

On the menu today

09/03/2021

Chapters 4

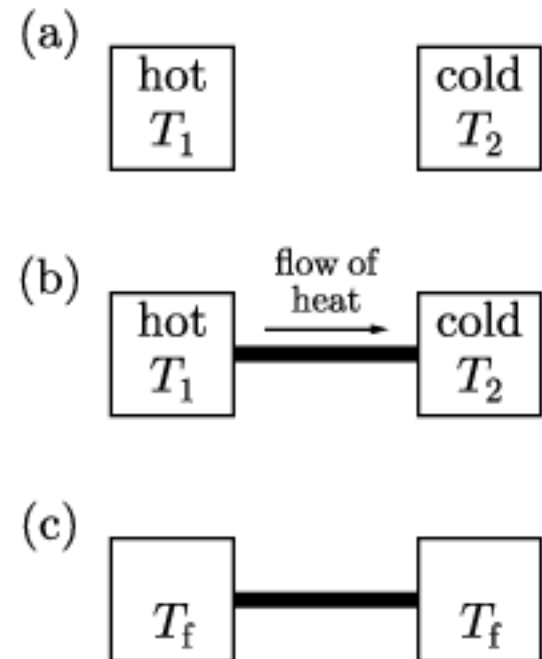
MEETING 2

Lecture 4. *Temperature and the Boltzmann factor*

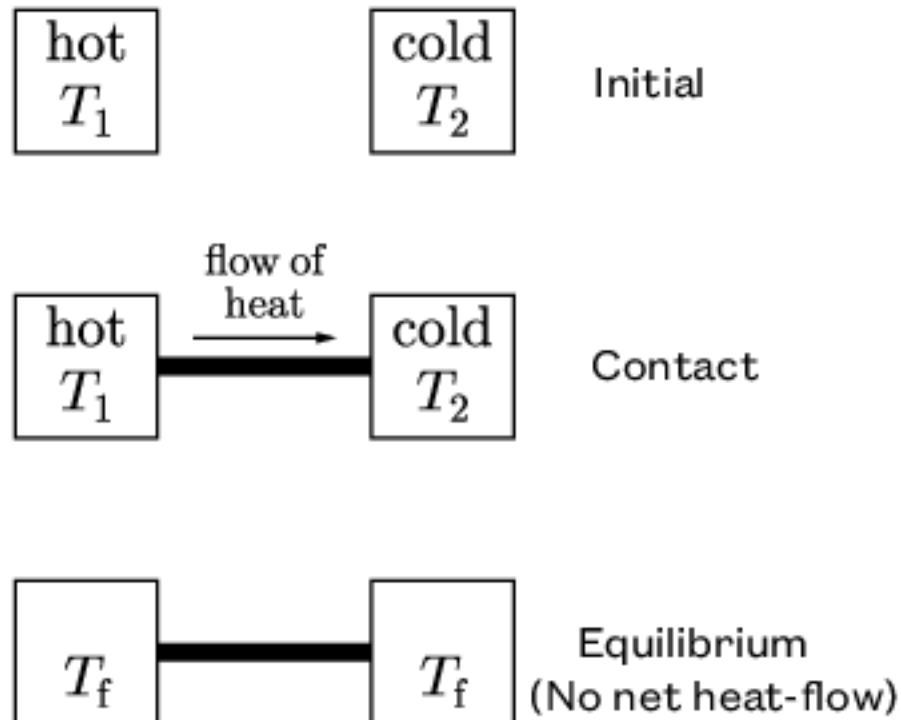
- In this unit we will learn about
 - Temperature

“A measure of hotness”

What does this really mean?



Thermal equilibrium



Thermalization

→ we say that the two bodies have the same temperature

Something irreversible just happened!

Zero-th law of thermodynamics

- The second body is called a **thermometer**. The zeroth law then guarantees that if we have calibrated this second body against any other standard thermometer, we should always get consistent results.
- Thus, a more succinct statement of the zeroth law is: "thermometers work".

Zeroth law of thermodynamics

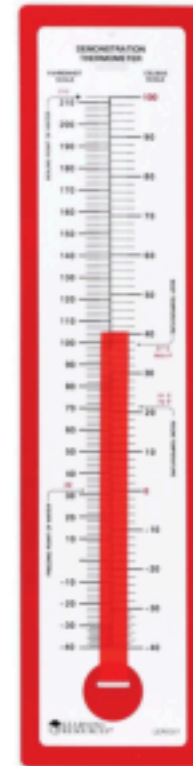
Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.

