

8 Task Theoretical Physics VI - Statistics

8.1 (Thermodynamics of the van der Waals gas)

Van der Waals gas:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

a, b constant, $R = N_A k_B$. n the number of moles (the equation given by the task seems to be wrong, since it says $N = nN_A$, which would be the number of particles). This can be rearranged to:

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (1)$$

(a)

First we will verify, that C_V will not depend on the volume.
definition:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V,N}$$

maxwell relation (will be used in the equation (2)):

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

It is equivalent to show that C_V doesn't depend on the volume V and that the derivative of C_V in terms of V is zero:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \frac{\partial^2 S}{\partial V \partial T} = T \frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V} \right)_T = T \frac{\partial}{\partial T} \left(\frac{\partial p}{\partial T} \right)_V = T \left(\frac{\partial^2 p}{\partial T^2} \right)_V \quad (2)$$

now using p from (1) we get:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \frac{\partial}{\partial T} \left(\frac{nR}{V - nb} \right) = 0$$

□

Therefore C_V indeed doesn't depend on the volume. Now we assume, that the heat capacity is:

$$C_V = \frac{3}{2}nR = \frac{3}{2}Nk_B$$

We can use, that the number of particles $N = \text{const.}$ and $U = U(T, V, N)$, which leads to:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV \quad (3)$$

while the definition of heat capacity is known:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

we still have to find $\left(\frac{\partial U}{\partial V}\right)_{T,N}$. We can get to know this using the entropy

$$dS = \frac{1}{T} \delta Q = \frac{1}{T} (dU - \delta W) = \frac{1}{T} (dU + p dV)$$

inserting (3):

$$\begin{aligned} dS &= \frac{1}{T} \left(\left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + p dV \right) \\ &= \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial V}\right)_{T,N} + p \right) dV \\ &= \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV \end{aligned} \quad (4)$$

Now using, that entropy is exact:

$$\frac{\partial}{\partial V} \frac{\partial S}{\partial T} = \frac{\partial}{\partial T} \frac{\partial S}{\partial V}$$

we can insert:

$$\begin{aligned} \frac{\partial}{\partial V} \left[\frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{V,N} \right] &= \frac{\partial}{\partial T} \left[\frac{1}{T} \left(\left(\frac{\partial U}{\partial V}\right)_{T,N} + p \right) \right] \\ \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} &= \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} - \frac{1}{T^2} \left(\frac{\partial U}{\partial V}\right)_{T,N} + \frac{1}{T} \frac{\partial p}{\partial T} - \frac{p}{T^2} \end{aligned} \quad (5)$$

while U is also exact:

$$\frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} = \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V}$$

and (5) can be rearranged to:

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = T \frac{\partial p}{\partial T} - p \quad (6)$$

Now we can express the internal energy as:

$$dU = C_V dT + \left(T \frac{\partial p}{\partial T} - p \right) dV$$

inserting (1):

$$\begin{aligned}
dU &= C_V dT + \left(T \frac{nR}{V-nb} - \frac{nRT}{V-nb} + \frac{an^2}{V^2} \right) dV \\
&= C_V dT + \frac{an^2}{V^2} dV
\end{aligned}$$

Now, while U is exact (this can be seen immediately, while both 2nd derivatives lead to zero), we can integrate:

$$U(T, V) = \int C_V dT - c(V) + U_0 = C_V T - c(V) + U_0$$

and

$$U(T, V) = an^2 \int \frac{1}{V^2} dV - c(T) + U_0 = -\frac{an^2}{V} - c(T) + U_0$$

this yields:

$$U(T, V) = C_V T - \frac{an^2}{V} + U_0$$

now we are looking at the limit $a = 0$ and we get:

$$U(T, V) = C_V T + U_0$$

with $C_V = \frac{3}{2} N k_B$ and $U_0 = 0$ this is:

$$U = \frac{3}{2} N k_B T$$

Now the entropy, using (4) and (6):

