

RECAP 7/12/2020

Maths

Probability Theory

Physics

Statistical Physics

Experiment:

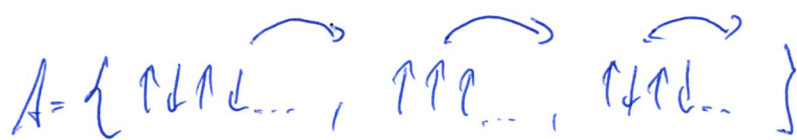
degrees of freedom

spins, atoms, gases...



← number of degrees of freedom

Output space:



M: # of states

dimension space of state

time evolution

thermodynamical ensemble

Measurement:

$A \rightarrow X(\omega)$:

Energy, particle-number

1.) $E(\omega)$

2.)

Probability: p_i

event space $\Omega \rightarrow p_i \in [0,1]$

← model

Physics :

thermodyn. equilibrium: $P_i = 1/M \quad \forall i$

Entropy: (Shannon)

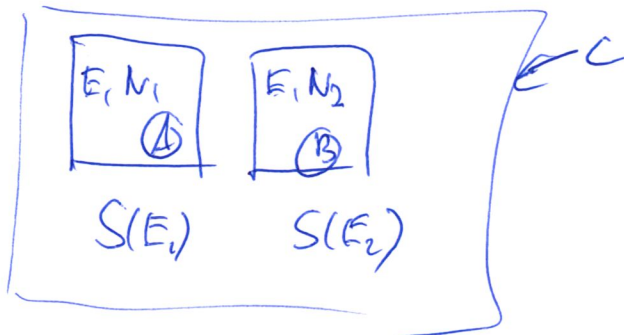
$$S = - \sum_{i=1}^M P_i \ln P_i$$

degrees of freedom + constraints: E (conserved)
 N particle number

A: thermodynamical ensemble

→ micro canonical ensemble

properties of entropy:



$$E = E_1 + E_2$$

$$S(E) = S(E_1) + S(E_2)$$

temperature: $\frac{1}{T(E)} = \frac{\partial S(E)}{\partial E} \Big|_N$

entropy in thermo. equilibrium:

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

$$p_i = \frac{1}{M}$$

$$= - \sum_{i=1}^M \frac{1}{M} \ln \left(\frac{1}{M} \right) = - M \cdot \frac{1}{M} \ln \left(\frac{1}{M} \right) = \underline{\underline{\ln M}}$$

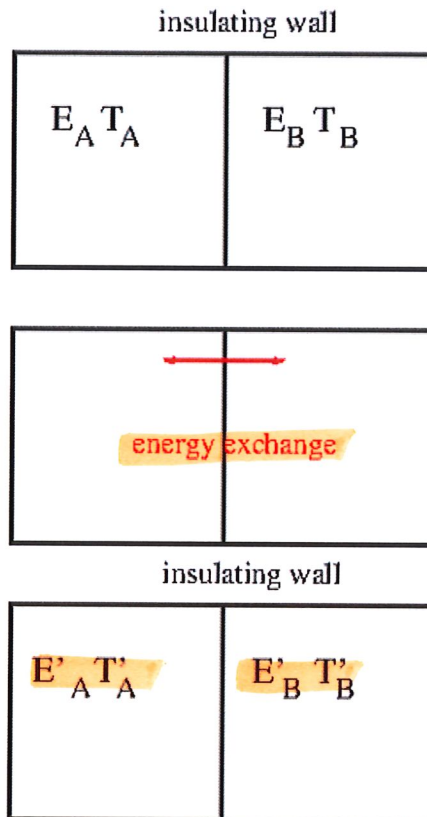
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3.4 Heat exchange

We still need to demonstrate that our definition of temperature is in line with everyday life experience. For example, if we bring together two containers with temperatures T_A and T_B and $T_A > T_B$, we would expect that energy flows from the hotter vessel into the colder vessel.

Mathematically this is a three stage process illustrated in the adjacent figure:

1. We prepare two systems in thermodynamical equilibrium with $E_A > E_B$. The wall between the containers is insulating.
2. We replace the insulating wall by a wall that allows energy exchange between the container. We wait until the combined systems reaches the thermodynamical equilibrium.
3. We re-insert the insulating wall and now have two containers with energy E'_A and E'_B . The temperatures might change to T'_A and T'_B .



