

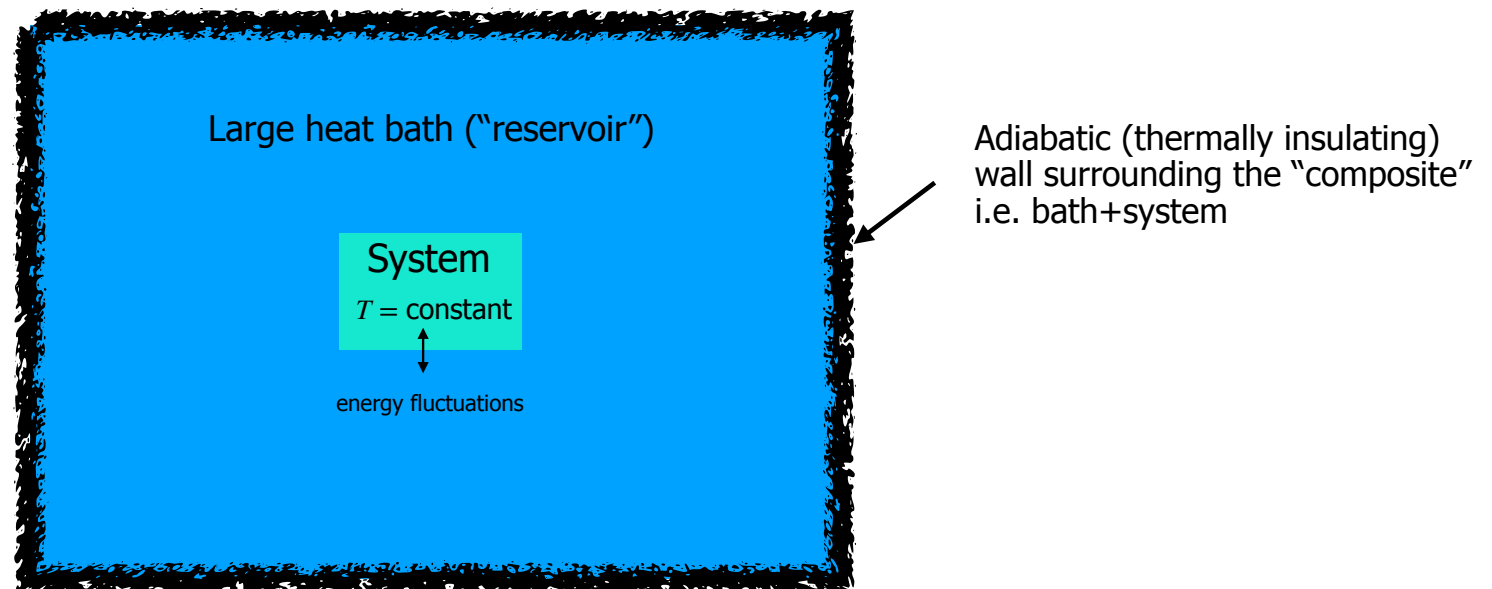


4. Boltzmann distribution

Boltzmann distribution



- Previously we have considered an isolated system of fixed N, E .
- Here we consider systems with fixed N but instead of E being fixed, we fix the temperature T by placing it in contact with a heat bath ("reservoir").
- Bath is assumed sufficiently large that energy can be exchanged with the system without its temperature changing. Thus by zeroth law, the temperature of the system is the same as the constant temperature of the reservoir.



Boltzmann distribution



Statistical Mechanics

- Total energy of composite system (system+bath) E_{TOT} fixed, but system energy **fluctuates**
- As the system energy can vary due to thermal fluctuations, it can explore microstates of **different** energy
- Recall: microstates of the same energy are explored with equal probability
- What are the relative probabilities of microstates of different energy?
- Let the probability that system is in a given microstate i , of energy E_i be P_i .
- If the system is in microstate i there is energy $E_{TOT} - E_i$ left for the bath, and this corresponds to many possible microstates for the bath.

Boltzmann distribution



- Since for the composite all microstates are equally likely,

$$P_i = \text{constant} \times \Omega_b(E_{TOT} - E_i)$$

$$\text{Planck equation} \Rightarrow \Omega_b(E_{TOT} - E_i) = \exp \left(\frac{S_b(E_{TOT} - E_i)}{k_B} \right)$$

$$\text{Since } E_i \ll E_{TOT} \quad S_b(E_{TOT} - E_i) = S_b(E_{TOT}) - E_i \frac{\partial S_b}{\partial E_b} + \frac{E_i^2}{2} \frac{\partial^2 S_b}{\partial E_b^2} + \dots$$

$$\simeq S_b(E_{TOT}) - E_i \frac{\partial S_b}{\partial E_b}$$

$$\simeq \underset{\substack{\uparrow \\ \text{Constant}}}{S_b(E_{TOT})} - \frac{E_i}{T}$$

- Thus $P_i \propto \exp \left(-\frac{E_i}{kT} \right)$

Boltzmann distribution



- Normalize probabilities by summing over all microstate

$$P_i = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_j \exp\left(-\frac{E_j}{kT}\right)} \equiv \frac{1}{Z} \exp\left(-\frac{E_i}{kT}\right) \quad \bullet \text{ This is the } \mathbf{Boltzmann distribution}$$