$$\begin{aligned}
dS &= \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_{V,N} dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial V} \right)_{T,N} + p \right) dV \\
&= \frac{C_V}{T} dT + \frac{1}{T} \left(T \frac{\partial p}{\partial T} - p + p \right) dV \\
&= \frac{C_V}{T} dT + \frac{\partial p}{\partial T} dV
\end{aligned}$$

now inserting (1):

$$dS = \frac{C_V}{T} dT + \left(\frac{nR}{V-nb} \right) dV$$

which again is exact and yields:

$$S(T, V) = C_V \int \frac{1}{T} dT + c(V) + S_0 = C_V \ln T + c(V) + S_0$$

and

$$S(T, V) = nR \int \frac{1}{V - nb} dV + c(T) + S_0 = nR \ln(V - nb) + c(T) + S_0$$

yielding the function:

$$S(T, V) = C_V \ln T + nR \ln(V - nb) + S_0$$

using $b = 0$:

$$S(T, V) = Nk_B \left(\ln VT^{\frac{3}{2}} \right) + S_0$$

Comparison with the entropy of the ideal gas (Sackur-Tetrode-equation)

$$S = Nk_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] = Nk_B \ln(VT^{\frac{3}{2}}) + Nk_B \left[\ln \left(\frac{1}{N} \left(\frac{4\pi mk_B}{3h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$

shows the same dependencies on V and T . Therefore:

$$S_0 = Nk_B \left[\ln \left(\frac{1}{N} \left(\frac{4\pi mk_B}{3h^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] = \text{const.}$$

because $N = \text{const.}$

(b)

definition free energy:

$$F = U - TS$$

inserting from Sackur-Tetrode:

$$\begin{aligned} F &= \frac{3}{2}Nk_B T + Nk_B T \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] \\ &= Nk_B T \left[4 + \ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{\frac{3}{2}} \right) \right] \end{aligned}$$

or for our result for the entropy from **a**):

$$F = Nk_B T \left(\frac{3}{2} + \ln VT^{\frac{3}{2}} \right) + TS_0$$

8.2 (Cycles)

We observe several cycles for the ideal gas. The ideal gas is defined by the equation:

$$pV = Nk_B T$$

definition of efficiency:

$$\eta = \frac{W}{\Delta Q_{abs}}$$

We can use:

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

which can be rewritten to:

$$\delta Q = dU + p \cdot dV = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + p \cdot dV$$

inserting $C_V = \left(\frac{\partial U}{\partial T} \right)_V$ and $\left(\frac{\partial U}{\partial V} \right)_T = 0$ we get:

$$\delta Q = C_V \cdot dT + p \cdot dV$$

now using the definition of the enthalpy:

$$dH = dU + pdV + Vdp$$

we get for adiabatic parts $\delta Q = 0 \Rightarrow dU + pdV = 0$:

$$\begin{aligned} C_V \cdot dT &= -p \cdot dV \\ dH &= Vdp \end{aligned}$$

which can be rewritten using $C_p dT = dH$ and $\frac{C_p}{C_V} = \gamma \Rightarrow C_p = \gamma C_V$:

$$\begin{aligned} \gamma C_V \cdot dT &= -\gamma p \cdot dV \\ C_p dT &= Vdp \end{aligned}$$

which means:

$$-\gamma \cdot \frac{dV}{V} = \frac{dp}{p}$$

integration leads to:

$$\begin{aligned} -\gamma \ln \left(\frac{V_f}{V_i} \right) &= \ln \left(\frac{p_f}{p_i} \right) \\ -\gamma \ln(V_f) + \gamma \ln(V_i) &= \ln(p_f) - \ln(p_i) \\ \gamma \ln(V_i) + \ln(p_i) &= \ln(p_f) + \gamma \ln(V_f) \\ \ln(p_i V_i^\gamma) &= \ln(p_f V_f^\gamma) \\ p_i V_i^\gamma &= p_f V_f^\gamma \end{aligned} \tag{7}$$

or using the ideal gas equation with $p = \frac{Nk_B T}{V}$:

