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Physics at negative absolute temperature

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Preface

Motivazioni e ringraziamenti

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Introduction

Everyone has an intuitive idea of what temperature is in everyday life: it is a quantity that tell us how *hot* or *cold* an object is.

Temperature is an intrinsic property of a system, which means that it does not depend on the object's dimensions nor on the quantity of matter contained in it.

Temperature is measured via thermometers and, since it is a physical quantity, it must be accompanied by physical unit. All the thermometers are expected to give the same number when used to measure the temperature of the same object, provided that the number is expressed always in the same physical unit. This can be possible if the thermometers are accurately calibrated according to some critera that make the calibration process reproducible. A roughly good calibration of a thermometer in the so called Celsius scale can be done by assigning the instrument a value of $0°$C (0 degrees Celsius) at the frozen point of water, and $100°$C at the boiling point of water. A more sophisticated and precise way to calibrate a thermometer on the Celsius scale consists in assigning the value of $-273.15°$C to the *coldest* temperature admitted according to nowadays' physics, and $0.01°$ C to the triple point of water, that is the point in which water coexists in liquid, solid and gaseous form. One can then extract a measure of all the other values of temperature by assuming a linear relation between temperature and the property in the material used as a thermometer, may it be the height of a liquid column in a bulb or an elastic deformation of a certain solid material.

Another interesting temperature scale is the one measured in degrees Kelvin (K), called the *absolute temperature*. This scale of temperature is defined in a way such that it gives a values of 0 K at the coldest possible situation admitted by physics, the so called *absolute zero* point: this means that no physical systems can be cooled more than a system whose absolute temperature is 0 K.

The purpose of this thesis is to introduce the concept of *negative absolute temperatures*. This does not constitutes a contradiction to what told before because negative absolute temperatures should not be searched below the absolute zero, but rather above infinity: negative absolute temperatures are hotter than all the positive ones. The world of negative absolute temperatures is often accompanied by strange phenomena: for example, when a system at negative temperature is put into contact with one at positive temperature, the former gives heat to the latter, leading the temperature of the former to be lowered and the temperature of the latter to be raised.

In the first chapter of this thesis I will first introduce the concept of temperature in a rigorous way according to physical laws, justifying the existence of negative absolute temperatures basing on thermodynamical arguments.

A simple system that admits negative temperatures will then be presented in chapter 2, namely the two level system.

In chapter 3 I will then show that negative absolute temperatures were experimentally observed by Purcell and Pound in 1950. After that discovery, some criticisms were moved against the definition of the entropy used to define the absolute scale, putting in doubt the existence of negative temperatures: this will be discussed in chapter 4.

Finally some simulations of a systems at negative temperature will be presented in the last chapter.

Contents

Chapter 1

Temperature

The purpose of this section is to provide a rigorous definition of temperature. The definition subsequently given is general and holds for every thermodynamical system.

1.1 Temperature as an equilibrium property

Temperature can be more sistematically defined starting from the concept of *equilibrium*. We consider a thermodynamic system to be in equilibrium when no changes are observed in any macroscopic observable and when the system does not exchange heat nor work with the environment. In particular we say that the system is at *thermal equilibrium* when no heat is exchanged by the system, and at *mechanical equilibirum* when no work is done by or on the system.

Let us consider three systems A, B, C whose equilibrium properties are described by the variables $\{X_1, X_2, \ldots, X_p\}$, $\{Y_1, Y_2, \ldots, Y_p\}$ and $\{Z_1, Z_2, \ldots, Z_p\}$ respectively.

If A and B are in equilibrium for some precise values of the coordinates $\{X_1, X_2, \ldots, X_p\}$ and $\{Y_1, Y_2, \ldots, Y_p\}$, then there must be a relation that connects the two set of values uniquely. Let us express this relation as

$$f_{AB}(X_1, X_2, \ldots, X_p, Y_1, Y_2, \ldots, Y_p) = 0 \tag{1.1}$$

In an analogous manner, if B and C are in equilibrium for some values $\{Y'_1, Y'_2, \ldots, Y'_p\}$ and $\{Z_1, Z_2, \ldots, Z_p\}$ of the coordinates, then there must be a constrain on the values $\{Y'_1, Y'_2, \ldots, Y'_p\}$ and $\{Z_1, Z_2, \ldots, Z_p\}$, which we express as

$$f_{BC}(Y'_1, Y'_2, \ldots, Y'_p, Z_1, Z_2, \ldots, Z_p) = 0 \tag{1.2}$$

The equations above can be inverted to espress one thermodynamic coordinate as a function of the others, or in other words, the above expressions may be written as

$$Y_1 = g_{AB}(X_1, X_2, \ldots, X_p, , Y_2, \ldots)$$
$$Y'_1 = g_{BC}(Y'_2, \ldots Y'_p, Z_1, Z_2, \ldots, Z_p)$$

Now let us bring the system B in the same state in both cases, which means imposing $Y_1 = Y_1'$, $Y_2 = Y_2'$, ..., $Y_p = Y_p'$. The last two equations implies that

$$g_{AB}(X_1, X_2, \ldots, X_p, Y_2, \ldots Y_p) = g_{BC}(Y_2, \ldots, Y_p, Z_1, Z_2, \ldots, Z_p) \tag{1.3}$$

or

$$G_{ABC}(X_1, X_2, \ldots, X_p, Y_2, \ldots, Y_p, Z_1, Z_2, \ldots, Z_p) = 0$$

One can use this relation to express X_1 as

$$X_1 = h_{ABC}(X_2, \ldots, X_N, Y_2, \ldots, Y_p, Z_1, Z_2) \tag{1.4}$$

According to the zeroth principle of thermodynamics if A and B are in equilibrium and B and C are in equilibrium then A and C are in equilibrium [1]. This means that the constrains 1.1, 1.2, lead to a new constrain between A and C there must be a constrain on the values $X_1, X_2, \ldots, X_p$, $Z_1, Z_2, \ldots, Z_p$ which can be expressed as

$$f_{AC}(X_1, X_2, \ldots, X_p, Z_1, Z_2, \ldots, Z_p) = 0$$

which means that X_1 can be expressed as

$$X_1 = g_{AC}(X_2, \ldots, X_p, Z_1, Z_2, \ldots, Z_p) \tag{1.5}$$

and imposing the equality between 1.4 and 1.5

$$g_{AC}(X_2, \ldots, X_p, Z_1, Z_2, \ldots, Z_p) = h_{ABC}(X_2, \ldots X_p, Y_2, \ldots, Y_p, Z_1, Z_2, \ldots, Z_p)$$

