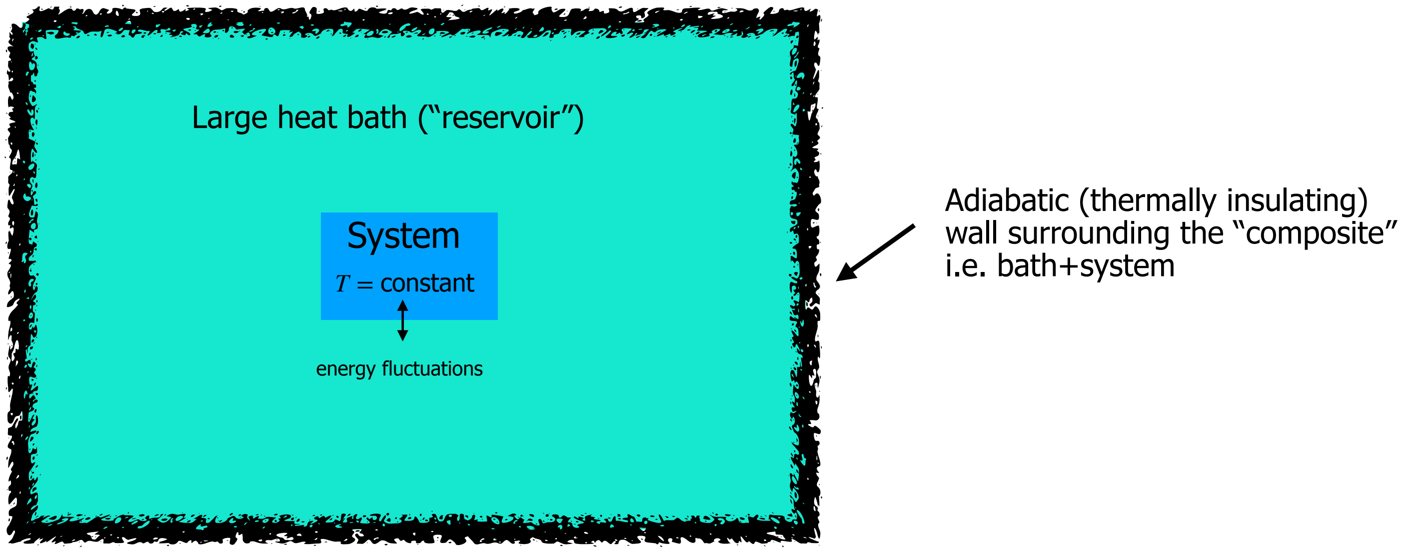
4. Boltzmann distribution

Boltzmann distribution

- Previously we have considered an isolated system of fixed N, E.
- Now 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 sufficiently large that energy can be exchanged with the system without its temperature changing. Zeroth law $\Rightarrow$ the temperature of the system is the same as the constant temperature of the reservoir.



Boltzmann distribution

- 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,

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

(see notes)

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

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

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

Key point 9

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

Independent of E_i

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

Boltzmann distribution

- Normalize probabilities by summing over all microstates

$$P_i = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_j \exp\left(-\frac{E_j}{kT}\right)} \equiv \frac{1}{Z}\exp\left(-\frac{E_i}{kT}\right)$$

- This is the **Boltzmann distribution**

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

Partition function. Sums Boltzmann factor over all microstates

Basic Hyperbolic Functions

$$\cosh x = \frac{e^x + e^{-x}}{2}, \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$\operatorname{sech} x = \frac{1}{\cosh x} = \frac{2}{e^x + e^{-x}}$$

$$\operatorname{cosech} x = \frac{1}{\sinh x} = \frac{2}{e^x - e^{-x}}$$

$$\coth x = \frac{\cosh x}{\sinh x} = \frac{1}{\tanh x} = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

Some derivatives of hyperbolic functions

$$\frac{d}{dx}(\sinh x) = \cosh x$$

$$\frac{d}{dx}(\cosh x) = \sinh x$$

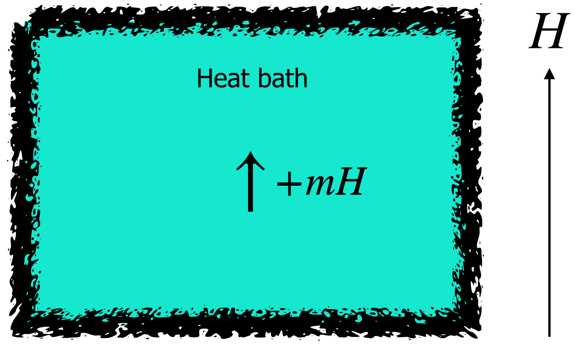
$$\frac{d}{dx}(\tanh x) = \operatorname{sech}^2 x$$