$$\begin{aligned}\frac{Nk_B T_i}{V_i} V_i^\gamma &= \frac{Nk_B T_f}{V_f} V_f^\gamma \\ T_i V_i^{\gamma-1} &= T_f V_f^{\gamma-1}\end{aligned}\tag{8}$$

or for $V = \frac{Nk_B T}{p}$:

$$\begin{aligned}p_i \left(\frac{Nk_B T_i}{p_i} \right)^\gamma &= p_f \left(\frac{Nk_B T_f}{p_f} \right)^\gamma \\ p_i^{1-\gamma} T_i^\gamma &= p_f^{1-\gamma} T_f^\gamma \\ \left(\frac{T_i}{T_f} \right)^\gamma &= \left(\frac{p_f}{p_i} \right)^{1-\gamma} \\ \frac{T_i}{T_f} &= \left(\frac{p_f}{p_i} \right)^{\frac{1-\gamma}{\gamma}} \\ T_i p_i^{\frac{1-\gamma}{\gamma}} &= T_f p_f^{\frac{1-\gamma}{\gamma}}\end{aligned}\tag{9}$$

(a) Otto cycle

to show:

$$\eta = 1 - (V_2/V_1)^{\gamma-1}$$

We first have a look at the cycle, where we see two adiabatic and two isochoric parts. Starting at the middle left point with V_1 , while the volume doesn't change ($dV = 0$) we get:

$$Q_1 = C_V dT$$

Integration leads to:

$$Q_1 = C_V \int_{T_{1,c}}^{T_{1,h}} dT = C_V \cdot (T_{1,h} - T_{1,c})$$

now looking at the upper point of V_2 :

$$Q_2 = C_V \int_{T_{2,h}}^{T_{2,c}} dT = C_V \cdot (T_{2,c} - T_{2,h})$$

with

$$W = Q_1 + Q_2 = C_V \cdot (T_{1,h} - T_{1,c} - (T_{2,h} - T_{2,c}))$$

and

$$\Delta Q_{abs} = Q_1 = C_V (T_{1,h} - T_{1,c})$$

we get:

$$\eta = \frac{W}{\Delta Q_{abs}} = 1 - \frac{T_{2,h} - T_{2,c}}{T_{1,h} - T_{1,c}}$$

Now we want to express the temperature terms in volumes. Therefore we can use the adiabatic parts of the cycle. We can insert the problem in (8):

$$T_{1,h}V_1^{\gamma-1} = T_{2,h}V_2^{\gamma-1} \quad \text{and} \quad T_{1,c}V_1^{\gamma-1} = T_{2,c}V_2^{\gamma-1}$$

leading to:

$$\begin{aligned} (T_{1,h} - T_{1,c})V_1^{\gamma-1} &= (T_{2,h} - T_{2,c})V_2^{\gamma-1} \\ \left(\frac{V_1}{V_2}\right)^{\gamma-1} &= \frac{(T_{1,h} - T_{1,c})}{(T_{2,h} - T_{2,c})} \end{aligned}$$

inserting in the efficiency equation:

$$\eta = 1 - \frac{T_{2,h} - T_{2,c}}{T_{1,h} - T_{1,c}} = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

□

Well, the result isn't the same like in the task, but while $V_1 < V_2$ and we don't want a negative η , this result seems physically correct. Since the exponent is non negative, we would have a negative efficiency for V_2/V_1 since it is bigger then one for $V_1 < V_2$.

(b) Joule cycle

to show:

$$\eta = 1 - (p_1/p_2)^{(\gamma-1)/\gamma}$$

We first have a look at the cycle, where we see two adiabatic and two isobaric parts. First we have a look at the isobaric parts, where $p = \text{const.}$. Starting at p_2 we use:

$$\begin{aligned} \delta Q &= dU + p \cdot dV \\ dH &= dU + pdV + Vdp \end{aligned}$$

for $p = \text{const.} \Rightarrow dp = 0$, therefore $\delta Q = dH = C_p dT$ and we can simply integrate:

$$Q_2 = C_p \int_{T_{2,r}}^{T_{2,l}} dT = C_p (T_{2,l} - T_{2,r})$$

and for p_1 :

$$Q_1 = C_p \int_{T_{1,l}}^{T_{1,r}} dT = C_p (T_{1,r} - T_{1,l})$$

With the definition of the efficiency we get:

$$\eta = \frac{W}{\Delta Q_{abs}} = \frac{Q_1 + Q_2}{Q_2} = 1 + \frac{Q_1}{Q_2} = 1 - \frac{T_{1,l} - T_{1,r}}{T_{2,l} - T_{2,r}} \quad (10)$$

