

## Recap:

E: Experiment

events  $\omega_1, \dots, \omega_2$

$X(\omega)$ : random variable

A: output space  $\{X_1, \dots, X_N\}$

F: event space: subset of A

$P(X_k) = p_k$ : probabilities

## Application:

Experiment A

Experiment B: repeat "A"  $N$ -times  
independently!

→ LLN

→ CLT



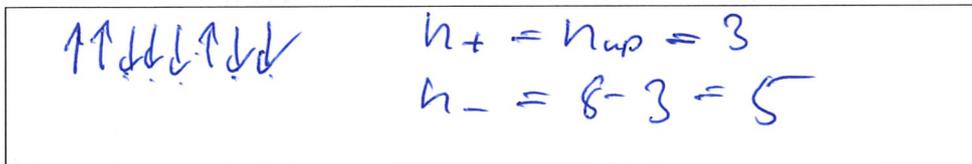
### 3 Microcanonical ensemble and temperature

#### 3.1 Entropy

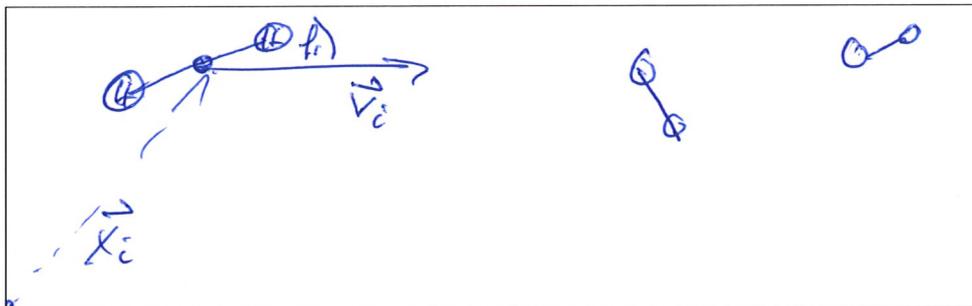
Consider a system of degrees of freedom coming out of a random process and call this state  $\omega_1$ .

Examples:

(A) 8 arrows, say spins, with orientation either *up* or *down*



(B) A container with  $N$  moving  $H_2$  molecules



The system evolves under the laws of physics into a new state  $\omega_2$ . We also introduce a *measurement*  $E(\omega) \in \mathbb{R}$ , which does not change under the evolution of the system. In particular, we have

$$E(\omega_1) = E(\omega_2)$$

$E$  is called a *conserved quantity*. An important example is the (*internal*) *Energy* of a closed system.

**Definition:** The fact that the total energy does not change during time evolution when the system adopt different elements of the output space is called the **First law of Thermodynamics**.

Examples:

(A) If a spin is parallel to an external magnetic field, it contributes the energy  $H$  to the internal Energy. If a spin is anti-parallel, its contribution is  $-H$ . If  $n_+$  is the numbers of spins parallel and  $n_- = N - n_+$  the number of anti-parallel spins, the internal energy is given by  $E = H(n_+ - n_-)$ .

example before:  $E = H \cdot (3 - 5) = -2H$   
 $\downarrow \uparrow \downarrow \uparrow \downarrow \downarrow \in \text{state (or event)}$

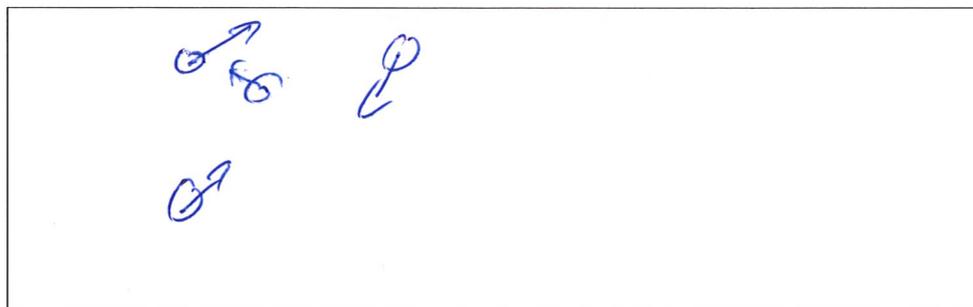
(B) If the  $i$ th molecule has velocity  $\vec{v}_i$  and if all molecules have the same mass  $m$ , the internal energy is given by the sum of their so-called kinetic energies:

$$E = \sum_{i=1}^N \frac{m}{2} v_i^2$$

We treat the evolution from  $\omega_1$  to  $\omega_2$  as a random process.