Boltzmann distribution

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

$$P(\downarrow) = \frac{\exp\left(-\beta mH\right)}{Z}, \quad P(\uparrow) = \frac{\exp\left(\beta mH\right)}{Z} \qquad \beta = \frac{1}{kT}$$

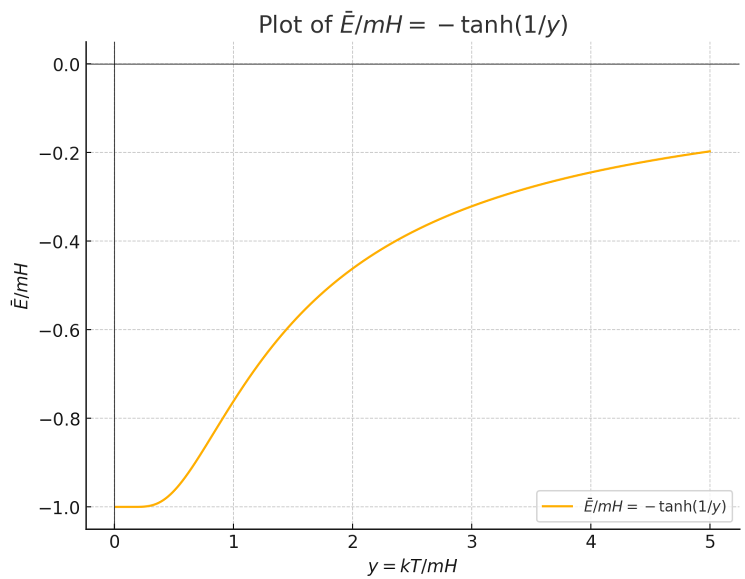
$$Z = \exp\left(\beta mH\right) + \exp\left(-\beta mH\right) = 2\cosh\left(\beta mH\right)$$



- Average energy as function of H and T

$$\overline{E} = \sum_i E_i P_i = \frac{1}{Z}[mHP(\downarrow) - mHP(\uparrow)]$$

$$= -mH\frac{\sinh\left(\beta mH\right)}{\cosh\left(\beta mH\right)} = -mH\tanh\left(\beta mH\right)$$



Worked example

Q: In a system of weakly-interacting particles, in equilibrium at temperature T, each particle has access to three states of energy $\epsilon = 0, \varepsilon_0, 3\varepsilon_0$. There are three times as many particles with energy ε_0 as there are with energy $3\varepsilon_0$. What fraction of the particles will be found with energy $\epsilon = 0$?

Solution

The probability P_i that a particle occupies a state with energy ϵ_i is given by the Boltzmann distribution:

$P_i = \dfrac{e^{-\beta\epsilon_i}}{Z}$, where $\beta = \dfrac{1}{kT}$ and $Z = \sum_i e^{-\beta\epsilon_i}$ is the partition function, ie. sum of the Boltzmann factors for all accessible microstates

Let the number of particles in the energy state $\epsilon_2 = 3\varepsilon_0$ be N_2, and the number of particles in the state $\epsilon_1 = \epsilon_0$ be $N_1 = 3N_2$.

We want to find the number of particles in the state $\epsilon = 0$, denoted N_0, relative to these populations.

From the question we have: $$\frac{N_1}{N_2} = \frac{P_1}{P_2} = \frac{e^{-\beta\varepsilon_0}}{e^{-\beta(3\varepsilon_0)}} = e^{\beta 2\varepsilon_0} = 3$$

and thus $$e^{-\beta\varepsilon_0} = \frac{1}{\sqrt{3}}$$

$$\frac{N_0}{N_{\text{total}}} = P_0 = \frac{e^{-\beta\times 0}}{Z} = \frac{1}{1 + e^{-\beta\varepsilon_0} + e^{-3\beta\varepsilon_0}} = \frac{1}{1 + \frac{1}{\sqrt{3}} + \frac{1}{3\sqrt{3}}} \approx 0.565$$