

4 The Boltzmann distribution

See Mandl chapter 2.5 and Blundell & Blundell chapter 20

Previously we have considered an isolated system of fixed N, E . Here we consider systems with fixed N but instead of E being fixed, the system is at some fixed temperature T .

To be specific our system is in equilibrium with a heat bath (or heat reservoir) at constant T . The zeroth law of thermodynamics then implies our system is at temperature T and the thermal contact with the reservoir means that energy can be exchanged. Therefore the energy of our system is not fixed and the system can explore microstates of different energy. We expect microstates of the same energy to have the same probabilities (we have no reason to believe otherwise). However since we are at fixed T we might think that microstates of different energy should have different probabilities. In the following we substantiate this.

4.1 Derivation of the Boltzmann distribution


Figure 1 illustrates the setup we shall use.

We will refer to the system of interest as the ‘system’ and the composite system (system plus heat bath) as the ‘composite’. The composite is isolated and has fixed total energy E_{TOT} . Thus for the composite all microstates are equally likely. But we are interested in microstates of the system.

Let the probability that system is in a given microstate labelled i , of energy E_i , be P_i . Now if the system is in this microstate there is energy $E_{TOT} - E_i$ left for the bath, and this corresponds to many possible microstates for the bath. Since for the composite all microstates are equally likely, we deduce

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

where the subscript b refers to the bath.

 If you don't follow this

Here is the reasoning. For fixed total energy E_{TOT} , the total number of microstates of the composite of system and bath is $\Omega = \Omega_s \Omega_b$, a constant. If we consider only the microstate of the system with energy E , then their number is $\Omega_s(E) = \Omega / \Omega_b(E_{TOT} - E)$. Now as all microstates of the system having a given energy are equally likely, the probability $P_i(E)$ of the system being in a specific microstate i with energy E is $P_i(E) = 1 / \Omega_s(E) = \Omega^{-1} \Omega_b(E_{TOT} - E)$.

Now using the Planck relation (key point 4)

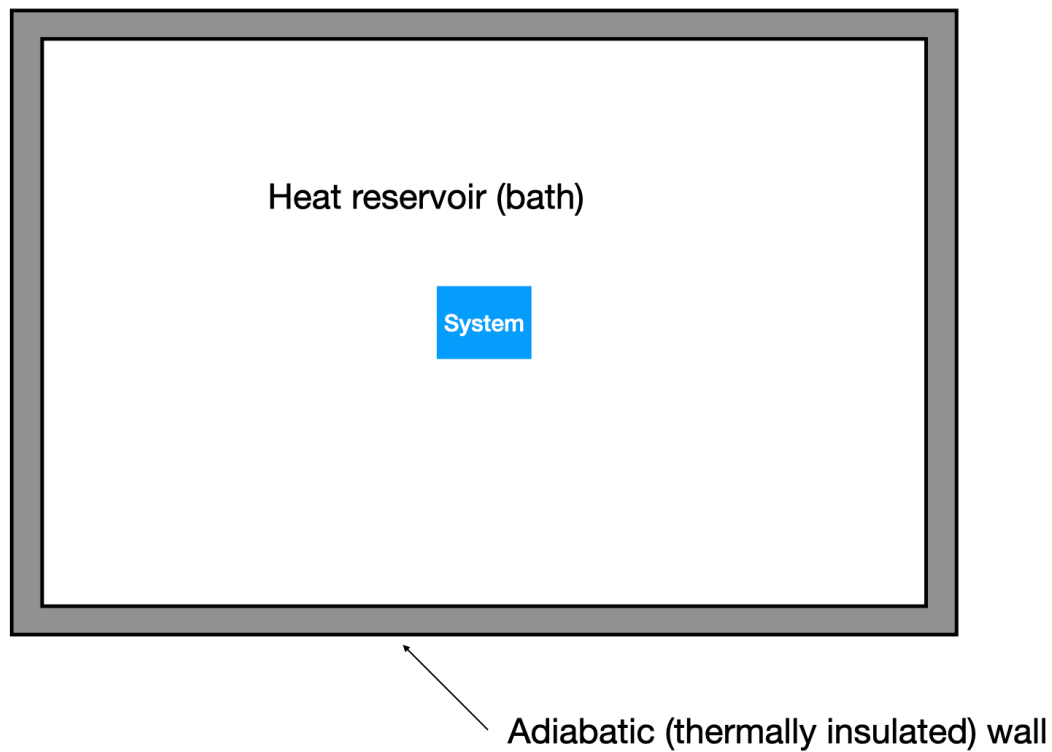


Figure 1: Composite system of a large heat reservoir within which is the system of interest

