

Exercise 8.1 Independent Dimers in a Magnetic Field

We consider a system of independent dimers described by the Hamiltonian

$$\mathcal{H}_0 = J \sum_i (\vec{S}_{i,1} \cdot \vec{S}_{i,2} + c) \quad (1)$$

where i numbers the dimers and $m = 1, 2$ correspond to their two magnetic sites, c is just some constant.

- What are the eigenstates and the eigenenergies of a single dimer? Choose the constant c in such a way that the groundstate energy vanishes.
- We now apply a magnetic field in z direction leading to an additional term in the Hamiltonian,

$$\mathcal{H}' = -g\mu_B H \sum_{i,m} S_{i,m}^z. \quad (2)$$

How do the eigenenergies change? Sketch the energies with respect to the applied field H and determine the particular groundstate. Discuss in this context also the entropy per dimer $s(T, H)$, in particular, in the limit $T \rightarrow 0$.

- Calculate the magnetization m and the magnetic susceptibility χ and discuss their dependence on H for different temperatures.

Exercise 8.2 The Ideal Paramagnetic Gas and the Law of Mass Action

The goal of this exercise is to understand the statistical mechanics of a mixture of ideal gases undergoing chemical reactions. An application is an ideal gas where paramagnetic atoms may combine to form molecules whose magnetic moment vanishes.

- Consider r different substances A_1, \dots, A_r (e.g. $A_1 = \text{H}_2$, $A_2 = \text{O}_2$, and $A_3 = \text{H}_2\text{O}$) that undergo s chemical reactions

$$\nu_1^\alpha A_1 + \dots + \nu_r^\alpha A_r = 0,$$

where $\alpha = 1, \dots, s$ and $\{\nu_i^\alpha\}$ are the *stoichiometric coefficients* of the reaction α (in the above example we have $s = 1$ and $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -2$).

Let N_i be the number of particles of the substance A_i . Now, if the system is materially closed the set of possible variations in the number of particles is given by

$$dN_i = \sum_{\alpha=1}^s \nu_i^\alpha d\lambda^\alpha,$$

with independent variations $d\lambda^1, \dots, d\lambda^s$. Show that, under constant temperature and pressure, the condition for thermodynamic equilibrium reads

$$\sum_{i=1}^r \nu_i^\alpha \mu_i = 0,$$

for each $\alpha = 1, \dots, s$ independently.

- b) Let each substance A_i be an ideal gas composed of point particles of mass m_i and with binding energy E_i . The Hamiltonian for the particles of type A_i then reads

$$\mathcal{H}_i = \sum_{j=1}^{N_i} \left(\frac{\vec{p}_j^2}{2m_i} + E_i \right).$$

Compute the grand canonical partition function \mathcal{Z} (fixed temperature, volume, and chemical potentials) of the system and show the *law of mass action*: At equilibrium one has

$$\prod_{i=1}^r \langle N_i \rangle^{\nu_i^\alpha} = f^\alpha(T, V, E_1, \dots, E_r) = \prod_{i=1}^r (V a_i e^{-\beta E_i})^{\nu_i^\alpha},$$

for each $\alpha = 1, \dots, s$. Here $a_i = (2\pi m_i k_B T)^{3/2}$.

- c) Consider now an ideal paramagnetic gas under the influence of an external magnetic field H (see also Section 3.5.4 in the lecture notes). The particles A_+ (resp. A_-) of mass m have a magnetic moment M parallel (resp. antiparallel) to the field. Furthermore, an A_+ and an A_- may combine to form a single molecule whose magnetic moment vanishes. The energy released in this reaction is E_b . The second possible “reaction” is a flip $A_\pm \mapsto A_\mp$. Use the above results to compute the relative magnetization per particle

$$\sigma = M \frac{\langle N_+ \rangle - \langle N_- \rangle}{\langle N_+ + N_- + 2N_0 \rangle}.$$

Discuss the high and low temperature limits. How do the laws of mass action read? Compare your results also with the prior exercise 8.1.