ETH
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Statistical Physics
Exercise Sheet 7

HS 11
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Exercise 7.1 Exact solution of the Ising chain

In this exercise we will investigate the physics of one of the few *exactly solvable interacting* 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)

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

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) Calculate the magnetic susceptibility in zero magnetic field using the fluctuation-dissipation relation of the form

$$\frac{\chi(T)}{N} = \frac{1}{k_B T} \sum_{j=-N/2}^{N/2} \Gamma_{0j}, \tag{2}$$

in the thermodynamic limit, $N \to \infty$. 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. The concepts will then be applied to an ideal gas of paramagnetic atoms which may combine to dimers whose magnetic moment vanishes.
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 $\alpha = 1, \dots, s$ 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

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

Compute the grand canonical partition function $\mathcal{Z}$ of the system and show that in equilibrium a *law of mass action*

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

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

c) As a concrete example, consider an ideal paramagnetic gas in an external magnetic field H. Two particle species A_+ (A_-) of mass m have a magnetic moment $|M|$ aligned parallel (antiparallel) to the field (with corresponding energy $E = -MH$).

Two reactions are considered here. On the one hand, 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. On the other hand we allow for a spin flip $A_\sigma \mapsto A_{-\sigma}$. Use the above results to compute average particle number of each species and 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. Express the laws of mass action explicitly for these reactions.

Office Hours: Monday, November 7, 9-10 am (Roland Willa, HIT K 23.3)