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

Since $E_i \ll E_{TOT}$ we can perform a Taylor expansion

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

Only keeping the first two terms (it turns out that the third term is small) and using key point 9 to identify

$$\frac{1}{T_b} = \frac{\partial S_b}{\partial E_b}$$

we find

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

The first term on the right hand side is a constant therefore when we insert this in the expression for P_i (or $\Omega_b(E_{TOT} - E_i)$) above we obtain

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

In order that the probability be normalised we require

$$\sum_i P_i = 1$$

where the sum is over all microstates of the system which implies

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

Thus the Boltzmann distribution for the probability that a system in equilibrium with a heat bath at temperature T is in microstate i is

💡 Key Point 10:

$$P_i = \frac{1}{Z} \exp(-\beta E_i) \quad \text{where } Z = \sum_j \exp(-\beta E_j) \quad \text{and } \beta = \frac{1}{kT}$$

You have met this distribution in year 1 properties of matter. for example in considering an isothermal atmosphere where particles of mass m have height probability distribution $P(h) \propto$

$\exp(-mgh)$. To see this is a Boltzmann distribution recall that the potential energy of kT such a particle is $mgh + \text{constant}$.

The Boltzmann distribution is also known as the canonical distribution (canonical simply means standard).

The quantity Z is known as the **partition function** or partition sum. Although introduced quietly here as a normalisation we shall see that it holds the key to calculating all properties of the system!

4.2 Boltzmann distribution for a single particle system

As a simple application of the Boltzmann distribution, let us consider a single magnetic dipole in equilibrium with a heat bath. (This is discussed in Baierlein 5.3 but with some differences in notation.)

Recall that a single dipole has two microstates \downarrow, \uparrow with energies $mH, -mH$.

A simple application of the Boltzmann distribution gives:

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

where the partition function Z is given by:

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

The average energy of the dipole is given by:

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

To see the temperature dependence of \bar{E} , we plot it as a function of $y = \frac{kT}{mH}$:

$$\bar{E} = -mH \tanh\left(\frac{1}{y}\right)$$

You should be able to sketch this curve by recalling the properties of the tanh function:

$$\tanh x \approx x \quad \text{for small } x, \quad \tanh x \approx 1 \quad \text{for } x \gg 1$$