The term on the lefts does not depend on the coordinates of B. This means that both g functions in equation 1.3 must be of the type

$$g_{AB}(X_1, X_2, \ldots, X_p, Y_2, \ldots, Y_p) = \Theta(X_1, X_2, \ldots, X_p) + \phi(Y_2, \ldots, Y_p)$$
$$g_{BC}(Y_2, \ldots, Y_p, Z_1, Z_2, \ldots, Z_p) = \Theta(Z_1, Z_2, \ldots, Z_p) + \phi(Y_2, \ldots, Y_p)$$

so that the dependence on $\{Y\}$ gets cancelled out when equating the two functions leading to

$$\Theta_A(X_1, X_2, \ldots, X_p) = \Theta_C(Z_1, Z_2, \ldots, Z_p)$$

We started this reasoning by assuming equilibrium between $A - B$ and $B - C$, but one could repeat this reasoning by assuming for example equilibrium between $A - C$ and $B - C$ obtaining an analogous result in terms of $\{Y_1, Y_2, \ldots, Y_p\}$. Because of the properties of the equivalence relation, one can extend the reasoning to an arbitrary number of systems. This means that if N systems are in equilibrium, then there must be a function Θ such that

$$\Theta_A(X_1, X_2, \ldots, X_p) = \Theta_B(Y_1, Y_2, \ldots, Y_p) = \Theta_C(Z_1, Z_2, \ldots, Z_p) = \ldots$$

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[1]or, alternatively, equilibrium is an equivalence relation

Let us call this function *empirical temperature*, and its value on a set of coordinates identifies a particular equivalence class of systems at equilibrium.

What just proven shows that systems at equilibrium are identified by the same value of a certain function Θ. By the way no specifications are given about the origin of this function and which precise value it has for a given set of systems at equilibrium. In fact there are multiple ways to define the values of such function, leading to many *temperature scales.*

An example of a possible way to define a scale of temperature is the one that concerns ideal gases. Practically it consists in assigning a value $\Theta = 273.16$ degrees Kelvin (K) at the triple point of water (coexistence of ice-water-gas) and then other values of temperature for ideal gases are defined via the relation

$$T(K) = \lim_{P \to 0} 273.16 \times \frac{(PV)_{system}}{(PV)_{ice-water-gas}}$$

because for an ideal gas $T \propto PV$.

Another possible definition of the function Θ, the one relevant for what follows, will be presented later in the next section.

1.2 Thermodynamic temperature

It is known from the first principle of thermodynamics that

$$dE = TdS - pdV$$

Once introducing an entropy as a function of the energy $S = S(E)$ it is possible to define a so called *thermodynamic temperature* via the above equation, yielding the relation

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

To see why this is coherent with what told before let us look at this example.

First let us consider a system isolated from the environment, so that it cannot exchange heat or work (energy fixed). Let us indicate a generical state of the system by the microscopic coordinates $\mathbf{x} = (q_1, \ldots, q_n, p_1, \ldots, p_n)$ where (q_i, p_i) is a pair of canonical coordinates. If $\mathcal{H}(\mathbf{x})$ denotes the hamiltonian of the system, the condition

$$\mathcal{H}(\mathbf{x}) = E \tag{1.6}$$

for a certain value of energy E, defines a microcanonical ensemble.

The central postulate of a priori probability in statistical mechanics states that all the microstates satisfying 1.6 are equally probable. In other words, one can define a probability density function

$$p(E, \mathbf{x}) = \frac{1}{\Omega(E, \mathbf{x})} \, \delta(H(\mathbf{x}) - E)$$

where $\Omega(E, \mathbf{x})$ denotes the volume of the phase space satisfying equation 1.6.
We also assume the Boltzmann definition of entropy [2]

$$S(E, \mathbf{x}) = k_B \log(\Omega(E, \mathbf{x})) \tag{1.7}$$

Let us now consider two separated systems with fixed energies E_1, E_2. By putting them
into contact and allowing them to exchange energy, one can create another system with
fixed energy $E = E_1 + E_2$ which can be studied in the microcanonical ensemble. For
fixed values E_1 and E_2 the phase space volume allowed for the system is

$$\Omega_{E_1}(E, \mathbf{x}) = \Omega_1(E_1, \mathbf{x}_1) \cdot \Omega_2(E_2, \mathbf{x}_2)$$

but E_1 (and as a consequence $E_2 = E - E_1$) is free to move between 0 and E, hence the
total phase space volume is given by an integral sum over E_1 and E_2 of the volumes at
fixed E_1, E_2 with the constrain $E_2 = E - E_1$

$$\Omega(E, \mathbf{x}) = \int_0^E dE_1 \int_0^E dE_2 \; \Omega_1(E_1, \mathbf{x}_1) \; \Omega_2(E_2, \mathbf{x}_2) \; \delta(E_1 + E_2 - E) =$$
$$= \int_0^E dE_1 \; \Omega_1(E_1, \mathbf{x}_1) \; \Omega_2(E - E_1, \mathbf{x}_2)$$

By using now equation 4.1 the last equation can be written as

$$\Omega(E, \mathbf{x}) = \int_0^E dE_1 \; e^{(S_1(E_1) + S_2(E - E_1))/k_B}$$

In the limit $N \to +\infty$ the integrand becomes sharply peaked around a value E_1^* and it
can be evaluated using the Laplace's method

$$\Omega(E, \mathbf{x}) \approx C e^{(S_1(E_1^*) + S_2(E - E_1^*))/k_B}$$

The energy value that maximes $\Omega(E, \mathbf{x})$ is the one that is represented by the largest
number of microstates, hence the most probable or, in other words, the one that it is
most likely at equilibrium. This value corresponds to the maximum of the exponential
factor $S_1(E_1^*) + S_2(E - E_1^*)$ and can then be found as

$$0 = \frac{\partial}{\partial E_1}(S_1(E_1) + S_2(E - E_1)) = \frac{\partial S_1(E_1)}{\partial E_1} - \frac{\partial S_2(E_2)}{\partial E_2}$$

or

$$\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2}$$

Hence any two systems at equilibrium satisfies this last equation. For what told in the
previous section the function $\frac{\partial S}{\partial E}$ must be an empirical temperature or, better, because

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[2]This assumption is non trivial and will be deeply discussed in section SECTION

of dimensional arguments, an inverse of a temperature. Hence the condition can be read as

$$T_1 = T_2$$

This justifies the definition given at the beginning of this section

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E} \tag{1.8}$$

The derivation of the last equation made use only of the zeroth principle of thermodynamics and physical consideration about equilibrium: in this sense the temperature defined via 1.8 sometimes is also called *absolute temperature*.

