$$

$$\mu - p_l v = \mu (n_l + n_g) - p_l (v_l n_l + v_g n_g)$$

$$\mu - p_l v = \mu - p_l (v_l n_l + v_g n_g)$$

$$v = v_l n_l + v_g n_g$$

$$v = v_l (1 - n_g) + v_g n_g$$

$$v - v_l = (v_g - v_l) n_g$$

$$n_g = \frac{v - v_l}{v_g - v_l}$$

and for  $n_l = 1 - n_g$ :

$$n_l = \frac{(v_g - v_l)}{(v_g - v_l)} - \frac{v - v_l}{v_g - v_l} = \frac{v_g - v}{v_g - v_l}$$

The result seems physically likely, while we will have no  $n_l$  for a volume  $v \geq v_g$  (while  $v_g > v_l$  is used to have a positive denominator), this means,  $n_l$  will become negative. A particle number cannot have a physical meaning when it is negative, therefore the number of particles will be zero. If we look at  $n_g$  the particle number will vanish if  $v \leq v_l$ . Therefore this relations just holds in the transition area, but in it, we can calculate the number of particles for a given volume  $v$ . A sketch of the dependancies can be seen in fig. (7). Interpreting this, we can say, that we have a measure, how close we are to one of the phases (gas or liquid).

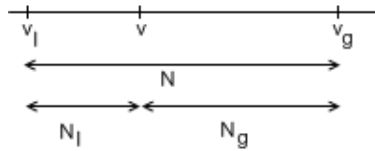


Figure 7: This sketch shows a geometric interpretation of **problem 9.2 (b)**

(f)

We are looking at a temperature  $T < T_c$ . We first need to find  $f(v)$ , using  $dF = dG - pdV - Vdp = dG + \left(\frac{\partial F}{\partial V}\right) dV + \left(\frac{\partial F}{\partial p}\right) dp$  we get:

$$\frac{\partial F}{\partial V} = \frac{\partial f}{\partial v} = -p$$

Integrating, while using  $p$  from (8):

$$\begin{aligned} f - f_0 &= - \int_{v_0}^v p dv \\ f(v) &= f_0 + \int_{v_0}^v \left( -\frac{RT}{(v-b)} + \frac{a}{v^2} \right) dv \\ f(v) &= f_0 + \left[ -RT \ln(v-b) - \frac{a}{v} \right]_{v_0}^v \\ f(v) &= f_0 + RT \ln \frac{(v_0-b)}{(v-b)} + a \frac{v-v_0}{vv_0} \\ f(v) &= c_0 - RT \ln(v-b) - \frac{a}{v} \end{aligned}$$

while  $c_0$  contains all constant terms. A sketch of the behavior of this function can be found in fig. (8). The problem to encounter is, that the form of the graph of  $f$  highly depends on the  $T$  used, when we plot it with *mathematica*. Therefore we are trying to think of the behavior using the equation:

$$f(v) = c_0 - RT \ln(v-b) - \frac{a}{v}$$

$c_0$  just gives us some constant axis intercept. While for high  $v$  the middle term will dominate and lead to  $-\infty$  for small  $v$  the last term will dominate and we will also have  $-\infty$  for  $f$ . For  $v = b$  we get  $f \rightarrow \infty$ , while  $\lim_{x \rightarrow 0} \ln x \rightarrow -\infty$ .

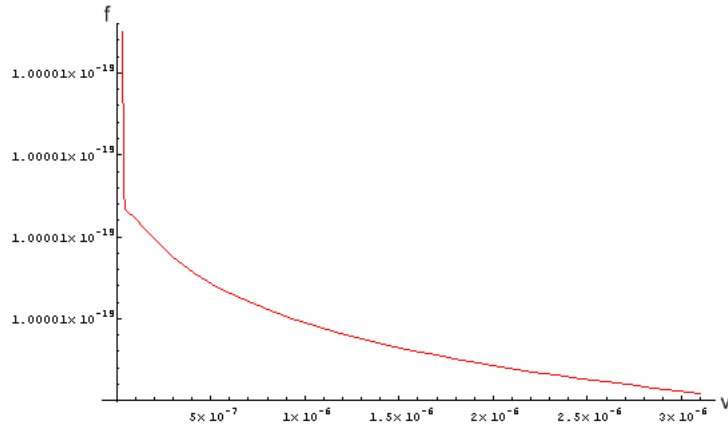


Figure 8: This sketch shows the free energy plotted over  $v$

We can now think of the effect of Maxwell's rule on  $f(v)$ . Using Maxwell's rule (10) in rewritten form:

$$\int_{v_l}^{v_g} p dv = p_{lg} (v_g - v_l)$$

This means, we will have a constant isotherm function behaviour in the part between  $v_l$  and  $v_g$ . We can look at the transition interval separately for  $f$  and write:

$$\begin{aligned} \frac{\partial f}{\partial v} &= -p \\ \int_{f_0}^{f(v_l)} df + \int_{f(v_l)}^{f(v_g)} df + \int_{f(v_g)}^{f(v)} df &= - \int_{v_0}^{v_l} p dv - \int_{v_l}^{v_g} p dv - \int_{v_g}^v p dv \\ f(v) &= f_0 - \int_{v_0}^{v_l} p dv - \int_{v_l}^{v_g} p dv - \int_{v_g}^v p dv \\ f(v) &= f_0 + RT \ln \frac{(v_0 - b)}{(v_l - b)} + a \frac{v_l - v_0}{v_l v_0} - p_{lg} (v_g - v_l) + RT \ln \frac{(v_g - b)}{(v - b)} + a \frac{v - v_g}{v v_g} \\ f(v) &= d_0(f_0, v_0, a, b, v_l, v_g, T, p_{lg}) - RT \ln (v - b) - \frac{a}{v} \end{aligned}$$

therefore we just experience a shift of the constant, meaning a constant shift of the whole free energy, while  $c_0(f_0, v_0, a, b, R, T) \neq d_0(f_0, v_0, b, v_l, v_g, R, T, p_{lg})$ .