Comment: This is a stark assumption since e.g. the laws of Newtonian mechanics would allow us to calculate the positions and the velocities of all the molecules from its initial values by solving an ODE. Note that the Newtonian laws are just an approximation, which works extremely well for macroscopic bodies, and the true underlying theory is Quantum Mechanics who adds an intrinsic random process to the time evolution. In case we do not invoke this theory, we could even turn Newtonian time evolution into a random process by just saying that we do not have any information on the positions of the molecules.

Example: This is best explained using hard-sphere collisions:



Time evolution is then a random process that sequentially generates a sequence of states

$$\omega_1 \rightarrow \omega_2 \rightarrow \omega_3 \rightarrow \omega_4 \dots$$

**Core definition:** The set of all events  $\Omega = \{\omega_1, \omega_2, \dots\}$  is called *thermodynamical ensemble*. Each ensemble is characterised by the set of conserved quantities such as energy  $E$  or particle number  $N$ .

We then can assign probabilities to  $p_i$  to each state  $\omega_i$ , which characterise the physical system. A good deal of history and experimental evidence then went to finding those probabilities that reproduce observations. A derived quantity which will help to analyse physical systems is the *Entropy*.

**Definition:** If  $M$  is the number of states of  $\Omega$ , the derived quantity

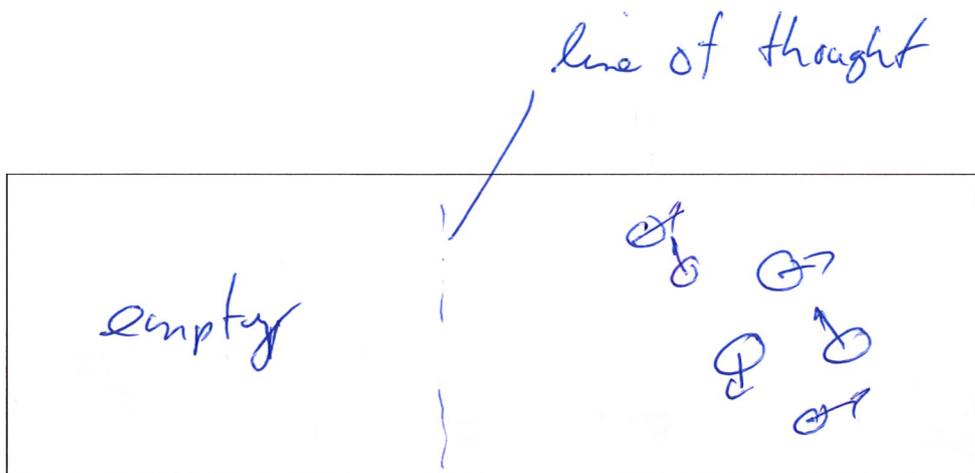
$$S = - \sum_{i=1}^M p_i \ln p_i$$

is called *Entropy*, where  $p_i$  is the probability for state  $i$  to occur. It is a function of the conserved quantities, e.g., of the internal energy  $E$ :  $S = S(E)$ .

In order to come up with a sensible definition for the  $p_i$ , let us consider a particular example, which will then lead us to a proper mathematical definition.

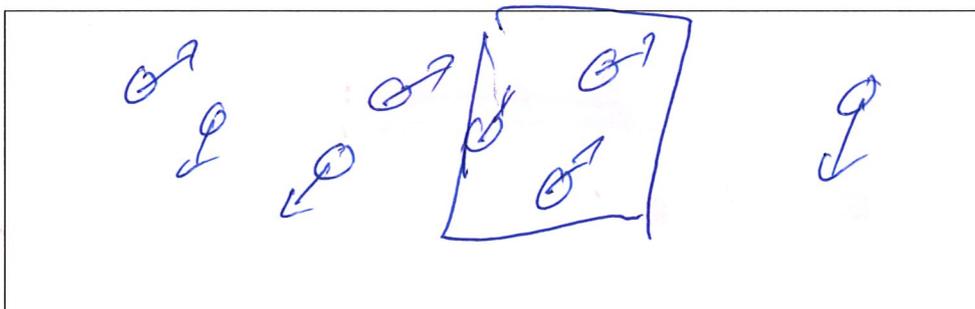
Example:

Let us assume we consider hard-sphere scattering and start with an improbable setting with small  $p_1$ . Only the right half of a container is filled with moving hard spheres, which scatter.