1.3   Insight on the thermodynamic temperature

Here I want to provide an insight into the meaning of the formal definition $\frac{1}{T} = \frac{\partial S(E)}{\partial E}$. According to this definition, the temperature is a measure of the tendency of a system to increase/decrease entropy when an amount of energy is added. When the temperature is positive, adding energy to the system always increases the entropy of the system, giving it access to more states. A negative temperature, on the other side, symbolizes the fact that the system decreases its entropy when an amout of energy is added: in other words this means that the number of accessible states for the system decreases as the energy increases. One can imagine that if the maximum energy state of a system is realised only by one or few microstates, the systems might admit a decreasing entropy as a function of energy, hence admitting negative temperatures. This idea will be formalized in the the *Ramsey*'s criteria which provide the conditions under which a system admits negative temperature.

A rather counterintuitive result at negative absolute temperatures concerns the direction of heat flow. Consider two systems $\mathcal{S}_1$ and $\mathcal{S}_2$ isolated and individually in thermal equilibrium at temperatures T_1 and T_2 respectively. We say that $\mathcal{S}_1$ is *hotter* and $\mathcal{S}_2$ is *colder* if, when $\mathcal{S}_1$ and $\mathcal{S}_2$ are put into contact, the heat flows from $\mathcal{S}_1$ to $\mathcal{S}_2$. When $\mathcal{S}_1$ and $\mathcal{S}_2$ are put into contact the change in $\mathcal{S}_1$'s entropy is $\delta S_1 = \frac{\delta Q}{T_1}$ and in $\mathcal{S}_2$'s is $\delta S_2 = -\frac{\delta Q}{T_2}$. If the process happens keeping the system $\mathcal{S} = \mathcal{S}_1 + \mathcal{S}_2$ thermally isolated from the environment, then we know that $\delta S = \delta S_1 + \delta S_2 > 0$ because of the second law of thermodynamics, which implies

$$\delta Q \left(\frac{1}{T_1} - \frac{1}{T2} \right) > 0$$

One can now note that

1. If $T_1, T_2 > 0$ and $T_1 > T_2$ then it must be $\delta Q < 0$

2. If $T_1, T_2 < 0$ and $T_1 > T_2$ then it must be $\delta Q > 0$

3. If $T_1 > 0$ and $T_2 < 0$ then it must be $\delta Q > 0$

According to the convention that $\delta Q > 0$ means that the system (S1) absorbs a heat δQ, condition 3. means that heat flows from the system at negative temperature to the one at positive temperature or, in other words, that systems at negative temperatures are hotter than those at positive ones. Instead, condition 2. means that when two systems at negative temperatures are put into contact, the system at lower temperature (or more negative temperature, that is $\mathcal{S}_2$) gives heat to the one at higher temperature (or less negative temperature, that is $\mathcal{S}_1$). If one would make a hierarchy of hotness of systems depending on the temperature, it would be

$$0^+ < +\infty < -\infty < 0^-$$

This fact will be further explored in chapter 2.

Chapter 2

Two levels system

2.1 Two-levels systems admit negative temperatures

The most simple system that can exhibit negative temperatures is the two levels system
(TLS).
A TLS is a system, for example a particle, for which only two values of energy are
admitted, say E_1 and E_2. Let us denote the corresponding eigenstates by $|1\rangle$ and $|2\rangle$.
An example of such a system, which we may consider in the following derivations, can be
a spin-1/2 fermion in a uniform magnetic field. Let us now consider a system composed
of N TLS. It is convenient to introduce the occupation numbers n_1, n_2 which denote,
respectively, the number of TLS at energy E_1 and E_2. If we set $E_1 = \epsilon$ and $E_2 = 0$ for
simplicity, the energy of the system is

$$E = n_1 E_1 + n_2 E_2 = n_1 \epsilon \tag{2.1}$$

where $n_1 + n_2 = N$.
One macrostate of the system is thus identified by its energy and the total number
of particles. The number of microstates corresponding to one given macrostate is the
number of ways in which one can rearrange the particles in a way such that the total
energy remains fixed, that is

$$\Omega(E, N) = \frac{N!}{n_1! \, n_2!} = \frac{N!}{n_1! \, (N - n_1)!}$$

which corresponds to the Boltzmann entropy

$$S(E, N) = k_B \ln \left(\frac{N!}{n_1! \, (N - n_1)!} \right) \tag{2.2}$$

In the limit of large N the last expression can be expanded by using the Stirling's formula
$\ln(N!) \approx N \ln N - N$ which yields

$$S(E, N) \approx N \ln \left(\frac{N}{N - n_1} \right) + n_1 \ln \left(\frac{N - n_1}{n_1} \right) \tag{2.3}$$

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By using relation 2.1

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n_1}\frac{\partial n_1}{\partial E} = \frac{k_B}{\epsilon}\ln\left(\frac{N-n_1}{n_1}\right) = -\frac{k_B}{\epsilon}\ln\left(\frac{E}{N\epsilon - E}\right) \qquad (2.4)$$

where in the last step I used equation 2.1 again inside the logarithm's argument.
A plot of the temperature as a function of the system's energy is reported in figure 2.1. Negative temperatures occure in the region in which $E > \frac{N\epsilon}{2}$, which correspond to the states in which there are more particles in the excited state than in the lower one. As mentioned at the end of chapter 1, negative temperatures occur above $+\infty$ rather than below the absolute zero. When a TLS is cooled down to $0\,^\circ$K all the spins lie in the ground state, i.e. the state of minimum energy. As soon as one adds energy to the system, the temperature starts increasing and more and more particles get excited to the higher energy state untill the point in which, on average, we expect the particles to be half excited and half in the ground state, that is we have the same probability of having an excited particle or a particle in the ground state. This happens when the temperature is ideally infinite, either positive or negative and this constitutes the state of maximum entropy. By keeping adding energy to the system one ends up having more particles in the excited state rather than in the lower one, experiencing the *population inversion*.
 Equation 2.4 can be rewritten as

$$\frac{1}{T} = \frac{k_B}{\epsilon}\ln\left(\frac{n_2}{n_1}\right)$$

which leads to

$$\frac{n_2}{n_1} = e^{-\epsilon/k_B T} \qquad (2.5)$$

This formula allows us to introduce the so called *spin temperature*.
In the derivation of the results for the two level system we implicitly assume that the spin system is isolated from the environment and that the spins do not interact each other or, in other words, that each spin is isolated from the rest of the thermodynamic universe. In practice this is not the case and in general such a system is described by a hamiltonian of the type