Now the adiabatic parts ($Q = 0$), for our problem using (9):

$$T_{1,l} p_1^{\frac{1-\gamma}{\gamma}} = T_{2,l} p_2^{\frac{1-\gamma}{\gamma}} \quad \text{and} \quad T_{2,r} p_2^{\frac{1-\gamma}{\gamma}} = T_{1,r} p_1^{\frac{1-\gamma}{\gamma}}$$

this can be rearranged to:

$$\begin{aligned} (T_{1,l} - T_{1,r}) p_1^{\frac{1-\gamma}{\gamma}} &= (T_{2,l} - T_{2,r}) p_2^{\frac{1-\gamma}{\gamma}} \\ \frac{T_{1,l} - T_{1,r}}{T_{2,l} - T_{2,r}} &= \left(\frac{p_2}{p_1} \right)^{\frac{1-\gamma}{\gamma}} \\ \left(\frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}} &= \frac{T_{1,l} - T_{1,r}}{T_{2,l} - T_{2,r}} \end{aligned}$$

Inserted in (10) this leads to:

$$\eta = 1 - \frac{T_{1,l} - T_{1,r}}{T_{2,l} - T_{2,r}} = 1 - \left(\frac{p_1}{p_2} \right)^{\frac{\gamma-1}{\gamma}}$$

□

(c) Diesel cycle

to show:

$$\eta = 1 - \frac{1}{\gamma} \frac{(V_2/V_1)^\gamma - (V_3/V_1)^\gamma}{(V_2/V_1) - (V_3/V_1)}$$

We again look at the cycle, where we got 2 adiabatic, one isobaric and one isochoric parts. Starting with the isobaric part we get:

$$Q_{p2} = C_p (T_{p2,l} - T_{p2,r})$$

now the isochoric part:

$$Q_{V1} = C_V (T_{V1,c} - T_{V1,h})$$

this leads to the efficiency:

$$\eta = \frac{W}{\Delta Q_{abs}} = \frac{Q_{p2} + Q_{V1}}{Q_{p2}} = 1 + \frac{C_V}{C_p} \frac{T_{V1,c} - T_{V1,h}}{T_{p2,l} - T_{p2,r}} = 1 - \frac{1}{\gamma} \frac{T_{V1,h} - T_{V1,c}}{T_{p2,l} - T_{p2,r}}$$

with the adiabatic parts using (8):

$$T_{V1,c} V_1^{\gamma-1} = T_{p2,l} V_3^{\gamma-1} \quad \text{and} \quad T_{p2,r} V_2^{\gamma-1} = T_{V1,h} V_1^{\gamma-1}$$

we can rearrange this:

$$\begin{aligned} T_{V1,c} &= T_{p2,l} \left(\frac{V_3}{V_1} \right)^{\gamma-1} \\ T_{V1,h} &= T_{p2,r} \left(\frac{V_2}{V_1} \right)^{\gamma-1} \end{aligned}$$

inserting in the efficiency equation we get:

