EXERCISE 3A: PARTITION FUNCTION

Objectives:

- Analyze a system in thermal equilibrium with a reservoir of known temperature. (Keywords: **canonical ensemble**, **partition function**.)
- Calculate the energy and **heat capacity** of a paramagnet vs. temperature.
- Derive and discuss the relationship between heat capacity and entropy.

Reading: Kittel & Kroemer, Ch. 3

Last time:

- We defined the temperature τ and inverse temperature $\beta \equiv 1/\tau = d\sigma/dE$.
- We derived the Boltzmann factor $e^{-\beta\varepsilon_s}$, where $\beta = 1/\tau$.

1. *Partition function.* Let X be a state function (e.g., magnetization; energy; volume or pressure of a gas) and X_s denote its value in a specific microstate s. Suppose that we know the *relative* probabilities of finding the system in different microstates, given by a set of weights w_s. How do we calculate the average value $\langle X \rangle$?

   a. The probability P_s of finding the system in microstate s is proportional to w_s, i.e., $P_s = w_s/Z$. What is the normalization factor Z?

   b. Write down a general expression for the average value $\langle X \rangle$ in terms of the weights w_s and Z.

   c. In the **canonical ensemble**, where the average is taken over identically prepared systems at **fixed temperature and particle number**, the quantity Z defined above is called the **partition function**. Write down explicit expressions for…

i. The **partition function** Z as a function of inverse temperature β and energies ε_s of the microstates s

ii. The average value $\langle X \rangle$ in terms of β and Z

d. Derive the following general relation between the expectation value of the energy and the partition function $Z = \sum_s e^{-\beta \varepsilon_s}$:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}. \tag{1}$$

2. *Energy and heat capacity of the paramagnet.* The **heat capacity** of a system at constant volume is

$$C_V \equiv \left(\frac{\partial E}{\partial \tau}\right)_V . \tag{2}$$

Calculate the energy E and heat capacity C_V of a paramagnet of N spins of magnetic moment μ in a magnetic field B at temperature τ. (Here, the volume plays no role.)

a. Show that the partition function for the paramagnet can be written in the form $Z = (a+b)^N$, where a and b depend on the energies $\pm\epsilon \equiv \pm\mu B$ of the two spin states and the inverse temperature $\beta = 1/(k_B T)$. What are a and b?

b. How else might you write out the partition function of the paramagnet? Why is the form in a. more convenient?

c. Use Eq. 1 to evaluate the energy $E(B, \tau)$ of the paramagnet.

d. Calculate the heat capacity C_V from the energy.

e. Sketch the heat capacity as a function of temperature. To this end, first determine the limiting behavior of the heat capacity …

   i. … for $\tau \ll \mu B$

   ii. … for $\tau \gg \mu B$

   iii. Based on the analysis above, sketch $C_V(\tau)$.

3. The heat capacity can alternatively be defined in terms of the temperature and entropy, without explicit reference to the energy.

   a. Derive a general expression for C_V in terms of σ and τ.
   Hint: Start by writing C_V/τ in terms of Eq. 2 and the definition of temperature.

   b. Suppose that you have measured the heat capacity of a solid as a function of temperature. Is this enough information to deduce the entropy $\sigma(\tau)$? Why or why not?

c. Physically, how do you interpret the peak in the heat capacity of the paramagnet? If you increased the magnetic field B, which way would you expect the peak to shift?

d. How do you explain the limiting behavior of the paramagnet's heat capacity at low and high temperature?