Problem E1

A system, which is in fact a defect in a crystal, is in thermal equilibrium with a heat reservoir with temperature T. The defect is characterized by its polarization vector $\vec{p}$, which has a constant length p and 8 possible directions given by the normal vectors in an xyz-coordinate system,

$$\vec{p} = (\pm 1, \pm 1, \pm 1)\frac{p}{\sqrt{3}}. \tag{1}$$

In an electric field pointing in the $(1, 1, 1)$ direction, i.e. $\vec{E} = (1, 1, 1) \cdot E/\sqrt{3}$, the energy of the defect is

$$E(\vec{p}) = -\vec{p} \cdot \vec{E}. \tag{2}$$

Question a:

Show that the defect has 4 different energies, and determine the degeneracy of each level.

Question b:

Show that the partition function for one defect can be written as

$$Z(T) = 8\cosh^3(x) \tag{3}$$

with $x = pE/(3kT)$.

Question c:

Determine the average energy $\bar{E}$ of one defect as a function of T and sketch it. Calculate $\bar{E}$ in the limits $T \to 0$ and $T \to \infty$.

Question d:

Determine the heat capacity C_V of one defect. Sketch also this function of T and comment on the limits $T \to 0$ and $T \to \infty$.

Question e:

Determine the entropy S of one defect as a function of T. Comment on the limits $T \to 0$ and $T \to \infty$.

Problem E2

We consider the chemical reaction $A + B \rightleftarrows AB$. The gases of A-atoms, B-atoms, and AB-molecules can be considered ideal, and they are confined in a container of volume V at constant temperature T. The total number of A-atoms and B-atoms are N_A^0 and N_B^0 so that there are $N_A = N_A^0 - N_{AB}$ and $N_B = N_B^0 - N_{AB}$ free A-atoms and B-atoms in the container. Here, N_{AB} denotes the number of AB-molecules. Let Z_i be the single-particle partition function given by Schroeder Eq. (6.84), where $i \in \{A, B, AB\}$.

Question a:

Calculate the free energy $F = U - TS$ of the mixture.

Question b:

Use that F is minimum for constant volume V and temperature T to show that in equilibrium

$$\frac{n_{AB}}{n_A n_B} = V \frac{Z_{AB}}{Z_A Z_B} \equiv K(T), \tag{4}$$

where $n_i = N_i/V$. Equation (4) is called the law of mass action.

Question c:

We now neglect any internal degrees of freedom, i.e. $Z_{\text{int}} = 1$ in Eq. (6.84). Discuss what happens if T increases. Discuss what happens if the ratio $m_{AB}/(m_A m_B)$ increases, where m_i is the mass of species i.

Problem E3

We consider an ideal gas of N identical atoms in a volume V and at temperature T. In addition to the translational degrees of freedom, each atom has two internal energy levels with energies ϵ_1 and ϵ_2. We have $\epsilon_2 > \epsilon_1$.

Question a:

Find the partition function Z_1 for a single atom in the gas and the partition function Z for all N atoms. Include the fact that the particles are indistinguishable only through the factor $N!$.

Question b:

Calculate the energy $U(T)$ and the heat capacity $C_V(T)$ of the gas, and sketch the two functions. What are $U(T)$ and $C_V(T)$ in the limits $T \ll (\epsilon_2 - \epsilon_1)/k$ and $T \gg (\epsilon_2 - \epsilon_1)/k$?

Question c:

Calculate the entropy $S(T)$ of the gas, and show that it can be written as $S = S_{\text{trans}} + S_{\text{int}}$. Determine S_{int} for $T \ll (\epsilon_2 - \epsilon_1)/k$ and $T \gg (\epsilon_2 - \epsilon_1)/k$.

Hand-in E

Consider two nuclei in a magnetic field B. One nucleus has spin $s = 1$ with the component $s_z = -1, 0, 1$ along the B field, and its energy in the three spin states is $-\epsilon_1$, 0, and ϵ_1, respectively. The other nucleus has spin $s' = 1/2$ with the component $s'_z = -1/2, 1/2$ along the B field, and its energy in the two spin states is $-\epsilon_2$ and ϵ_2, respectively. The total energy of the system is therefore

$$\epsilon_{\text{tot}} = s_z \epsilon_1 + 2 s'_z \epsilon_2.$$

We have $\epsilon_1 > 0$ and $\epsilon_2 > 0$, and the two nuclei are in thermal equilibrium with a reservoir at temperature T. The system is illustrated in figure 1.

Question a:

Give the partition function Z of the system.

Question b:

Calculate the average energy $E(T) = \overline{\epsilon_{\text{tot}}}$ of the system as a function of T. Find $\lim_{T\to 0} E(T)$ and $\lim_{T\to\infty} E(T)$, and give a physical interpretation of these limits.

We now take into account that the two spins interact with each other, so that the energy decreases by the amount U, when they are parallel, see figure 1. Thus, the energy of the system is $\epsilon_1 + \epsilon_2 - U$ when both spins are parallel with the B field, and the energy is $-\epsilon_1 - \epsilon_2 - U$ when both spins are anti-parallel to the B field. The energy of all other states is unchanged.

Question c:

Calculate the probability P that the two spins are parallel. Find $\lim_{U\to\infty} P$, and give a physical interpretation of this limit.

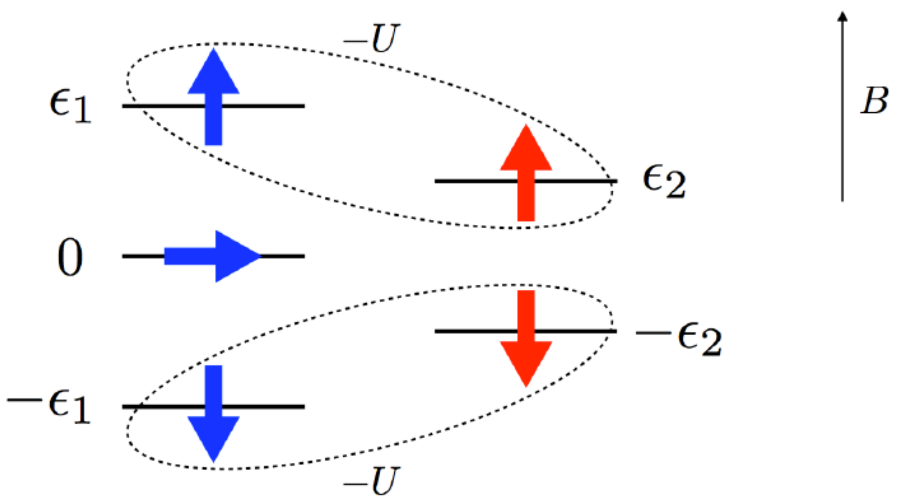

Figure 1. Energy levels of the two nuclei with spin 1 and spin 1/2. In question c, we include that the energy decreases by U, when the two spins are parallel.