Thermometers

- For a thermometer to work well, its heat capacity must be much lower than that of the object whose temperature one wants to measure.
- If this is not the case, the action of measurement (placing the thermometer in thermal contact with the object) could alter the temperature of the object.

Thermometers

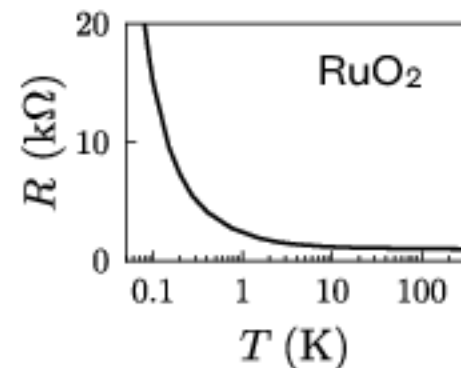
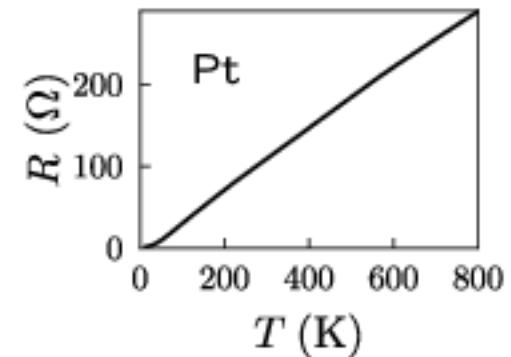
- A common type of thermometer utilizes the fact that liquids expand when they are heated.
- Galileo Galilei used a water thermometer based on this principle in 1593, but it was Daniel Gabriel Fahrenheit (1686–1736) who devised thermometers based on alcohol (1709) and mercury (1714) that bear most resemblance to modern household thermometers.
- He introduced his famous temperature scale, which was then superseded by the more logical scheme devised by Anders Celsius (1701–1744).



<http://www.stargis.com/stockroom/thermometer/>

Thermometers

- Another method is to measure the electrical resistance of a material which has a well-known dependence of resistance on temperature.
- Platinum is a popular choice since it is chemically resistant, ductile (so can be easily drawn into wires) and has a large temperature- coefficient of resistance;
- Other commonly used thermometers are based on doped germanium (a semiconductor that is very stable after repeated thermal cycling), carbon sensors and RuO₂ (in contrast with platinum, the electrical resistance of these thermometers increases as they are cooled).



Thermometers

- Using the ideal gas equation, one can measure the temperature of a gas by measuring its pressure with its volume fixed (or by measuring its volume with its pressure fixed)
- This works well as far as the ideal gas equation works, although at very low temperature gases liquefy and show departures from the ideal gas equation.

$$pV = Nk_{\text{B}}T$$

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- All of these methods use some measurable property, like resistance or pressure, which depends in some, sometimes complicated, manner on temperature.
 - However, none of them is completely linear across the entire temperature range of interest: mercury solidifies at very low temperature and becomes gaseous at very high temperature, the resistance of platinum saturates at very low temperature and platinum wire melts at very high temperature, etc.
 - It is clear that we need some absolute definition of temperature based on fundamental physics.
 - In the nineteenth century, one such definition was found, and it was based on a hypothetical machine, which has never been built, called a Carnot engine. Subsequently, it was found that temperature could be defined in terms of a purely statistical argument using ideas from probability theory, and this is the definition we will use, which we introduce later.

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- **Step 1:** put 100 coins in a box and shake it well
 - **Step 2:** look inside; some are up, some are down
 - Suppose each configuration is equally likely, thus each configuration has a probability of 2^{-100} . Each configuration is a *microstate* of the system. *You know the state of EACH coin*
 - In practice, you are more interested in knowing *how many* coins are head and how many are tail. This refers to a *macrostate*. Note: There are 101 macro states

Likelihood of observation

- The system could be described by a very large number of equally likely microstates
- You actually measure a *property* of the macrostate of the system. Some macrostates are more likely than others *because they correspond to a different number of microstates.*

The most likely macrostate that the system will find itself in is the one that corresponds to the largest number of microstates.

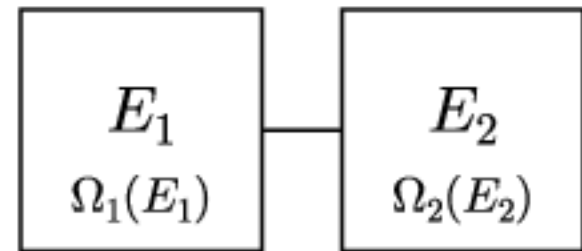
Thermal systems behave in a very similar way to the example we have just considered. To specify a microstate for a thermal system, you would need to give the microscopic configurations (e.g., position and velocity, or perhaps energy) of each and every atom in the system.