### 9.3 (Thermodynamics of ice skating)

Clausius-Clapeyron-equation:

$$\frac{dp}{dT} = \frac{q_{12}}{T(v_2 - v_1)} = \frac{\Delta p}{\Delta T} \quad (12)$$

with  $q_{12}$  the latent heat.

(a)

Given information:

$$\begin{aligned} m &= 80 \text{ kg} \\ l &= 0.2 \text{ m} \\ w &= 4 \cdot 10^{-3} \text{ m} \\ v_{water} &= 1.0 \cdot 10^{-3} \frac{\text{m}^3}{\text{kg}} \\ v_{ice} &= 1.1 \cdot 10^{-3} \frac{\text{m}^3}{\text{kg}} \\ q_{ice} &= 3.4 \cdot 10^5 \frac{\text{J}}{\text{kg}} \end{aligned}$$

With  $p = \frac{F}{A}$  and  $F = m \cdot g$  ( $g = 9.81 \frac{\text{m}}{\text{s}^2}$ ), while  $A = w \cdot l$  we get for the pressure on the ice from the blade:

$$\Delta p = p_{blade} = \frac{m \cdot g}{w \cdot l} = 9.81 \cdot 10^5 \frac{\text{N}}{\text{m}^2}$$

Using  $T = 0^\circ\text{C} = 273.15\text{ K}$  and inserting in rearranged (12) we get:

$$\Delta T = \frac{T(v_2 - v_1)}{q_{12}} \Delta p = \frac{273.15(1.0 - 1.1) \cdot 10^{-3}}{3.4 \cdot 10^5} 9.81 \cdot 10^5 \text{ K} = -\frac{273.15 \cdot 10^{-4}}{3.4} 9.81 \text{ K} = -0.0788 \text{ K}$$

The freezing point therefore is decreased by 0.0788 K. This means the ice/water will be liquid at  $-0.0788\text{ K}$ .

We now want to estimate if this effect is sufficient to produce a film of water on which the skates can glide. Therefore we will start at  $T = 0^\circ\text{C} = 273.15\text{ K}$  again, this time calculating (12) in it's given form, while  $\Delta T$  should be the difference between temperature  $0^\circ\text{C}$  and the temperature of the ice, while  $\Delta p$  is the needed pressure to melt the ice, therefore we calculate the pressure, which is needed to melt ice at a temperature  $\Delta T$  below  $0^\circ\text{C}$ :

$$\frac{\Delta p}{\Delta T} = \frac{q_{12}}{T(v_2 - v_1)} = \frac{3.4 \cdot 10^5}{273.15 \cdot 10^{-4}} \frac{\text{J}}{\text{m}^3 \text{K}} = \frac{3.4 \cdot 10^5}{273.15 \cdot 10^{-4}} \frac{\text{J}}{\text{m}^3 \text{K}} = 12.45 \cdot 10^6 \frac{\text{Pa}}{\text{K}}$$

This means it needs a pressure of:

$$\Delta p = 12.45 \cdot 10^6 \frac{\text{Pa}}{\text{K}} \cdot \Delta T$$

to melt ice at a temperature  $\Delta T$  below  $0^\circ\text{C}$ . This would mean, that we can only ice skate as long as the ice temperature isn't below  $T = -0.0788^\circ\text{C}$  if we only have a look at this effect. Well, while ice skating is actually possible (even at temperatures smaller than  $-20^\circ\text{C}$ ), we can think of other effects. The main effect is found to be the friction and the heat it produces when skating over the ice. While at high temperatures about  $0^\circ\text{C}$  or little less, there is a naturally liquid film on the ice, which might allow the skating, at lower temperatures this film decreases till it vanishes, but skating remains possible. Therefore the skating experience might change in dependance of the ice temperature. The temperature of  $-7^\circ\text{C}$  was found to have a friction minimum, therefore it is used in indoor iceskating rinks. More information about the theory of melting can be found in one of the books of Prof. Kleinert<sup>2</sup>.

**(b)**

Assuming  $v_l \ll v_g$ ,  $v_g = \frac{k_B T}{p}$  and  $q_{lg} \neq q_{lq}(T)$  we can get using (12):

$$\frac{dp}{dT} = \frac{q_{lg}}{T(v_g - v_l)} \approx \frac{q_{lg}}{T(v_g)} = \frac{q_{lg}}{k_B T^2} p$$

separating variables:

$$\begin{aligned} \frac{dp}{p} &= \frac{q_{lg}}{k_B} \frac{dT}{T^2} \\ \int_{p_0}^p \frac{dp'}{p'} &= \frac{q_{lg}}{k_B} \int_{T_0}^T \frac{dT}{T^2} \\ \ln\left(\frac{p}{p_0}\right) &= \frac{q_{lg}}{k_B} \left(-\frac{1}{T} + \frac{1}{T_0}\right) \\ p(T) &= p_0 \exp\left[\frac{q_{lg}}{k_B} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \end{aligned}$$

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<sup>2</sup>Kleinert, Hagen, Gauge Fields in Condensed Matter, Vol. II, "STRESSES AND DEFECTS; Differential Geometry, Crystal Melting", pp. 743-1456, World Scientific (Singapore, 1989); Paperback ISBN 9971-5-0210-0