Exercise 05

Name:	Matriculation number:
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The exercise is due on Wednesday, May 23, 8 am.

5.1 Text book

Read sections 2.2 to 2.4 in G.H. Findenegg, T. Hellweg „Statistische Thermodynamik".

5.2 Canonical ensemble

Show explicitly the transition from the microcanonical ensemble to the canonical ensemble. Define and use the words: Particle partition function, System partition function and Degeneracy. Additionally, prove that $\beta \propto T^{-1}$.

5.3 Additivity of the entropy

From classical thermodynamics we know that the entropy of a combined system $S_{A,B}$ can be calculated as the sum of the entropy of the subsystems S_A and S_B.

$$S_{A,B} = S_A + S_B \tag{1}$$

In terms of statistical thermodynamics the (Gibbs) entropy is defined as:

$$S_{A,B} = -k_b \sum_{i,j} p_{ij} \log p_{ij} \tag{2}$$

where p_{ij} denotes the probability that subsystem A is in state i and subsystem B is in state j. Show that the entropy in terms of statistical thermodynamics is additive. The entropy of the single subsystem is defined as:

$$S_A = -k_b \sum_{i} p_i \log p_i \tag{3}$$

where p_i is the probability that subsystem A is in state i.

5.4 Energy fluctuation in the canonical ensemble

The energy fluctuation in a canonical ensemble is defined as

$$\Delta E^2 = \langle E^2 \rangle - \langle E \rangle^2 \tag{4}$$

where $\langle E \rangle$ is defined as

$$\langle E \rangle = \frac{1}{Q} \sum_j E_j \mathrm{e}^{-\beta E_j}. \tag{5}$$

Show that for this case

$$\Delta E^2 = k_b T^2 c_V$$

is fulfilled.

5.5 Calculation of state functions for a 3-level system

Consider a 3-level system at 400 K with

$$g_0 = g_1 = 2 \text{ and } g_2 = 4$$

and

$$\Delta E_1 = 4 \cdot 10^{-21}\text{J and } \Delta E_2 = 12 \cdot 10^{-21}\text{J.}$$

The partition function for this system is then defined as:

$$z = g_0 + g_1 \exp\left(-\beta \Delta E_1\right) + g_2 \exp\left(-\beta \Delta E_2\right) \tag{6}$$

(a) Calculate the internal energy U.

(b) Calculate the entropy S.

(c) Calculate the Helmholtz free energy A.