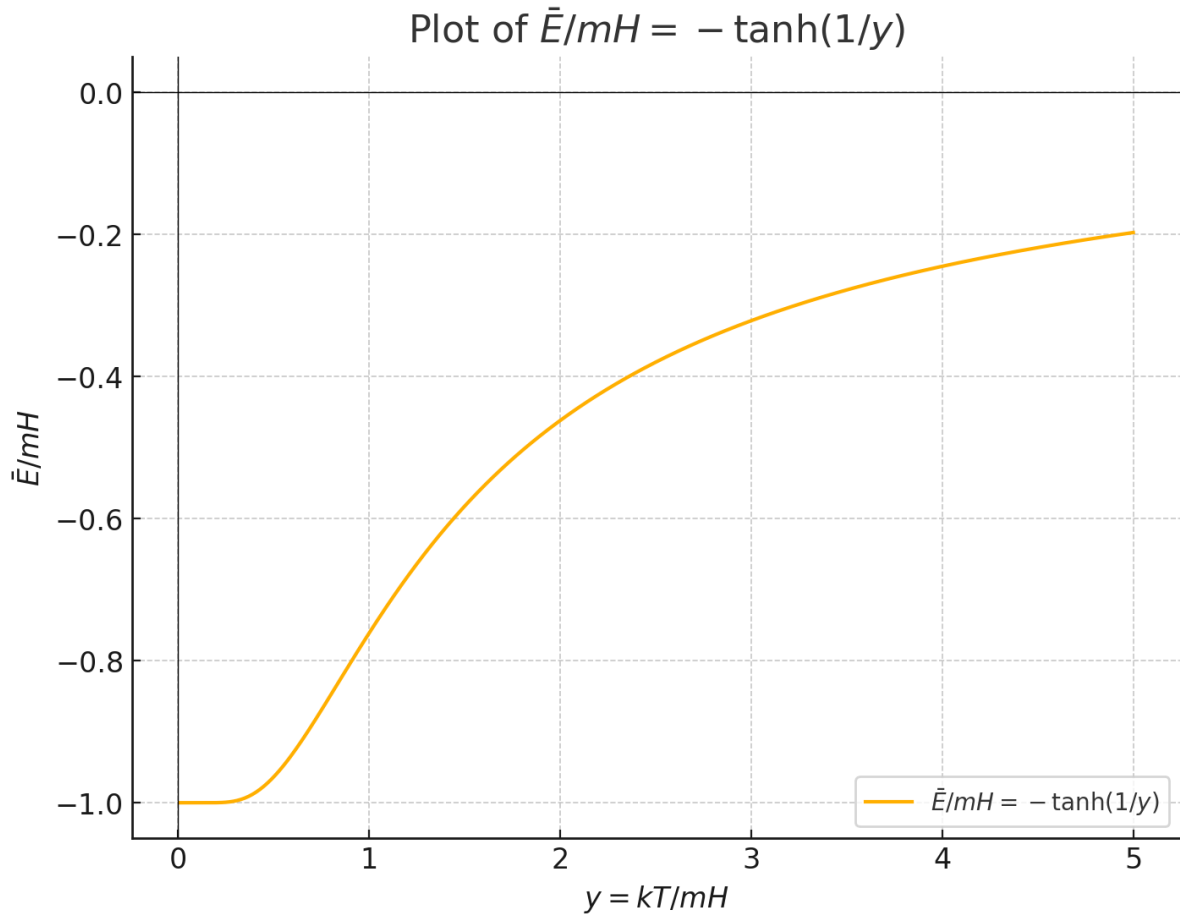



Figure 2: Mean energy \bar{E}/mH versus scaled temperature for a single dipole

The curve is plotted in [Figure 2](#).

 Expand to learn about hyperbolic functions and their identities

Hyperbolic Identities

The hyperbolic functions satisfy a number of identities. These allow expressions involving the hyperbolic functions to be written in different, yet equivalent forms. Several commonly used identities are given below.

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

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

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

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

Fundamental Identities

$$\cosh^2 x - \sinh^2 x = 1$$

$$1 - \tanh^2 x = \operatorname{sech}^2 x$$

$$\coth^2 x - 1 = \operatorname{cosech}^2 x$$

4.3. Single constituent in an isolated system for large N

In order to gain more insight into the generality of the Boltzmann distribution, we return briefly to the scenario of chapters 3 and 4 where we considered an isolated system with a large number N of constituents. We saw we could define an entropy $S(E)$ through the Planck relation and a temperature through key point 9.

In particular, for the model magnet, we used the Planck relation to find the entropy:

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

where n is the number of excited dipoles and N is the total number of dipoles.

Using key point 9, we find:

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

Inverting this, we find:

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

so that:

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

The frequency definition of probability implies that $\frac{n}{N}$ 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!

At first, this seems very confusing: for an isolated system, we have all microstates equally likely—so where did the Boltzmann distribution suddenly appear from?

The answer is to realize that a single dipole exchanges energy with the $N - 1$ other dipoles. Therefore, for large N , the other dipoles act as a heat bath for the single dipole, which is why we recover the Boltzmann distribution for a single dipole.

Another way of thinking about this is to remember that although all microstates of the isolated system are equally likely, we have the constraint of total fixed energy. Therefore, for a single dipole, its two states are not equally likely since the state it is in dictates how much energy is left to share among the other dipoles. Therefore, the global constraint of fixed energy induces a Boltzmann distribution for a single dipole.