It is probable that some of the spheres will be scatter to the left half of the container over time. It is also likely that we reach a sort of steady state after many collisions, which is “macroscopically” only characterised by the conserved quantities. We call this steady state the *thermodynamical equilibrium*. If we zoom into a fraction of the volume into states, we could exchange those volumes and would still arrive at a state that is plausible.

Example:



This leads us to the mathematical definition:

**Core definition:** A physical system with state space  $\Omega$  and set of probabilities  $\{p_i, i = 1 \dots M\}$  is in *thermodynamical equilibrium*, if all probabilities are equal

$$p_i = 1/M .$$

We draw a first conclusion: If a physical system  $(\Omega, \{p_i, i = 1 \dots M\})$  is in thermodynamical equilibrium, the entropy is given by

$$S = - \sum_{i=1}^M \frac{1}{M} \ln \left( \frac{1}{M} \right) = \ln M . \quad (10)$$

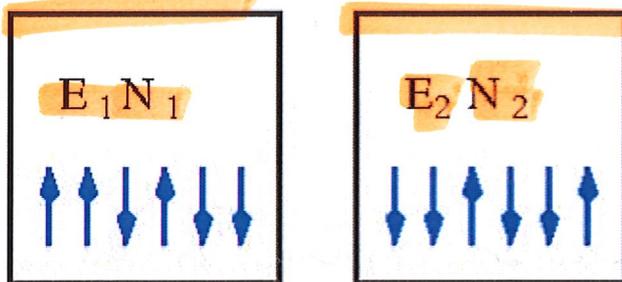
Example:

A chain of  $N$  spins (without constraints, i.e.,  $H = 0$ ) has the entropy in thermodynamical equilibrium:

A handwritten diagram showing a chain of  $N$  spins represented by a sequence of arrows:  $\uparrow \downarrow \uparrow \downarrow \downarrow \uparrow \dots \uparrow \downarrow$ . A horizontal line below the arrows is labeled  $N$ . To the right, a vertical bracket groups the arrows and is labeled  $M$ . Next to the arrows are labels:  $\leftarrow$  one event,  $\leftarrow$  two event,  $\vdots$ , and  $\leftarrow$   $N$ th event. Below the diagram, the entropy formula is written as  $S = \ln M = \ln(2^N) = N \cdot \ln 2$ . The  $N \cdot \ln 2$  part is underlined.

### 3.2 Properties of Entropy

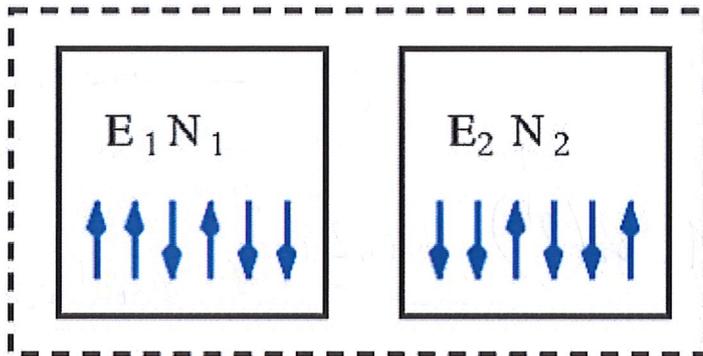
Let us <sup>two</sup> consider an isolated statistical system visualised as boxes below. We could think of our 1-dimension spin chain in an external field. Each of the systems is characterised by the internal Energy  $E_{1/2}$  and the number  $N_{1/2}$  of degrees of freedom, here spins. The state of the system is the box on the left side is described by probabilities  $p_i, i = 1 \dots M(E_1)$  where  $M(E_1)$  is the total number of states. The probabilities  $q_k, k = 1 \dots M(E_2)$  characterise the state of the system in the right box. Both systems are not necessarily in the thermodynamical equilibrium, where the set of states in either box would have the same probability.