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{ss} + \mathcal{H}_{sl} \qquad (2.6)$$

where H_0 represents the single particle hamiltonian implicitly assumed in the previous derivation, H_{ss} represents the spin-spin interaction and H_{sl} represents the spin-lattice interaction.
The term H_{ss} can be conveniently considered negligible but cannot be zero: indeed this therm plays a fundamental role for guaranteeing the *ergodicty* of the system.
The spin-lattice interaction on the other side can be characterized by a typical interaction time τ_L. The time τ_L characterizes the speed under which the spins adapts to a change in the lattice temperature. When the observation time of the experiment τ_s is much smaller than the typical interaction time $\tau_s \ll \tau_L$ the change in the system due to the spin-lattice interaction is negligible and equation 2.5 defines a temperature which is
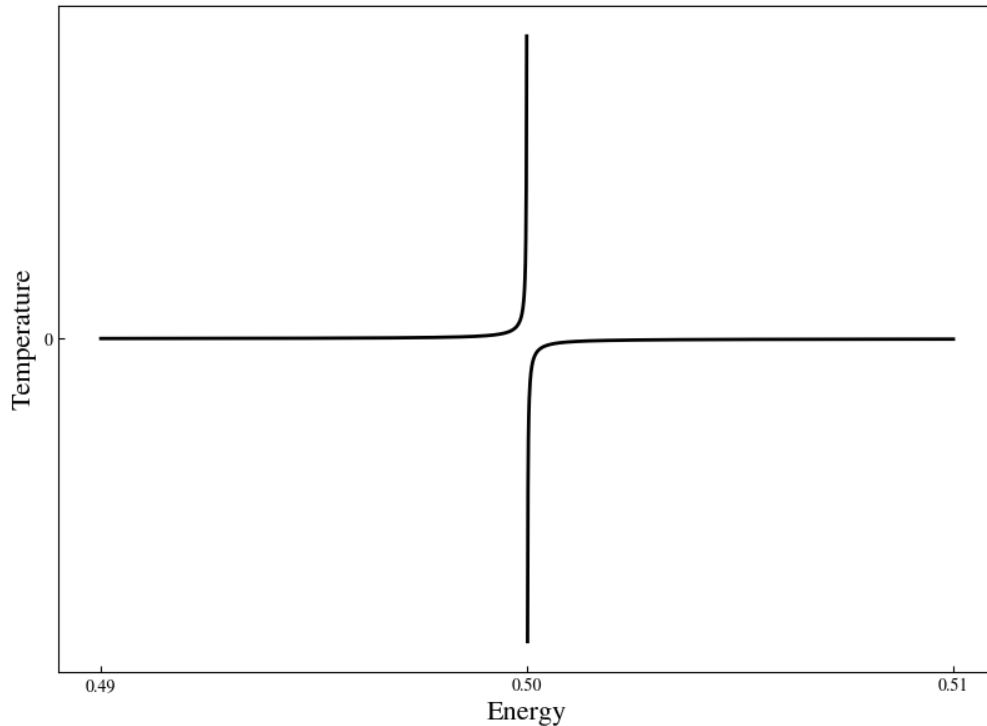
Figure 2.1: The plot reports the temperature as a function of the energy $(E/N\epsilon)$ in a two-levels system. When there are more excited particles than those in the lower state (energy > 0.5), the system exhibits negative absolute temperatures.

dependent only on the spins' configuration.

We call this temperature *spin temperature* [1]: Note that for $t \ll \tau_L$ this temperature may differ by the one of the lattice while for $t \gg \tau_L$ the two temperature coincide.

Let us now recall what we mentioned at the end of chapter 1: a system whose maximum energy state is allowed by only one or few microstates may exhibit a decreasing entropy as a function of the energy, hence admitting negative temperatures. This is exactly the case of a TLS for which the maximum energy state corresponds to exactly one precise microstate, that is when all the particles are in the excited state. This of course corresponds to a null entropy. Analogously, the same happens at the minimum energy for which there is only one corresponding microstate and the entropy is null. For all the other states the entropy is non-zero and is given by formula 2.3. The whole expressions as a function of the energy can be easilly obtained by 2.2 by multiplying and

diving by ϵ both inside and outside the logarithm

$$S(E,N)/k_B = N \ln \left(\frac{N\epsilon}{N\epsilon - E} \right) + \frac{E}{\epsilon} \ln \left(\frac{N\epsilon - E}{\epsilon} \right) \tag{2.7}$$

and is reported in figure 2.2.

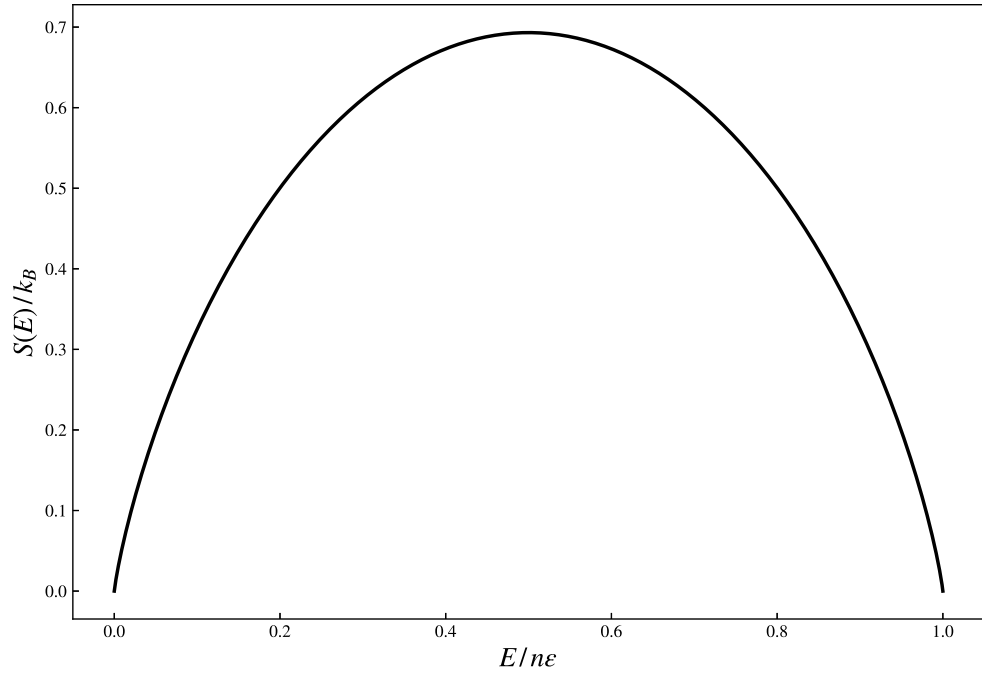   This insight can be formalized into the *Ramsey's criteria*.

