Exercises for
Theoretical physics IV

WiSe 2022/23 **Sheet 4** **08.11.2022**

Exercise 8 *Thermodynamic potentials and Maxwell Relations*

Thermodynamic potentials are functions from which all thermodynamic quantities can be derived. The prerequisite for this is that the correct variables (natural variables) are used for the respective thermodynamic potential. In addition to the internal energy U, there are further thermodynamic potentials, of which we will describe the enthalpy H, the free energy F, the free enthalpy G, the great potential *Omega* and finally the Helmholtz free potential Consider energy A.

a) The change in the internal energy $U(S, V, \vec{H})$ of a body with a magnetic moment $\vec{M}$ in a homogeneous external magnetic field is $\vec{H}$

$$dU = T\,dS - p\,dV - \vec{M}\cdot d\vec{H} = T\,dS - p\,dV - \sum_i M_i\,dH_i \tag{1}$$

for a constant number of particles. Based on the free energy $F(T, V, \vec{H})$, we define the so-called Helmholtz free energy $A = A(T, V, \vec{M})$ via

$$A = F + \vec{M}\cdot\vec{H} = F + \sum_i M_i\,H_i\,. \tag{2}$$

Based on the equations (1) and (2), derive the follow relations

$$\left(\frac{\partial U}{\partial S}\right)_{V,H_i} = T\,,\quad \left(\frac{\partial U}{\partial V}\right)_{S,H_i} = -p\,,\quad \left(\frac{\partial U}{\partial H_i}\right)_{S,V,H_k\neq H_i} = -M_i,$$
$$\left(\frac{\partial A}{\partial T}\right)_{V,M_i} = -S\,,\quad \left(\frac{\partial A}{\partial V}\right)_{T,M_i} = -p\,,\quad \left(\frac{\partial A}{\partial M_i}\right)_{T,V,M_k\neq M_i} = H_i\,,$$

and thus prove the Maxwell relations

$$\left(\frac{\partial M_i}{\partial V}\right)_{S,H_k} = \left(\frac{\partial p}{\partial H_i}\right)_{S,V,H_k\neq H_i}\,,\quad \left(\frac{\partial M_i}{\partial S}\right)_{V,H_k} = -\left(\frac{\partial T}{\partial H_i}\right)_{S,V,H_k\neq H_i}\,,$$
$$\left(\frac{\partial H_i}{\partial V}\right)_{T,M_k} = -\left(\frac{\partial p}{\partial M_i}\right)_{T,V,M_k\neq M_i}\quad \left(\frac{\partial H_i}{\partial T}\right)_{V,M_k} = -\left(\frac{\partial S}{\partial M_i}\right)_{T,V,M_k\neq M_i}\,.$$

(2 points)

Exercise 9 *Partial Trace*

Let us consider two Hilbert spaces that are combined into one via a tensor product: $\mathfrak{H} = \mathfrak{H}_1 \otimes \mathfrak{H}_2$. The dimensions of the Hilbert spaces are D_1 and D_2. Furthermore, each Hilbert space is spanned by a basis, denoted by $\{|a_i\rangle\}$ and $\{|b_i\rangle\}$. Let $\hat{X}$ be an operator defined over $\mathfrak{H}$. Its trace can be written as

$$\mathrm{Tr}[\hat{X}] = \sum_{i=1}^{D_1} \sum_{j=1}^{D_2} \langle a_i| \otimes \langle b_j|\hat{X}|a_i\rangle \otimes |b_j\rangle. \tag{3}$$

This operation results in a scalar. Similarly, we define the partial trace over $\mathfrak{H}_2$ as

$$\hat{X}_1 = \mathrm{Tr}_2[\hat{X}] = \sum_{j=1}^{D_2} \langle b_j|\hat{X}|b_j\rangle, \tag{4}$$

where one obtains an operator defined over $\mathfrak{H}_1$.

a) Let us consider a state of two spins $|\Psi\rangle$ such that

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle). \tag{5}$$

Determine the form of the density matrix $\hat{\rho} = |\Psi\rangle\langle\Psi|$.

(1 point)

b) Determine the expression of the reduced density matrices $\hat{\rho}_1 = \mathrm{Tr}_2[\hat{\rho}]$ and $\hat{\rho}_2 = \mathrm{Tr}_1[\hat{\rho}]$.

(1 point)

Exercise 10 *Properties of paramagnetic systems*

We consider a system of N non-interacting spin-1/2 particles which are in a static magnetic field $\vec{B} = B_0\vec{e}_z$. The Hamiltonian operator is then given by

$$\hat{H} = -B_0\hat{M}^z = \mu_B B_0 \sum_{j=1}^{N} \hat{\sigma}^z \tag{6}$$

where $\hat{M}^z$ is the magnetisation operator in the z-direction and μ_B is the Bohr magneton. Furthermore, let $\hat{\rho}_N$ be the density matrix of the entire system of N spins.

a) Show that in a homogeneous system the following statement is true

$$\langle\hat{M}^z\rangle = N\mu_B \mathrm{Tr}\{\hat{\rho}_1\hat{\sigma}_1^z\} \tag{7}$$

where $\hat{H}_1 = \mu_B B_0 \hat{\sigma}_1^z$ and $\hat{\rho}_1 = \mathrm{Tr}_{N-1}\{\hat{\rho}_N\}$, where Tr_{N-1} is the trace over $N-1$ spins.

(1 point)

b) Let us assume a Boltzmann-Gibbs distribution of spins. The density matrix of a single spin is then given by

$$\hat{\rho}_1 = \frac{e^{\beta\epsilon_0}|+\rangle\langle+| + e^{-\beta\epsilon_0}|-\rangle\langle-|}{\mathcal{Z}_1}, \tag{8}$$

with the normalisation constant $\mathcal{Z}_1 = e^{\beta\epsilon_0} + e^{-\beta\epsilon}$ and $\epsilon_0 = \mu_B B_0$. Show that the expectation value of the magnetisation in the z-direction is given by

$$\langle\hat{M}^z\rangle = N\mu_B \tanh\left(\frac{\mu_B B_0}{k_B T}\right) \tag{9}$$

with $\beta = 1/(k_B T)$.

(1 point)

c) Determine the expression for the standard deviation $\Delta M^z = \sqrt{\langle(\hat{M}^z)^2\rangle - \langle\hat{M}^z\rangle^2}$ of the magnetisation. Comment on the scaling of the standard deviation with respect to the system size N.

(1 point)