By definition, both entropies are

$$S_1 = - \sum_{i=1}^{M(E_1)} p_i \ln p_i, \quad S_2 = - \sum_{k=1}^{M(E_2)} q_k \ln q_k.$$

We do now do not change the physics of the systems at, but shift our point of view and consider the two boxes as *one* statistical system:

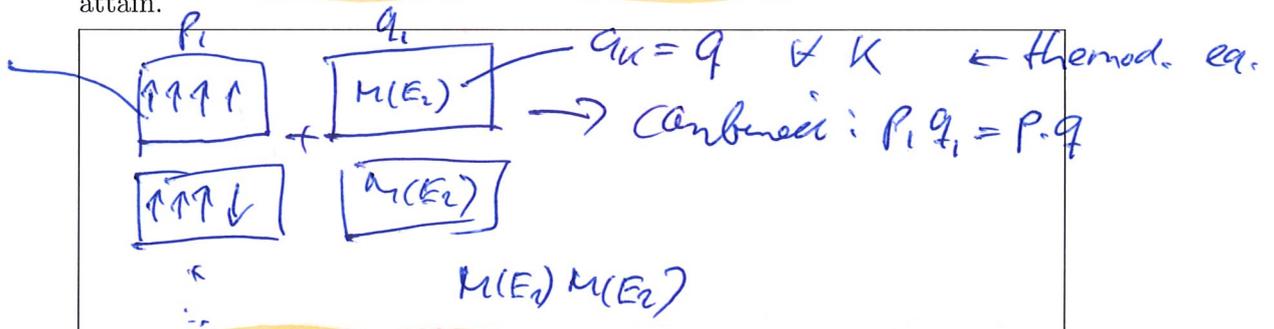


What is the Entropy of the in-thoughts combined system?

Now, we need to enumerate all possible states the combined system can attain.

$$P_i = P$$

$\forall i$



Hence, there are  $M(E_1)M(E_2)$  states in total. Since both systems are “isolated”, or in mathematical terms, “statistically independent”, the probability that system 1 is in state  $i$  and system 2 is in state  $k$  is given by  $p_i q_k$ . We then find for the Entropy of the combined system:

total combined system is thermodynamical equilibrium!

even "away" from thermodynamical equilibrium:  
entropy of combined system

$$\begin{aligned}
 S &= - \sum_{i=1}^{M(E_1)} \sum_{k=1}^{M(E_2)} p_i q_k \ln(p_i q_k) \\
 &= - \sum_i \sum_k p_i q_k [\ln p_i + \ln q_k] \\
 &= - \sum_{i,k} p_i q_k \ln p_i - \sum_{i,k} p_i q_k \ln q_k \\
 &= - \left( \sum_k q_k \right) \sum_i p_i \ln p_i - \left( \sum_i p_i \right) \sum_k q_k \ln q_k \\
 &= S(E_1) + S(E_2)
 \end{aligned}$$

$$\begin{aligned}
 \sum_{i=1}^M p_i &= 1 \\
 \sum_{k=1}^M q_k &= 1
 \end{aligned}$$

Hence, we observe that the Entropy of two individual isolated systems adds up, i.e.,  $S = S_1 + S_2$ , if both systems are *considered* as one statistical system. Of course, we can add now a third box with another statistical system and would find that its entropy adds to  $S_1 + S_2$  and so on.

**Key observation** The Entropies of statistically independent (isolated) systems add up to form the Entropy of the combined system.