Figure 2.2: Entropy of a TLS as a function of the energy.

2.2 Ramsey's criteria

Ramsey [2] provided 3 conditions under which a thermodynamic system exhibits negative temperatures

1. *The various elements of the thermodynamic system under analysis must be at equilibrium each other.*
   This condition must be verified in order to define a temperature for the whole system.

2. *There must be an upper bound on the energy of the system*
   In fact it is known from statistical mechanics that the probability (or probability density) for the system to be in a state of energy E is

   $$p(E) \propto e^{-\beta E} \tag{2.8}$$

   where $\beta = 1/k_B T$. If negative temperatures are admitted by the system and the latter does not admit an upper bound on the energy, the exponential factor in equation 2.8 becomes infinitely large for increasing energy. This means that if the system admits negative temperature, the higher the energy, the higher the probability of the system to be in that state. The most probable state would then be the one at infinite energy making the other states negligible in probability. Clearly, an infinite amount of energy cannot be put into the system, meaning that such a system cannot exists.

3. *The thermodynamic system under analysis must be thermally isolated from other systems that do not satisfy the above conditions.*
   In good approximation one can think that the time required to reach equilibrium between the elements of the system is small compared to the time of interaction between the system and the environment or another system.

The above conditions are all satisfied by the TLS described above. Indeed it admits negative temperatures.

Chapter 3

The experiment by Purcell and Pound

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The existence of negative absolute temperatures was first predicted by Lars Onsager in 1949 [3] in the context of 2D confined turbulence vortices.

The confinement of the vortices caused the phase space of the system to be bounded and Onsager showed that this results in a peak of the entropy as a function of the energy, in accordance to what stated by the Ramsey's criterion.

The first experimental evidence of negative temperatures was the experiment carried by Purcell and Pound [4] in 1951, who managed to bring the spins of a LiF crystal in a negative absolute temperatures state for several minutes. In this section I want to illustrate the experimental procedure followed by Purcell and Pound to realize such a state.

The experiment used a system of nuclear spins on a LiF crystal lattice immersed in a uniform magnetic field $\mathbf{h}$. The energy of the system is given by the analogous of equation 2.6

$$E = -\mathbf{h} \cdot \mathbf{M} + \mathcal{H}_{ss} + \mathcal{H}_{sl}$$

where $\mathbf{M}$ is the magnetic moment vector $\mathbf{M} = g\frac{q}{2m}\mathbf{S}$, $\mathbf{S}$ is the spin and g is the Landé factor.

As before we consider negligible the spin-spin interaction term but still considering it non-zero since it is fundamental for keeping the system in internal equilibrium [5].

The spin-lattice interaction is characterized by the typical relaxation time τ_L which was found to be around 5 minutes for the considered system. For times much smaller than τ_L, the system can be considered as in a transient equilibrium, and the particle's states distribution defines a spin temperature according to equation 2.5. This temperature is precisely the one that was deduced to be negative. The effective energy for the system for the experiment was then
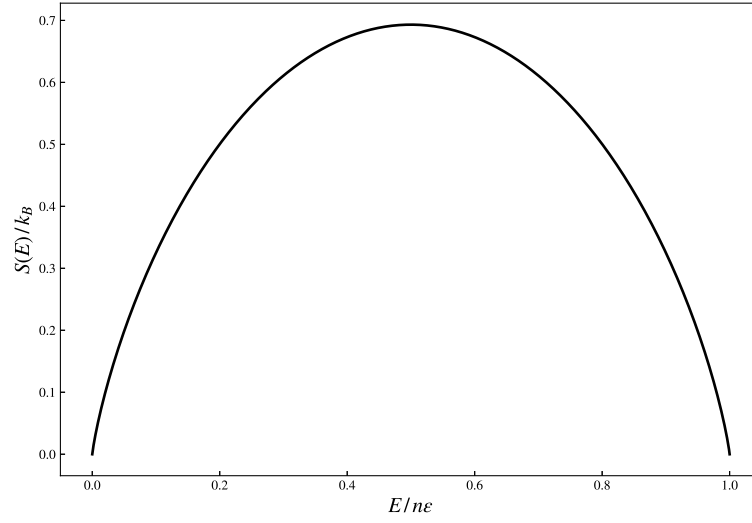
$$E \approx -\mathbf{h} \cdot \mathbf{M} \tag{3.1}$$

Figure 3.1

Initially the system was brought into equilibrium aligning all the spins with the magnetic field in either a parallel or antiparallel way: for positive temperatures, for what said in chapter 2, we expect the majority of the spins to be parallel causing the energy given by equation 3.1 to be negative.

Then, suddenly, the magnetic field is switched in direction, causing the majority of the spins to be antiparallel to the magnetic field, hence giving raise to a positive energy. This state is characterized by a negative spin temperature. Figure 3.1 illustrates the effect of the magnetic field making use of the entropy-energyrelation given by equation 2.7.
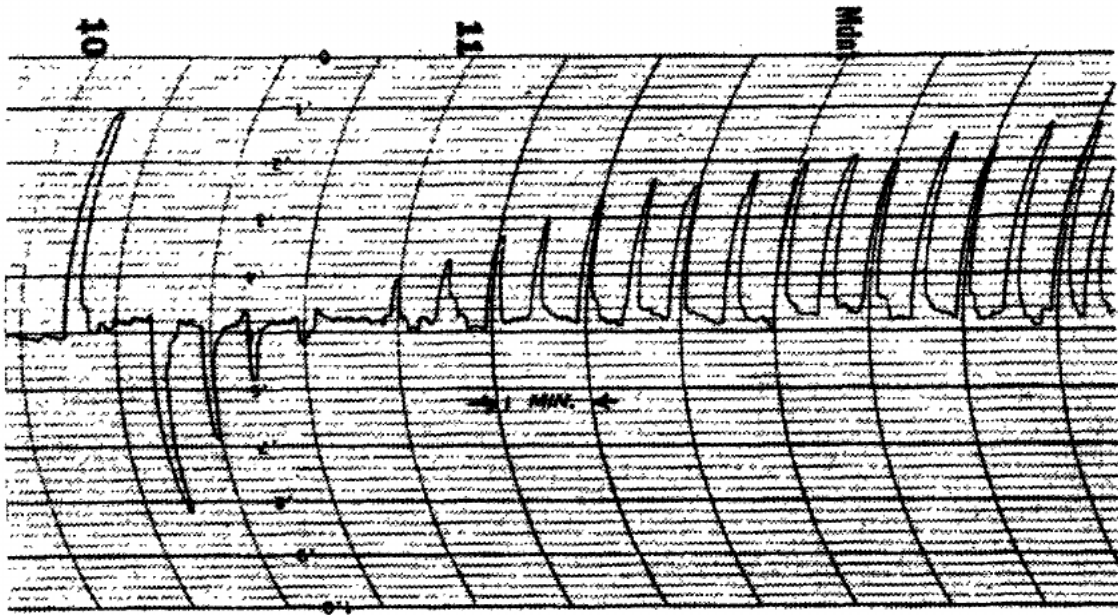
Figure 3.2: The plot (adapted from [4]) reports the record of the nuclear magnetization during the experiment. The first peak denotes the initial equilibrium state in which the spins are aligned with the magnetic field in the lowest energy state. As the magnetic field is istantaneously reversed, the spins remained aligned in the opposite direction of the field, remaining in the highest enery state and causing the second (negative) peak. After a relaxation time τ_L the spin system returns in equilibrium in the lowest energy state.