We will consider the case where E_A is not so much different from E_B so that we can expect

$$E'_{A/B} = E_{A/B} + \Delta E_{A/B}, \quad \frac{\Delta E_A}{E_A} \ll 1, \quad \frac{\Delta E_B}{E_B} \ll 1,$$

let us briefly focus on system A: it evolves from the thermodynamical system at stage 1 into the the thermodynamical system at stage 3. We know that the number of states (and hence the entropy) only depends on the energy.

We assume that we can expand the entropy in a Taylor series:²

$$\begin{aligned}
 \text{thermcd. eq.:} \quad S(E'_A) &= S(E_A) + \Delta E_A \\
 \text{(Taylor)} \quad &= S(E_A) + \left(\frac{\partial S}{\partial E} \Big|_{E_A} \right) \Delta E_A + \dots \\
 &= S(E_A) + \frac{1}{T_A} \cdot \Delta E_A + \dots
 \end{aligned}$$

Def. of temperature

The combined system at stage 3 is made of two isolated systems and therefore the combined entropy is the sum of the entropies of the individual systems (see subsection 3.2):

$$S_C = S_A(E'_A) + S_B(E'_B).$$

From the Second Law of Thermodynamics (see subsection 3.2), we know

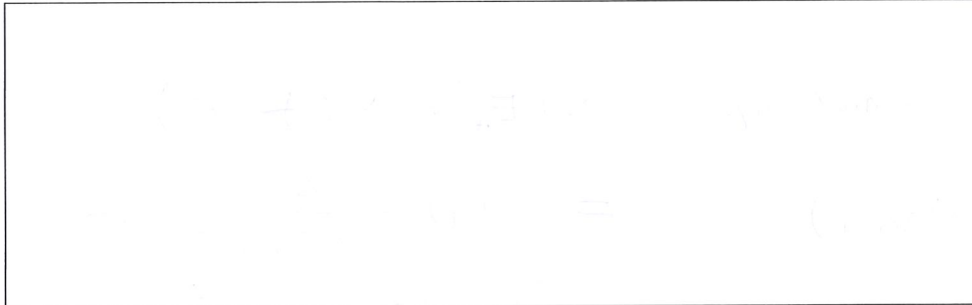
$$S_C = S_A(E'_A) + S_B(E'_B) > S_A(E_A) + S_B(E_B).$$

Using the above result from the Taylor expansion, we observe:

$$\begin{aligned}
 S(E_A) + \frac{\Delta E_A}{T_A} + S(E_B) + \frac{\Delta E_B}{T_B} &> S(E_A) + S(E_B) \\
 E'_A + E'_B = E_A + E_B &\rightarrow \Delta E_A + \Delta E_B = 0 \\
 \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta E_A &> 0
 \end{aligned}$$

We are now using energy conservation (or the First Law of Thermodynamics), and observe:

²This is true for most systems such as ideal gases. Near so-called 1st order phase transition, we need to revise this assumption later.



Combining both results, we arrive at the important finding:

$$\left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta E_A > 0 .$$

Without any loss of generality, we assumed that T_A is bigger than T_B , and, thus, the bracket in the above equation is negative. To satisfy the Second Law of Thermodynamics (i.e., the above inequality), we can conclude that (and since $\Delta E_A + \Delta E_B = 0$):

$$\Delta E_A < 0 , \rightarrow \Delta E_B > 0 .$$

The important observation is that energy is flowing from the hot system into the cold system.

SUMMARY:

- Entropy is a mathematical tool and e.g. also used in information theory (where it is called Shannon Entropy).
- We defined a statistical system as the output space of a random process, where the events are generated by the law of physics during time evolution. Since the underlying physical processes obey energy conservation, the measurement of energy of an event is the same for all elements of the statistical ensemble (First Law of Thermodynamics).
- The statistical system is said to be in thermodynamical equilibrium when all the events (also called states) have equal probability.

- Physics input: The ergodicity conjecture is that almost any statistical system evolves towards the thermodynamical equilibrium.
- Mathematical consequence: in thermodynamical equilibrium, the entropy is only a function of the conserved quantities.
- Definition: Temperature quantifies the change in entropy when the total energy of the system changes (all in thermodynamical equilibrium).
- Mathematical consequence: the entropy increases over time (Second Law of Thermodynamics).
- Mathematical consequence: energy flows from a hot container into a cold container (and not vice versa!).