Statistical Physics   HS 09
Exercise Sheet 7   Prof. M. Sigrist

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Exercise 7.1   Exact solution of the Ising chain

In this exercise we will investigate the physics of one of the few exactly solvable models, the *one-dimensional Ising model* (Ising chain). Consider a chain of $N + 1$ Ising-spins with free ends and nearest neighbor coupling J ($J < 0$ for ferromagnetic coupling)

$$
\mathcal{H} = J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} , \quad \sigma_i = \pm 1 . \tag{1}
$$

In this exercise we will be interested in the thermodynamic limit of this system, i.e. we assume N to be very large.

a) Compute the partition function Z_{N+1} using a recursive procedure.

b) Calculate the magnetization density $m = \langle \sigma_j \rangle$ where the spin σ_j is far away from the ends. Which symmetries does the system exhibit? Interpret you result in terms of symmetry arguments.

c) Show that the *spin correlation function* $\Gamma_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle$ decays exponentially with increasing distance $|j - i|$ on the scale of the so-called *correlation length* ξ, i.e. $\Gamma_{ij} \sim e^{-|j-i|/\xi}$. Show that $\xi = -[\log(\tanh -\beta J)]^{-1}$ and interpret your result in the limit $T \to 0$.

d) Use the fluctuation-dissipation relation in the thermodynamic limit $N \to \infty$,

$$
\frac{\chi(T)}{N} = \frac{1}{k_B T} \left(\sum_j \langle \sigma_0 \sigma_j \rangle - N \langle \sigma_0 \rangle^2 \right) , \tag{2}
$$

to calculate the magnetic susceptibility in zero magnetic field. Here the sum over j runs from $-N/2$ to $N/2$, where $N \to \infty$ (for simplicity we assume N to be even). Note that $\chi(T)$ is defined to be extensive, such that we obtain the intensive quantity by normalization with N, for details consider sections (3.4.5) and (3.4.6) of the lecture notes.

Exercise 7.2   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.

a) Consider a gaseous mixture of r different substances $A_1, \ldots, A_r$ (e.g. $A_1 = H_2$, $A_2 = O_2$, and $A_3 = H_2O$) that undergo s chemical reactions

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

where $\alpha = 1, \ldots, s$ and $\{\nu_i^\alpha\}$ are the *stoichiometric coefficients* of the reaction α (in the above example we have $s = 1$ and $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -2$). Note that these kind of equations allow for both directions of every chemical reaction process.

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 $d\lambda^1, \ldots, d\lambda^s$ of the particle numbers according to the s reaction processes. 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. This means that the proportions of the different species will assume the value that corresponds to the condition of detailed balance.

b) Let each substance A_i be an ideal gas composed of particles of mass m_i and with potential energy E_i (E_i can be a binding energy of a molecule or a Zeeman energy for substances with atomic or molecular magnetic moments). 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 T, volume V, and chemical potentials μ_i) of the system and show the *law of mass action*: At equilibrium one has

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

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

This law states that in thermodynamic equilibrium, every chemical reaction is characterized by a value $K^\alpha(T, V)$, determined only by the stoichiometric coefficients of the reaction, the binding energies and the mass of the particles. This value can only be changed by the external parameters such as the temperature or the system volume but is independent of the proportion of species in the mixture.

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 A_0 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?

Office Hours: Friday, October 30, 8-10 am (HIT K 12.2)