Chapter 4

Definition of Entropy

The temperature definition via

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E}$$

is strictly dependent on the definition of the entropy and the existence of negative temperatures is mainly a consequence of this definition. It was already discussed in chapter 1 why it is legitimate to define the temperature as the derivative of the entropy with respect to the energy. The purpose of this section, on the other side, is to discuss the definition of the entropy with particular regards to the definitions given by Gibbs and Boltzmann. since they have direct consequences on the existence of negative temperatures.

After a brief introduction over the two perspectives, which would require an entire thesis themselves to be deeply developed, the focus of the discussion will be on the comparison between the two definitions with particular emphasis on the direct consequences on the negative temperatures.

4.1 Boltzmann's framework

The conceptual basis for the Boltzmann's approach to statistical mechanics presented in Boltzmann's paper (1877b) relies on the attempt to explain the Second Law of thermodynamics via probability calculus.

To introduce the idea let us consider a system of N particles and let us work in a $6N$ dimensional phase space with coordinates $q_1, ..., q_{3N}, p_1, ...p_{3N}$ and let us consider also the μ-space associated to each particle in the system, i.e. the phase space in which each single particle moves.

Let us parition each μ-space into m disjoint rectangular cells of volume $\Delta\omega$ so that $\mu = \omega_1 \cup ... \cup \omega_m$ and each cell ω_i is charaterized by an energy value ϵ_i. Once specifying the mechanical state of the system, a point $x \in \Gamma$, one can associate a collection of N points in the μ-spaces, one for each particle (they are the same for each particle). For each x, also called *microstate* of the system, one can define a *macrostate* for the system by specifying the number of particles n_i included in each cell ω_i in the μ-space. Formally

$Z = (n_1, ..., n_m)$ where n_i is the number of particles in the cell $\omega_i \subset \mu$.

By this definition it is clear that more than one microstate can describe the same macrostate of the system. For each macrostate Z_0 the corresponding phase space volume, that is the set of corresponding microstates, is

$$\Gamma_{Z_0} \equiv \{x \in \Gamma : Z(x) = Z_0\}$$

The Boltzmann's entropy of a system in a macrostate Z is then defined as

$$S = k_B \ln \left(\text{Vol}(\Gamma_Z) \right) \tag{4.1}$$

4.2   Gibbs' framework

Gibbs' approach to statistical mechanics is based on the idea of a statistical ensemble. To introduce this concept let us work again in a phase space Γ and describe the system via $3N$ canonical coordinates, so that Γ is a $6N$ dimensional space. A point in Γ denotes a precise configuration of the system and it is referred to as a *representative point*.

A given macroscopic configuration for the system can correspond to multiple microscopic configurations of the system, that is multiple points in the Γ space might correspond to the same macroscopic state.

In other words, when specifying a precise macroscopic configuration, we are not referring to one system, but rather to a collection of systems which we call an *ensemble*.

An ensemble is conveniently described my means of a *density function* $\rho(q, p, t)$ such that $\rho(q, p, t) d^{3N} q d^{3N} p$ is the number of representative points in a phase space volume $d^{3N} q d^{3N} p$.

Given the value of ρ at time $t = 0$, the evolution of the function is completely determined by means of the Hamilton equation

$$\frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i}$$
$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}$$

More precisely the evolution of ρ is determined by the *Liouville's theorem* which states that

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right) = 0 \tag{4.2}$$

or

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}$$

ADD PROOF OF THE Liouville's theorem.

In developing his theory, Gibbs' main goal was to produce a rational fundation for thermodynamics. Hence, Gibbs's work was guided by analogies between his theory and

thermodynamics.

In his book [6] Gibbs derived a relation in the canonical ensemble that is

$$d\langle H \rangle = \theta d\sigma - \sum_i \langle A \rangle \, da_i \tag{4.3}$$

which is formally analogue to the fundamental equation of thermodynamics

$$dU = TdS + \sum_i F_i da_i$$

where $\langle H \rangle$ in equation 4.3 denotes the expectation value of the hamiltonian in the canonical ensemble. The analogy suggests that θ, the so called *modulus of the ensemble*, can be identifies as the temperature of the system and and σ, defined as

$$\sigma[p_\theta] = -\int p_\theta(x) \ln \rho_\theta(x) \, dx$$

can be identified as the entropy of the system, namely the *Gibbs entropy*.

One important point to note is that in the Gibbs' entropy is not a function on the phase space but rather a functional on the ensemble density ρ_θ. This implies that there is no function χ on the phase space such that

$$\langle \chi \rangle_\theta = \sigma[\rho_\theta] \quad \forall \theta$$

The next step is to understand whether an equation such 4.3 can be obtained in the microcanonical ensemble. Gibbs proposed (see [6] page 124-128, 169,171) the following definitions

$$\begin{aligned} T &\longleftrightarrow \left(\frac{\partial \ln \Omega(E)}{\partial E}\right)^{-1} \\ S &\longleftrightarrow \ln \Omega(E) \end{aligned}$$

where

$$\Omega(E) \equiv \int_{H(x) \leq E} dx \tag{4.4}$$

is called *integrated density of states*.