$$\begin{aligned}
\eta &= 1 - \frac{1}{\gamma} \frac{T_{V1,h} - T_{V1,c}}{T_{p2,l} - T_{p2,r}} \\
&= 1 - \frac{1}{\gamma} \frac{T_{p2,l} \left(\frac{V_3}{V_1}\right)^{\gamma-1} - T_{p2,r} \left(\frac{V_2}{V_1}\right)^{\gamma-1}}{T_{p2,l} - T_{p2,r}} \\
&= 1 - \frac{1}{\gamma} \frac{\left[\frac{T_{p2,l}}{V_3} \left(\frac{V_3}{V_1}\right)^\gamma - \frac{T_{p2,r}}{V_2} \left(\frac{V_2}{V_1}\right)^\gamma\right]}{\frac{1}{V_1} (T_{p2,l} - T_{p2,r})} \\
&= 1 - \frac{1}{\gamma} \frac{\frac{T_{p2,r}}{V_2} \left(\frac{V_2}{V_1}\right)^\gamma - \frac{T_{p2,l}}{V_3} \left(\frac{V_3}{V_1}\right)^\gamma}{\frac{T_{p2,r}}{V_2} \left(\frac{V_2}{V_1}\right) - \frac{T_{p2,l}}{V_3} \left(\frac{V_3}{V_1}\right)}
\end{aligned}$$

using, that $p_2 = \text{const.}$ and $\frac{p_2}{Nk_B} = \frac{T_{p2,r}}{V_2}$ and $\frac{p_2}{Nk_B} = \frac{T_{p2,l}}{V_3}$ (meaning both T, V combinations are on the same isobaric line) we can rewrite to:

$$\eta = 1 - \frac{1}{\gamma} \frac{\left(\frac{V_2}{V_1}\right)^\gamma - \left(\frac{V_3}{V_1}\right)^\gamma}{\left(\frac{V_2}{V_1}\right) - \left(\frac{V_3}{V_1}\right)}$$

□

8.3 (Thermodynamic potentials)

Given equation of state:

$$m = \frac{DH}{T} \Rightarrow M = n \frac{DH}{T} \Leftrightarrow H = \frac{MT}{nD} \quad (11)$$

m is molar magnetization, H magnetic field, T temperature and D is a constant, n number of moles.

further conditions:

$$\begin{aligned}
c_M &= \frac{C_M}{N} \\
c_M &= c
\end{aligned}$$

N number of particles and c is constant.

At first we will get ourselves the hamiltonian for this problem. We interpret the task as a solid body with magnetic moments in an extern magnetic field, where those magnetic moments will be forced parallel to the extern field (the total magnetisation will be parallel, while the magnetic moments can for sure point in an arbitrary direction, but this effect is middled out over all magnetic moments). The magnetisation is:

$$\vec{M} = \frac{1}{V} \sum_{i=1}^N \vec{\mu}_i$$

while the magnetisation is parallel to the magnetic field the equation $\vec{M} \cdot \vec{H} = MH$ holds and the hamiltonian is:

$$\hat{H} = - \sum_{i=1}^N \vec{\mu}_i \cdot \vec{H} = -VMH$$

Now we can use (11) to get:

$$\hat{H} = -\frac{VT}{nD}M^2$$

We now follow the hint:

molar internal energy

First we consider the situation, while we got a solid there will be no change in the pressure, volume or number of particles, therefore $dp = 0$, $dV = 0$, $dN = 0$. Therefore we get:

$$dU = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM \quad (12)$$

while we know $\frac{c_M}{N} = c_M = \left(\frac{\partial U}{\partial T}\right)_M$ the term $\left(\frac{\partial U}{\partial M}\right)_T$ is not known. We try to find it in a similar way to **8.1**.

Using the Gibbs-Duhem-Relation:

$$dS(U, M) = \frac{1}{T}dU - \frac{1}{T} \left\langle \frac{\partial \hat{H}}{\partial M} \right\rangle dM$$

now using (lecture 28.11.2007 thermodynamic limes) $X_\alpha = \langle X_\alpha \rangle = \left\langle \frac{d\hat{H}}{d\xi_\alpha} \right\rangle \Rightarrow \left\langle \frac{\partial \hat{H}}{\partial M} \right\rangle = \frac{\partial \hat{H}}{\partial M}$ we get:

$$dS(U, M) = \frac{1}{T}dU + \frac{1}{T} \frac{2VT}{nD} M dM = \frac{1}{T}dU + \frac{2V}{nD} M dM$$