In general it is impossible to measure which microstate the system is in. The macrostate of a thermal system on the other hand would be specified only by giving the macroscopic properties of the system, such as the pressure, the total energy, or the volume.

A macroscopic configuration, such as a gas with pressure 10^5 Pa in a volume 1 m^3 , would be associated with an enormous number of microstates.

A statistical definition of temperature

- Two systems are in thermal contact with each other (and isolated from the rest of the universe; $E = E_1 + E_2$ is assumed fixed)
- Systems have $\Omega_1(E_1)$ and $\Omega_2(E_2)$ microstates, each with equal probability
- Thus the whole system can be in any one of $\Omega_1(E_1) \times \Omega_2(E_2)$ microstates
- Suppose now that the systems are in thermal equilibrium.
- **The system will appear to choose a macroscopic configuration that maximizes the number microstates**



Two systems that can exchange energy between themselves

This works if:

- (1) Each one of the possible microstates of a system is equally likely to occur;
- (2) The system's internal dynamics are such that the microstates of the system are continually changing;
- (3) Given enough time, the system will explore all possible microstates and spend an equal time in each of them (**ergodic** hypothesis).

These assumptions imply that the system will most likely be found in a configuration that is represented by the most microstates. For a large system our phrase “most likely” becomes “absolutely, overwhelmingly likely”; what appears at first sight to be a somewhat weak, probabilistic statement becomes an utterly reliable prediction!

Most probable macrostate?

- For our problem of two connected systems, the most probable division of energy between the two systems is the one that maximizes $\Omega_1(E_1) \times \Omega_2(E_2)$, because this will correspond to the greatest number of possible microstates.
- Our systems are large and hence we can use calculus to study their properties; we can therefore consider making infinitesimal changes to the energy of one of the systems and seeing what happens. Therefore, we can maximize this expression with respect to E_1 by writing:

$$\frac{d}{dE_1} (\Omega_1(E_1) \Omega_2(E_2)) = 0$$

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2}$$

Ensembles

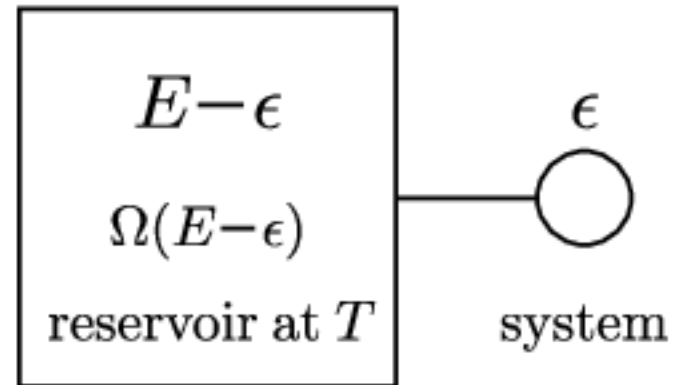
- (1) **The microcanonical ensemble:** an ensemble of systems that each have the same fixed energy.
- (2) **The canonical ensemble:** an ensemble of systems, each of which can exchange its energy with a large reservoir of heat. As we shall see, this fixes (and defines) the temperature of the system.
- (3) **The grand canonical ensemble:** an ensemble of systems, each of which can exchange both energy and particles with a large reservoir. (This fixes the system's temperature and a quantity known as the system's chemical potential.)

Canonical ensemble

- Assume that there is only one single micro-state for each value of the energy
- We fix the total energy of the system to be E
- Probability the system has energy ϵ is proportional to the number of micro states:

$$P(\epsilon) \propto \Omega(E - \epsilon) \times 1$$

Systems can exchange energy



(reservoir or heat bath;
large because it keeps its
 T even if you remove/add
energy)

$$P(\epsilon) \propto e^{-\epsilon/k_{\text{B}}T}$$

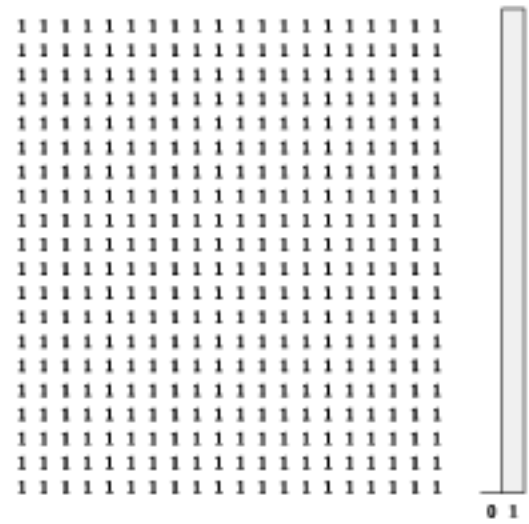
Normalization and partition function

- If a system is in contact with a reservoir and has a micro state r with energy E_r