4.3 Consistent thermodynamics forbids negative temperatures

The difference between the Gibbs entropy [1]

$$S_G = k_B \ln \Omega(E) \tag{4.5}$$

---

[1]the Boltzmann's constant is added for dimensional arguments

and the Boltzmann's entropy

$$S_B = k_B \ln \omega(E) \tag{4.6}$$

has a direct and important consequence on the existence of negative temperatures. Indeed it is easy to see that the integrated density of states defined in equation 4.4, that is the number of states whose energy is less than or equal to E, is a monotonically increasing function of the energy, hence the temperature is always positive. On the other side, the density of states $\omega(E)$ that enters in the Boltzmann's entropy denotes the number of states in the range $(E, E + dE)$ and there is no reason to believe that is a monotonically increasing function of the energy. In fact we have already seen that in the case of a non interacting two level system the Boltmann's entropy leads to negative temperatures.

The choice of the correct microcanonical entropy is not a straightforward process since different definitions of entropy can be used untill they are able to reproduce the thermodynamics.

In 1991 Berdichevsky *et al.* [7] pointed out some arguments in favour of the Gibbs' entropy, which have then been developed by many authors. The main arguments were proposed by Dunkel and Hillbert in 2014 [8] introducing the so called *thermostatistical consistency condition*.

Let us suppose that the system is described by some control variables $\{E, V, A_i\}$ so that $S = S(E, V, A_i)$. By differentiating S with respect to the control variables

$$\begin{aligned}
\mathrm{d}S &= \left(\frac{\partial S}{\partial E}\right) \mathrm{d}E + \left(\frac{\partial S}{\partial V}\right) \mathrm{d}V + \sum_i \left(\frac{\partial S}{\partial A_i}\right) \mathrm{d}A_i \\
&\equiv \frac{1}{T}\,\mathrm{d}E + \frac{p}{T}\,\mathrm{d}V + \sum_i \frac{a_i}{T}\,\mathrm{d}A_i
\end{aligned}$$

If one now considers an isoentropic process for which only energy and one control variable are allowed to change, one gets that

$$T\left(\frac{\partial S}{\partial A_\mu}\right)_E = -\left(\frac{\partial E}{\partial A_\mu}\right)_S = -\left\langle \frac{\partial H}{\partial A_\mu}\right\rangle \tag{4.7}$$

Now, since

$$\begin{aligned}
T_{\mathrm{B}}(E, V, A) &= \left(\frac{\partial S_{\mathrm{B}}}{\partial E}\right)^{-1} = \frac{1}{k_{\mathrm{B}}}\frac{\Omega'}{\Omega''} \\
T_{\mathrm{G}}(E, V, A) &= \left(\frac{\partial S_{\mathrm{G}}}{\partial E}\right)^{-1} = \frac{1}{k_{\mathrm{B}}}\frac{\Omega}{\Omega'}
\end{aligned} \tag{4.8}$$

where the prime indicates the differentiation with respect to the energy of the system, one has that

$$\begin{aligned}
T_B\left(\frac{\partial S_B}{\partial A_\mu}\right) &= \frac{1}{\Omega''}\frac{\partial \Omega'}{\partial A_\mu} \\
T_G\left(\frac{\partial S_G}{\partial A_\mu}\right) &= \frac{1}{\Omega'}\frac{\partial \Omega}{\partial A_\mu}
\end{aligned}$$

so in general we expect that if one of the two definitions of the entropy satisfies condition 4.7, the other one does not, and it is easy to see that the Gibbs entropy does

$$
\begin{aligned}
T_G\left(\frac{\partial S_G}{\partial A_\mu}\right) &= \left(\frac{\partial S_G}{\partial E}\right)^{-1}\left(\frac{\partial S_G}{\partial A_\mu}\right) = \frac{1}{\omega}\frac{\partial}{\partial A_\mu}\mathrm{Tr}[\theta(E-\mathcal{H})] \\
&= \frac{1}{\omega}\mathrm{Tr}\left[\frac{\partial\theta(E-\mathcal{H})}{\partial A_\mu}\right] = -\frac{1}{\omega}\mathrm{Tr}\left[\delta(E-\mathcal{H})\frac{\partial\mathcal{H}}{\partial A_\mu}\right] \\
&= -\mathrm{Tr}\left[\frac{\delta(E-\mathcal{H})}{\omega}\frac{\partial\mathcal{H}}{\partial A_\mu}\right] = -\mathrm{Tr}\left[\rho\frac{\partial\mathcal{H}}{\partial A_\mu}\right] = -\left\langle\frac{\partial\mathcal{H}}{\partial A_\mu}\right\rangle
\end{aligned}
$$

Another argument in favour of the Gibbs' entropy, still proposed by Dunkel and Hillbert [8], is that the Gibbs' entropy satisfies the generalized equipartition theorem (proof in appendix)

$$nulla \tag{4.9}$$

while the Boltzmann's does not. To see this one can consider the simple example of an ideal gas confined in a cubic box of side L. In this case the hamiltonian reads

$$
\mathcal{H}(t,\mathbf{q},\mathbf{p}) = \sum_i \frac{\mathbf{p}_i^2}{2m} + V(\mathbf{q}_i)
$$

where

$$
V(\mathbf{q}_i) = \begin{cases} 0 & \text{if } \mathbf{q}_i \in \text{box} \\ +\infty & \text{otherwise} \end{cases}
$$

The integrated density of states, that is the number of states with energy less than or equal to E, can be computed as

$$
\begin{aligned}
\Omega(E) &= \frac{1}{h^{3N}}\int d^{3N}p\int d^{3N}q \quad \theta(\mathcal{H}(t,\mathbf{q},\mathbf{p})-E) = \\
&= \frac{V^N}{h^{3N}}\int d^{3N}p \quad \theta\left(\sum_i\frac{\mathbf{p}_i^2}{2m}-E\right) = \frac{V^N(2\pi mE)^{3N/2}}{h^{3N}\Gamma(\frac{3N}{2}+1)}
\end{aligned}
$$

so that the density of states is

$$
\omega(E) = \frac{\partial\Omega(E)}{\partial E} =
$$

One can now calculate the two temperatures using 4.8

$$T_B, T_G$$

and rearrangin terms

$$eq1, eq2 \tag{4.10}$$

leading to the desired result.

Chapter 5

Ising model at negative temperatures

In this last section I move the focus towards the the study of a more complex model, namely the Ising model.

After a brief introduction on the 2D Ising model, I will move towards the description of the simulations. The results of the simulations are then presented and discussed according to what said in the previous chapters.

5.1 The Ising model

The Ising model is a mathematical model initially used to describe magnetic properties of materials in statistical mechanics. It consists in a collection of spins organised in a lattice that can assume two values, either 1 or -1.