**Definition:** A measurement, which is additive for isolated subsystems, is called *extensive*.

Other examples for *extensive* measurements are the internal energy  $E$  and the number of degree of freedoms,  $N$ , since

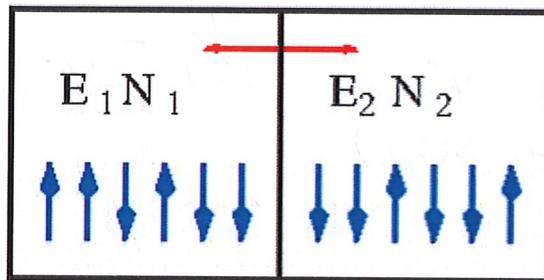
$$E = E_1 + E_2, \quad N = N_1 + N_2.$$

Let us now change the physical situation:

1. We will now assume that the system in either box is in thermodynamical equilibrium with all  $p_i = p$  are the same as well as  $q_k = q$ . The corresponding entropies are hence given by

$$S_1 = \ln M(E_1), \quad S_2 = \ln M(E_2).$$

- Note that we naturally assume that  $p \neq q$ . Nevertheless, the *combined* system is *also* in thermodynamical equilibrium, since every state has the same probability  $p_i q_k = pq$ .
- Thermal contact:** The crucial change is now that we allow the two systems to exchange energy. Of course, the total energy  $E = E_1 + E_2$  is conserved, but now the energy content of each box can change.



Before we allow thermal contact, we found that the total entropy is  $S(E) = S(E_1) + S(E_2)$ ,  $E = E_1 + E_2$ . We now allow a thermal contact and let the total system reach thermal equilibrium.

What is the entropy  $S(E)$  of the thermalised system now?

Since the “big” system is in thermal equilibrium, we need to find the total number of states  $M(E)$  since

$$S(E) = \ln M(E).$$

We consider the total energy  $E$  and the energy of system  $e_1$  as variables: the energy in box 2 is then given by  $e_2 = E - e_1$ <sup>1</sup> If it happens that system 1 has energy  $e_1$ , the total number of states for this configuration is

$$M(e_1) M(E - e_1).$$

However, due to energy exchange, any value  $0 \leq e_1 \leq E$  is also permissible. Hence, the total number of states is now:

$$M(E) = \sum_{e_1=0}^E M(e_1) M(E - e_1) > M(E_1) M(E - E_1) = M(E_1) M(E_2).$$

<sup>1</sup>I use small letters since  $E_1$  and  $E_2$  are reserved for the energies in the initial state before we allowed thermal contact.

$(E_{12} \rightarrow 0)$   
 $e_{12}$

The inequality is true since all terms are positive and since  $e_1 = E_1$  is one of them. We therefore derive the important result.

$$\begin{aligned}
 S(E) &= \ln M(E) = \ln \left[ \sum_{e_1} M(e_1) M(E - e_1) \right] \\
 &> \ln (M(E_1) M(E - E_1)) \\
 &= \ln M(E_1) + \ln M(E - E_1) \\
 &= \ln M(E_1) + \ln M(E_2) \\
 &= S(E_1) + S(E_2)
 \end{aligned}$$

**Key observation** If two systems, which are in thermodynamic equilibrium with entropies  $S(E_1)$  and  $S(E_2)$ , are allowed to exchange energy (i.e., are in “thermal contact”), the entropy  $S(E_1 + E_2)$  of the combined system in equilibrium satisfies:

$$S(E_1 + E_2) > S(E_1) + S(E_2).$$

The entropy always increases! This is called the Second Law of Thermodynamics.

At least for the discrete systems, for which we can count states, the entropy is bounded from above. Hence, a thermalisation process increases the entropy until it is limited by the upper bound and reaches a maximum.

**Key observation:** A system in thermodynamical equilibrium is a state of maximal entropy.

Let us check that this observation is consistent with our earlier definition of equilibrium, namely a state for which all states of the system have the same

probability  $p$ . We are led to the task:

$$S = - \sum_i p_i \ln p_i \rightarrow \max, \quad \sum_i p_i = 1.$$

new variable

To solve this problem, we use a Lagrange multiplier:

$$\begin{aligned} \text{extended: } \bar{S} &= - \sum_i p_i \ln p_i + \lambda \left( \sum_i p_i - 1 \right) \\ \text{maximise: } (p_i, \lambda) \quad \frac{\partial \bar{S}}{\partial \lambda} &= 0 = \sum_i p_i - 1 \\ \frac{\partial \bar{S}}{\partial p_k} &= - \ln p_k - p_k \frac{1}{p_k} + \lambda \cdot 1 = 0 \\ p_k &= e^{-\lambda+1} = c \forall k; \quad \sum_{i=1}^M p_i = \sum_{i=1}^M c = c \cdot M = 1 \\ &\quad \boxed{p_k = 1/M \quad \forall k} \quad c = 1/M \end{aligned}$$

We indeed find that the entropy is maximal for  $p_i = 1/M$ , which was our definition of thermodynamical equilibrium before!