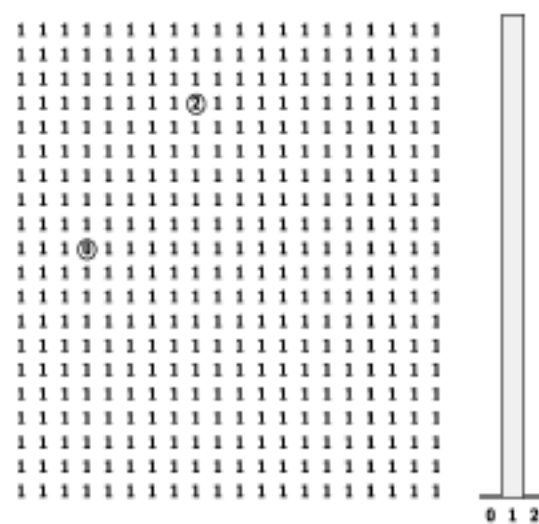
$$P(\text{ microstate } r) = \frac{e^{-E_r/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

- The **partition function** is defined as

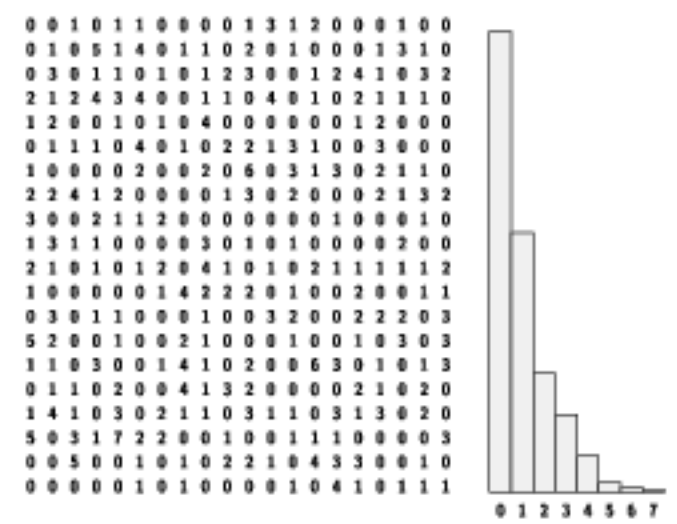
Example



Initial



First step

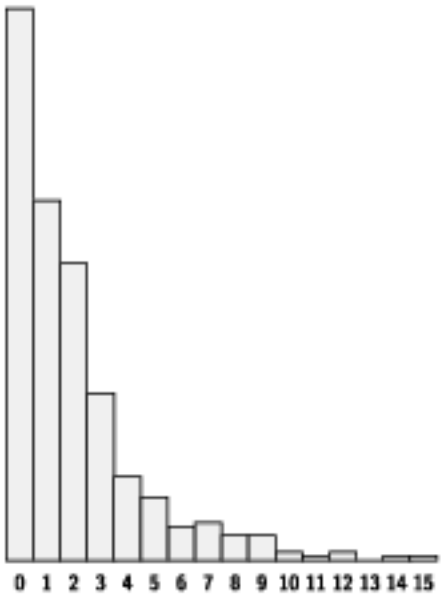


Equilibrium

Higher “Temperature”

Starting with two quanta per site:

