ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Statistical Physics
Exercise 8

HS 12
Prof. M. Sigrist

Exercise 8.1   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.

Consider a gaseous mixture of r different substances $A_1, \ldots, A_r$ that undergo s chemical reactions,

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

indexed by $\alpha \in \{1, \ldots, s\}$, with $\{\nu_i^\alpha\}$ the *stoichiometric coefficients* of the reaction α.
Example: The reaction of water formation would be expressed through, $A_1 = H_2$, $A_2 = O_2$, and $A_3 = H_2O$, with $\nu_1 = 2$, $\nu_2 = 1$, and $\nu_3 = -2$.

Let N_i be the number of particles of the substance A_i. For a materially closed system, 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 $d\lambda^1, \ldots, d\lambda^s$ of the particle numbers according to the s reaction processes.

a) Show that, assuming constant temperature and pressure, the condition for thermodynamic equilibrium constrains the chemicals potentials μ_i of the r species to obey

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

for each $\alpha = 1, \ldots, s$ independently, and interpret this result.

b) Let each substance A_i be an ideal gas composed of particles of mass m_i and with potential 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 $\mathcal{Z}$ of the system and show that in equilibrium a *law of mass action*

$$\prod_{i=1}^{r} \langle N_i \rangle^{\nu_i^\alpha} = \prod_{i=1}^{r} \left[V(2\pi m_i k_B T)^{3/2} e^{-\beta E_i} \right]^{\nu_i^\alpha} \equiv K^\alpha(T, V),$$

is obtained for each reaction α.

This law states that in thermodynamic equilibrium, every chemical reaction is characterized by one value $K^\alpha(T, V)$, which depends only on the coefficients ν_i^α, the binding energies E_i and the particle masses m_i. In particular, $K^\alpha(T, V)$ is independent of the proportion of species in the mixture.

Remark: E_i can be a binding energy of a molecule or a Zeeman energy for substances with atomic or molecular magnetic moments

Exercise 8.2   Independent Dimers in a Magnetic Field. Quantum vs Ising

We consider a system of N independent dimers of two spins, $s = 1/2$, described by the Hamiltonian

$$\mathcal{H}_0^{\text{quantum}} = J \sum_i \left(\vec{S}_{i,1} \cdot \vec{S}_{i,2} \right), \tag{1}$$

where i is the dimer index and $m = 1, 2$ denotes the spin state along z direction ($|\uparrow\rangle$ or $|\downarrow\rangle$). For simplicity, we use $\hbar = 1$. To this quantum system corresponds a classical Ising dimer, described by:

$$\mathcal{H}_0^{\text{Ising}} = \frac{1}{2} J \sum_i \left(\sigma_{i,1} \cdot \sigma_{i,2} - \frac{1}{2} \right), \tag{2}$$

where $\sigma_{i,m} = \pm 1$. The spins are aligned along the z axis. We will use eigenstates and eigenenergies to denote also the classical states and energies.

a) What are the eigenstates and the eigenenergies of a single dimer for the two cases?

b) For both cases consider the macroscopic system and determine the Helmholtz free energy, the entropy, the internal energy and the specific heat as a function of temperature and N. Discuss the limit $T \to 0$ and $T \to \infty$ for both signs of J (antiferromagnetic and ferromagnetic case).

Note: The following exercises are left for the fun of the interested reader.

c*) We now apply a magnetic field along z direction leading to an additional term in the Hamiltonian,

$$\mathcal{H}_{\text{mag}}^{\text{quantum}} = -g\mu_B H \sum_{i,m} S_{i,m}^z \tag{3a}$$

$$\mathcal{H}_{\text{mag}}^{\text{Ising}} = -g\mu_B H \sum_{i,m} \frac{\sigma_{i,m}}{2}. \tag{3b}$$

How do the eigenenergies change? Sketch the energies with respect to the applied field H, the partition functions and determine the ground state for both cases. For the antiferromagnetic case you should notice a critical field. What differences do you notice between the classical and quantum system when the the critical field is reached? For the quantum case discuss in this context the entropy per dimer in the limit $T \to 0$.

d*) Calculate the magnetization m for the two cases. In which limit are they the same? Moreover compute the magnetic susceptibility χ for the quantum case and discuss its dependence on H for different temperatures.

Office Hours: Monday, November 12, $8 - 10$ am (Juan Osorio, HIT G 32.4)