- *Key point 10:* $P_i = \frac{1}{Z} \exp(-\beta E_i)$ where $Z = \sum_j \exp(-\beta E_j)$ and $\beta = \frac{1}{kT}$

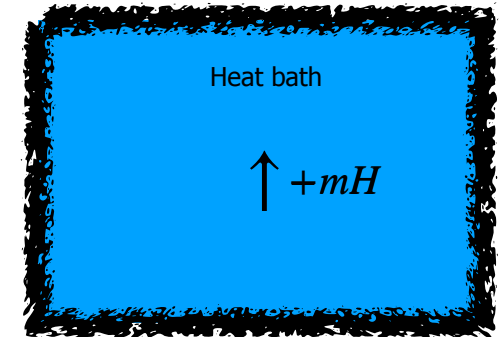
Boltzmann distribution



- Example 1: Single dipole two microstates \downarrow, \uparrow with energies $-mH, +mH$

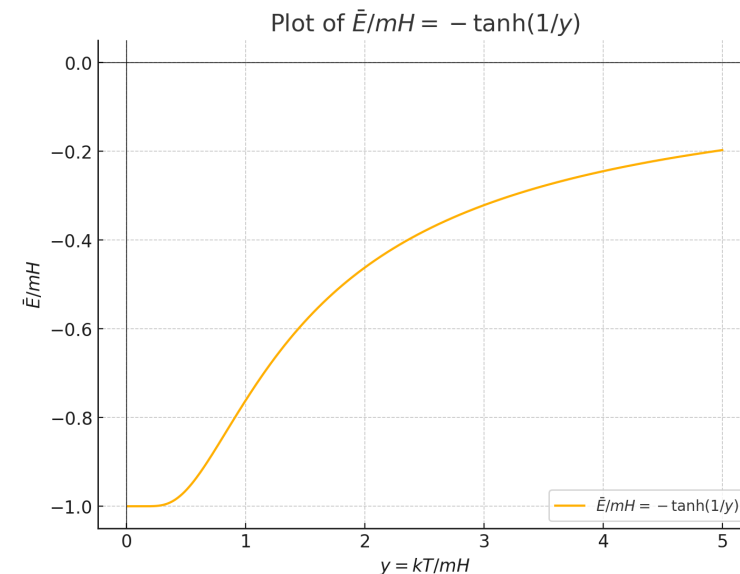
$$P(\downarrow) = \frac{\exp\left(\frac{mH}{kT}\right)}{Z}, \quad P(\uparrow) = \frac{\exp\left(-\frac{mH}{kT}\right)}{Z}$$

$$Z = \exp\left(\frac{mH}{kT}\right) + \exp\left(-\frac{mH}{kT}\right) = 2 \cosh\left(\frac{mH}{kT}\right)$$



- Average energy as function of H and T

$$\begin{aligned} \bar{E} &= \sum_i E_i P_i = \frac{1}{Z} [-mH P(\downarrow) + mH P(\uparrow)] \\ &= -mH \frac{\sinh\left(\frac{mH}{kT}\right)}{\cosh\left(\frac{mH}{kT}\right)} = -mH \tanh\left(\frac{mH}{kT}\right) \end{aligned}$$



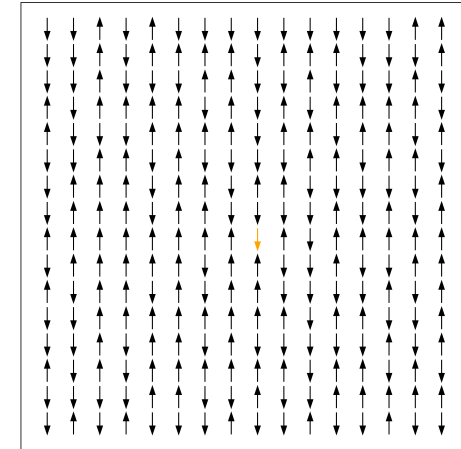
Boltzmann distribution



- Example 2: Single constituent in an isolated system for large N
- Recall that for our isolated system

$$S(E) = -Nk \left[x \ln x + (1 - x) \ln(1 - x) \right], \quad x = \frac{n}{N} = \frac{1}{2} \left(1 + \frac{E}{NmH} \right)$$

where n is the number of excited dipoles



$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{dx}{dE} \frac{\partial S}{\partial x} = -\frac{Nk}{2NmH} \left[\ln x + 1 - \ln(1 - x) - 1 \right] = -\frac{k}{2mH} \ln \left(\frac{x}{1 - x} \right)$$

$$\exp \left(-\frac{2mH}{kT} \right) = \frac{x}{1 - x}$$

$$x = \frac{n}{N} = \frac{\exp \left(-\frac{2mH}{kT} \right)}{1 + \exp \left(-\frac{2mH}{kT} \right)} = \frac{\exp(-\beta mH)}{\exp(\beta mH) + \exp(-\beta mH)}$$

Boltzmann distribution



Statistical Mechanics

- The frequency definition of probability implies that n/N is the probability that a single dipole is in the excited state.
- We see we recover the Boltzmann distribution of the previous subsection for a single dipole!
- Why?
- Because a single dipole exchanges energy with the $N - 1$ other dipoles. For large N , the other dipoles act as a heat bath for the single dipole.