### 3.3 Temperature

As discussed in the previous subsections, in *thermodynamical equilibrium* (see above for the precise definition!), the entropy only depends on the conserved macroscopic parameters such as the number  $N$  of degrees of freedom or the internal energy  $E$ . In fact, we have

$$S(E) = \ln M(E),$$

where  $M$  is the total number of states of a given physical system. In everyday life, we are used to temperature rather than  $E$  to characterise a thermodynamical system. Here, I give a precise mathematical definition of temperature, and we will then check that this definition meets with our expectations.

**Core definition:** If a system is in thermodynamical equilibrium (and only then!) specified by the entropy  $S(E)$  as a function of the internal energy  $E$ , the temperature  $T$  is defined by the derivative

$$\frac{1}{T(E)} = \left. \frac{\partial S}{\partial E} \right|_N \quad (11)$$

for a fixed number  $N$  of degrees of freedom.

**Worked example:** Consider a chain of  $N$  spins - with orientation up or down - in an external magnetic field  $H$ . If  $n_+$  is the number of spins with orientation up and  $n_-$  the number of down-spins, the energy of the system is given by

$$E = H(n_+ - n_-). \quad (12)$$

Def. of "measurement"  $\chi(\omega)$

The system of spins is exposed to a "heat bath" and undergoes random fluctuations in the spin orientation while the energy  $E$  is conserved. The system is in thermodynamical equilibrium.

Sketch the spin configuration with minimal energy  $E_{\min}$  and find  $E_{\min}$ .

$\uparrow \rightarrow E = H$        $\uparrow \downarrow \uparrow \uparrow \downarrow \uparrow \uparrow$   
 $\downarrow \rightarrow E = -H$        $+H -H$   
 $E_{\min} = -NH$        $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$   
 $E_{\max} = NH$        $\uparrow \uparrow \uparrow \uparrow \uparrow$

Find the entropy  $S$  and the temperature  $T$  of the system as a function of  $E$  for the case  $N \gg 1$ .

For the entropy, we need to find the total number of states for a given energy

lecture start

$E$ . Note that  $n$  completely specifies  $E$ , and we only need to find the number of states for a given  $n$ :

$$M(E) = \binom{N}{n}, \quad n = (E/H + N)/2.$$

We define  $\nu = E/H$  and note that  $\nu + N$  is even because of (12). Thus, we find:

$$S(E) = \ln M(E) = \ln \left( \frac{N!}{(\nu + N)/2!} \right). \quad \text{for } N \gg 1$$

For large  $N$  and with the help of a tutorial result, we find:

$$S(E) \approx \ln \left( \frac{2^N}{\sqrt{2\pi N}} \exp \left\{ -\frac{\nu^2}{2N} \right\} \right) = N \left[ \ln 2 - \frac{\nu^2}{2N^2} \right] - \frac{1}{2} \ln(2\pi N).$$

We can now calculate the temperature:

$$\frac{1}{T(E)} = \left. \frac{\partial S}{\partial E} \right|_N = \frac{1}{H^2} \frac{E}{N}.$$

fix  
Only energy dependence  
 $E_{\min} = -NH$

### Observations:

- The lowest temperature is reached for  $E = E_{\min}$ :

$$T_{\min} = H$$

and is *not* zero. This is specific to the spin system, and e.g. classical gases encapsulated in a box can reach zero temperature.

- If we raise the temperature from  $E_{\min}$  to  $E \leq 0$ , we find

$$\lim_{E \rightarrow 0} T(E) = \infty.$$

This is an ensemble where we have as many *up* as *down* spins.

- Can we have negative temperatures? Mathematically "Yes", namely for  $E > 0$ . Note, however, that those systems do not naturally occur in nature: we would need to transfer energy in to the spin system by e.g. a Laser and then isolate the spins.

lecture end

4/2/2020