inserting (12):

$$\begin{aligned} dS(U, M) &= \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{1}{T} \left(\frac{\partial U}{\partial M}\right)_T + \frac{2V}{nD} M\right) dM \\ &= \frac{c_M}{T} dT + \left(\frac{1}{T} \left(\frac{\partial U}{\partial M}\right)_T + \frac{2V}{nD} M\right) dM \\ &= \left(\frac{\partial S}{\partial T}\right)_M dT + \left(\frac{\partial S}{\partial M}\right)_U dM \end{aligned} \quad (13)$$

while entropy should be an exact differential:

$$\begin{aligned} \frac{\partial}{\partial M} \frac{\partial S}{\partial T} &= \frac{\partial}{\partial T} \frac{\partial S}{\partial M} \\ \frac{\partial}{\partial M} \frac{c_M}{T} &= \frac{\partial}{\partial T} \frac{1}{T} \left(\frac{\partial U}{\partial M}\right)_T + \frac{\partial}{\partial T} \frac{2V}{nD} M \end{aligned}$$

$$\begin{aligned}
0 &= \frac{\partial}{\partial T} \frac{1}{T} \left(\frac{\partial U}{\partial M} \right)_T \\
0 &= -\frac{1}{T^2} \left(\frac{\partial U}{\partial M} \right)_T + \frac{1}{T} \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial M} \right)_T \\
\frac{1}{T} \left(\frac{\partial U}{\partial M} \right)_T &= \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial M} \right)_T
\end{aligned}$$

now using, that U is exact, too:

$$\frac{\partial^2 U}{\partial M \partial T} = \frac{\partial^2 U}{\partial T \partial M} = \frac{\partial}{\partial M} c_M = \frac{\partial}{\partial M} c = 0$$

therefore we get:

$$\frac{1}{T} \left(\frac{\partial U}{\partial M} \right)_T = 0$$

which shows, that U is independant of M or equivalently u is independant of m . Now we can use this in (12):

$$dU = \left(\frac{\partial U}{\partial T} \right)_M dT$$

and integration yields:

$$U = c_M T + U_0$$

entropy

using (13) with U independant of M :

$$dS = \frac{c_M}{T} dT + \frac{2V}{nD} M dM$$

we can integrate:

$$S(T, M) = c_M \int \frac{1}{T} dT + c(M) + S_0 = c_M \ln T + c(M) + S_0$$

and

$$S(T, M) = \frac{2V}{nD} \int M dM + c(T) + S_0 = \frac{VM^2}{nD} + c(T) + S_0$$

which leads to:

$$S(T, M) = c_M \ln T + \frac{VM^2}{nD} + S_0$$

enthalpy

definition (with help of lecture from 2./7.11.2007 $p = - \left\langle \frac{\partial \hat{H}}{\partial V} \right\rangle$):

$$H = U + p \cdot V = U - \left\langle \frac{\partial \hat{H}}{\partial V} \right\rangle \cdot V$$

now using thermodynamic limes $\left\langle \frac{\partial \hat{H}}{\partial V} \right\rangle = \frac{\partial \hat{H}}{\partial V}$ and inserting \hat{H} leads to:

$$H = U + \frac{TM^2}{nD} \cdot V = c_M T + \frac{TV}{nD} \cdot M^2 + U_0$$

free energy

definition:

$$\begin{aligned} F &= U - TS \\ &= c_M T + U_0 - T \cdot \left(c_M \ln T + \frac{VM^2}{nD} + S_0 \right) \\ &= c_M T (1 - \ln T) - \frac{VM^2 T}{nD} + U_0 - TS_0 \end{aligned}$$

Gibbs free energy

definition:

$$G = U - TS + pV = F + pV = H - TS$$

this means:

$$\begin{aligned} G &= c_M T (1 - \ln T) - \frac{VM^2 T}{nD} + U_0 - TS_0 + \frac{TV}{nD} \cdot M^2 \\ &= c_M T (1 - \ln T) + U_0 - TS_0 \end{aligned}$$