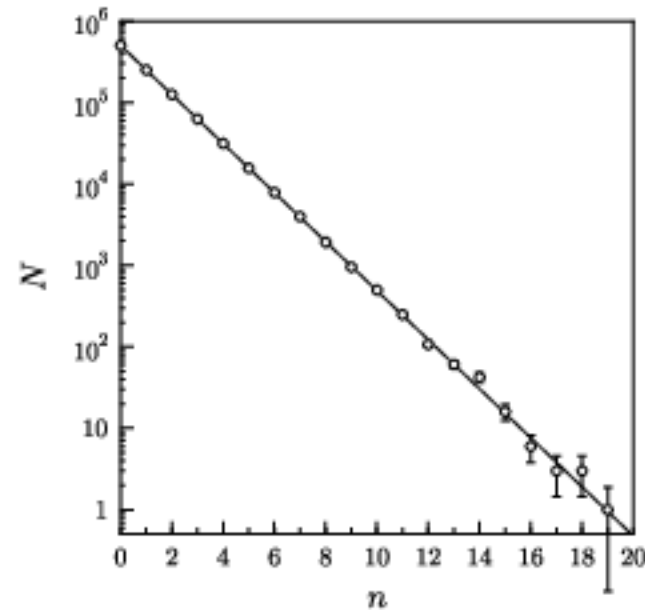
2	8	0	4	1	0	2	1	2	1	1	4	0	1	2	0	3	1	9	4
15	1	3	0	2	1	3	2	8	2	0	3	0	0	0	5	1	8	2	0
2	0	0	2	0	0	5	4	2	3	2	3	0	1	0	0	1	4	0	2
2	1	2	3	0	2	0	1	10	2	5	0	1	0	0	1	0	2	2	0
2	1	6	1	1	1	1	0	0	2	0	3	2	1	1	1	0	0	0	2
0	0	0	10	1	0	5	2	0	2	4	0	0	3	0	1	1	1	0	3
0	1	4	2	2	0	0	4	5	1	1	0	0	0	3	1	1	3	1	0
3	1	3	0	3	1	0	7	1	4	3	2	0	6	0	3	2	1	4	1
0	0	7	0	2	2	0	0	9	0	2	7	0	1	1	0	0	0	0	1
1	5	1	1	5	1	0	4	9	1	1	1	0	5	1	3	2	2	4	2
1	1	11	4	2	0	7	0	1	0	2	2	7	0	5	2	0	6	0	3
5	0	5	3	0	0	0	7	0	1	1	8	0	0	3	9	1	7	3	0
4	0	2	0	0	2	2	0	2	3	2	1	0	1	3	0	0	0	0	0
0	2	1	2	5	1	2	3	1	0	7	2	0	0	0	0	2	1	4	0
1	1	3	2	4	0	2	0	2	12	1	2	0	0	0	0	5	5	0	2
3	0	0	2	1	4	2	0	6	2	1	0	3	7	6	1	3	1	0	12
9	0	0	1	5	1	2	2	1	3	3	1	1	0	0	1	3	0	9	8
6	1	3	0	4	3	2	0	1	2	6	2	0	2	2	1	0	0	4	3
0	14	2	2	0	0	1	2	2	0	3	0	6	0	1	0	0	3	8	0
0	0	1	3	0	0	1	0	1	3	1	2	2	4	2	1	0	1	1	3



Bigger lattice

Let us now start with a bigger lattice, now containing 10^6 sites, and place a quantum of energy on each site.

The straight line is a fit to the expected Boltzmann distribution.



The final distribution for a lattice of size 1000×1000 with one quantum of energy initially placed on each site. The error bars are calculated by assuming Poisson statistics and have length \sqrt{N} , where N is the number of sites having n quanta.

$$\beta \equiv \frac{1}{k_{\text{B}}T}$$

Application of the Boltzmann distribution:

(1) The two-state system

- Only two states!

- $E_1 = 0$ $P(0) = \frac{1}{1 + e^{-\beta\epsilon}}$

- $E_2 = \epsilon > 0$

- Energy of the system?

Application of the Boltzmann distribution:

(2) Isothermal atmosphere

- What is the number of molecules in an isothermal atmosphere as a function of height?

$$P(z) \propto e^{-mgz/k_B T}$$

- Because of the potential energy is mgz
- The number density is therefore

Application of the Boltzmann distribution:

(3) The Sun

- Main reaction in the sun is $p^+ + p^+ \rightarrow d^+ + e^+ + \bar{\nu}$
- The main barrier is the electrostatic repulsion of the two protons

- For $r = 10^{-15}$ m, $E \approx 1\text{MeV}$
- Temperature at the center of the sun: $T \approx 10^7$ K
- Thus, the Boltzmann factor for this process is
- The sun is thus unlikely to undergo fusion
- Why does it occur? Quantum mechanics reduces the barrier through tunneling!

Summary

1) The temperature T of a system is given by $\beta \equiv \frac{1}{k_B T} = \frac{d \ln \Omega}{dE}$

where k_B is the Boltzmann constant, E is its energy, and Ω is the number of microstates (i.e., the number of ways of arranging the quanta of energy in the system).

2) The microcanonical ensemble is an idealized collection of systems that each have the same fixed energy.

3) The canonical ensemble is an idealized collection of systems, each of which can exchange its energy with a large reservoir of heat.

4) For the canonical ensemble, the probability that a particular system has energy E is given by $P(E) = \frac{e^{-\beta E} \Omega(E)}{Z}$ (Boltzmann distribution), and the factor $e^{-\beta E}$ is known as the Boltzmann factor.