

EXERCISE 2B: THERMAL EQUILIBRIUM*Objectives:*

- Arrive at a definition of **temperature**, a quantity that is the same for two systems in **thermal equilibrium**.
- Understand the meaning of “hot” and “cold.”
- Derive the **Boltzmann factor**

Reference: Kittel & Kroemer, Ch. 2 + beginning of Ch. 3 (Eqs. 1-9)

1. Two systems in thermal equilibrium are said to be at equal temperature. But what exactly is temperature? To arrive at a definition, consider a generic composite system $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$ formed by allowing two subsystems $\mathcal{A}_1, \mathcal{A}_2$ to equilibrate at fixed total energy E .
 - a. Write down an expression for the multiplicity $g(N, E)$ of microstates of the total system \mathcal{A} by summing the multiplicities for configurations of variable energy E_1 in subsystem \mathcal{A}_1 . (Let us assume that each subsystem has a discrete energy spectrum; otherwise, you could replace the sum by an integral.)
 - b. The most probable configuration is found by maximizing the summand in part a. Show that the summand is maximized when

$$\frac{d\sigma_1}{dE_1} = \frac{d\sigma_2}{dE_2}, \quad (1)$$

where the **entropy** $\sigma_i = \ln g(N_i, E_i)$ represents the amount of information that would be required to specify the microstate of subsystem \mathcal{A}_i given its energy E_i .

- c. Based on your result in Equation 1, propose a definition of **temperature**.
- d. Explain in words the relation between temperature and energy. What does it mean for a system to be “hot” or “cold”?

- e. What is the entropy σ of the composite system $\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2$ with known total energy E ?
- i. First, write σ in terms of the sum from part a.

- ii. How does your expression in i. simplify in the thermodynamic limit? Explain.
Hint: It may help to sketch the typical behavior of the multiplicity $g(E_1, E_2 = E - E_1)$ of states with energy E_1 in subsystem \mathcal{A}_1 .

2. Very often, we are interested in the properties of a system \mathcal{A} that is in thermal equilibrium with a much larger reservoir \mathcal{R} . Let us take the system to be a single spin with two energy states $E_{\uparrow}, E_{\downarrow}$ and the reservoir to be its surrounding environment at temperature τ . Calculate the ratio of probabilities $P_{\uparrow}/P_{\downarrow}$ for finding the spin in the $|\uparrow\rangle$ or $|\downarrow\rangle$ state, as follows:
- Write down an expression for $\ln(P_{\uparrow}/P_{\downarrow})$, noting that the probability of finding the spin in a given state is proportional to the multiplicity of available microstates for the composite system including the reservoir.
 - Express your result from part a. in terms of temperature τ and use it to evaluate $P_{\uparrow}/P_{\downarrow}$.
 - What are the limiting values of $P_{\uparrow}/P_{\downarrow}$ as $\tau \rightarrow 0$ and as $\tau \rightarrow \infty$? Assume $E_{\uparrow} > E_{\downarrow}$. Are the results consistent with your physical intuition? Why or why not?

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- d. To familiarize yourself with more common notational conventions, reexpress your result from b. in terms of
 - i. The temperature T (which has units of Kelvin)
 - ii. The inverse temperature $\beta \equiv 1/\tau$

3. *Boltzmann factor.* Consider a generic system \mathcal{A} in thermal equilibrium with a reservoir \mathcal{R} , and consider two microstates of the system with energies E_1 and E_2 . Show that the probabilities of finding the system in these two microstates are related by the **Boltzmann factor**

$$\frac{P_1}{P_2} = e^{-\beta(\varepsilon_1 - \varepsilon_2)}. \quad (2)$$

4. *A closer look at multiplicity and entropy.* We have been somewhat sloppy in treating the multiplicity $g(E)$ sometimes as a function defined for only a discrete set of energy levels E and sometimes as a continuous function.

a. Why might it be a good approximation to regard $g(E)$ as a continuous function in the thermodynamic limit?

b. Suppose that our system has a discrete energy spectrum, but the spacing ϵ between energy levels is smaller than some resolution δE quantifying the smallest energy difference that we can measure. How much does the energy uncertainty δE change our lack of knowledge of the microstate, as quantified by the entropy?

i. Let $\bar{g}(E)$ represent the multiplicity of states with energies between E and $E + \delta E$. How is $\bar{g}(E)$ related to the multiplicity $g(E)$, in terms of ϵ and δE ?

ii. How is the entropy $\bar{\sigma} = \ln \bar{g}$ related to $\sigma = \ln g$?

- iii. Consider the case of a paramagnet, where $\epsilon = 2\mu B$. Suppose that $\delta E = n\epsilon$ is the change in energy when n spins are flipped, with $1 \ll n < N$. How does the fractional correction $(\bar{\sigma} - \sigma)/\sigma$ to the entropy scale with N and n ?
- iv. Suppose $N = 10^{23}$ and $n = 10^{20}$. Give an order-of-magnitude estimate for $(\bar{\sigma} - \sigma)/\sigma$. Does the finite resolution $\delta E = n\epsilon$ matter?

When the energy spectrum is best approximated as continuous, it is often useful to refer not to the multiplicity but to the density of states $\mathcal{D}(E)$ per unit energy, defined such that $\bar{g}(E) = \mathcal{D}(E)\delta E$. We shall return to this concept later in the course.