The spins are allowed to interact with their neirest neighbors and in the most general form the hamiltonian assumes the form

$$\mathcal{H}(\{\sigma_k\}) = -\sum_{\langle ij \rangle} J_{ij}\sigma_i\sigma_j - \sum_j B_j\sigma_j \tag{5.1}$$

where B_j indicates the intensity of the magnetic field on the spin j and J_{ij} indicates the strength of the interaction between the spin i and the spin j. In the following analysis I will assume $J_{ij} = J, B_j = B \ \forall i, j$.

The sign of the interaction parameter J determines whether we are dealing with ferromagnetic materials ($J > 0$) or paramagnetic materials ($J < 0$). In the case of $J = 0$ we return to the two levels system discussed in chapter 2.

Let us first restrict the analysis to the purely interacting case setting $B = 0$. In this case the hamiltonian initially given by 5.1 becomes

$$\mathcal{H}(\{\sigma_k\}) = -J\sum_{\langle ij \rangle} \sigma_i\sigma_j$$

At fixed temperature T the probability of a state is given by the Boltzmann factor

$$p(\{\sigma_k\}) = \frac{e^{-\beta \mathcal{H}(\{\sigma_k\})}}{Z} \tag{5.2}$$

where $\beta = \frac{1}{k_B T}$ and Z is the canonical partition function

$$Z(\beta, V, N) = \sum_{\{\sigma_k\}} e^{-\beta \mathcal{H}(\{\sigma_k\})}$$

Let us consider the probability factor 5.2, which explicitly becomes

$$p(\{\sigma_k\}) \propto e^{-\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j}$$

and let us define a new new parameter $\xi = \beta J$ so that

$$p(\{\sigma_k\}) \propto e^{-\xi \sum_{\langle ij \rangle} \sigma_i \sigma_j} \tag{5.3}$$

Ferromagnetic systems

In the ferromagnetic case $J > 0$, hence $\xi > 0$. For $\xi \to 0$, which can be either a high temperature or a weak coupling, one can see that $p(\{\sigma_k\}) \to 1$ independently on the values σ_k so that we expect the spins to be almost evenly distributed between up and down.
Instead for $\xi \to +\infty$ which can be either a low temperature or a strong coupling, one has that the exponential in 5.3 except when $\sum_{\langle ij \rangle} \sigma_i \sigma_j$ is close to zero, hence we expect, again, the spins to be evenly distributed between up and down.

Paramagnetic systems

In this case $J > 0$, hence $\xi > 0$. For $\xi \to 0$ the result is the same as for ferromagnetic systems.
When $\xi \to -\infty$ the exponential factor in 5.3 grows indefinetely if $\sum_{\langle ij \rangle} \sigma_i \sigma_j > 0$, that is when the spins are aligned. Thus no preference is given to the configuration in which two neighbor spins are aligned both up or down, and we expect it to depend on the history of the system.

The study is carried in a 2D lattice which is of the shape reported in figure 5.1. Let us focus the attention on a $2x2$ subset of the lattice. The possible energies are

$$\begin{pmatrix} \uparrow & \uparrow \\ \uparrow & \uparrow \end{pmatrix}_1 \quad E = 4J$$

$$\begin{pmatrix} \downarrow & \uparrow \\ \uparrow & \uparrow \end{pmatrix}_1 \quad E = 4J$$

$$\begin{pmatrix} \downarrow & \downarrow \\ \uparrow & \uparrow \end{pmatrix}_1 \quad E = 4J$$

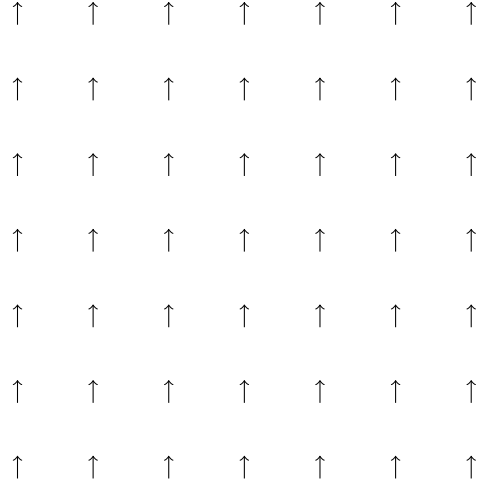$$\begin{pmatrix} \downarrow & \downarrow \\ \downarrow & \uparrow \end{pmatrix}_1 \quad E = 4J$$

$$
\begin{pmatrix} & \uparrow & \\ \uparrow & \uparrow & \uparrow \\ & \uparrow & \end{pmatrix}_1 \implies \begin{pmatrix} & \uparrow & \\ \uparrow & \downarrow & \uparrow \\ & \uparrow & \end{pmatrix}_2 \qquad \Delta E = 2J \cdot 4 = 8J
$$

$$
\begin{pmatrix} & \uparrow & \\ \downarrow & \uparrow & \uparrow \\ & \uparrow & \end{pmatrix}_1 \implies \begin{pmatrix} & \uparrow & \\ \downarrow & \downarrow & \uparrow \\ & \uparrow & \end{pmatrix}_2 \qquad \Delta E = 2J \cdot 2 = 4J
$$

$$
\begin{pmatrix} & \downarrow & \\ \downarrow & \uparrow & \uparrow \\ & \uparrow & \end{pmatrix}_1 \implies \begin{pmatrix} & \downarrow & \\ \downarrow & \downarrow & \uparrow \\ & \uparrow & \end{pmatrix}_2 \qquad \Delta E = 2J \cdot 0 = 0
$$

$$
\begin{pmatrix} & \downarrow & \\ \downarrow & \uparrow & \uparrow \\ & \downarrow & \end{pmatrix}_1 \implies \begin{pmatrix} & \downarrow & \\ \downarrow & \downarrow & \uparrow \\ & \downarrow & \end{pmatrix}_2 \qquad \Delta E = 2J \cdot (-2) = -4J
$$

$$
\begin{pmatrix} & \downarrow & \\ \downarrow & \uparrow & \downarrow \\ & \downarrow & \end{pmatrix}_1 \implies \begin{pmatrix} & \downarrow & \\ \downarrow & \downarrow & \downarrow \\ & \downarrow & \end{pmatrix}_2 \qquad \Delta E = 2J \cdot (-4) = -8J
$$

Figure 5.1

5.2 Markov Chain Monte Carlo

To study the physical properties of the system at equilibrium in a certain macrostate X, one needs to perform ensemble averages (er expectation values). The expectation value of a physical quantity A is computed as

$$
\bar{A} = \frac{\int A e^{-\beta H} d\tau}{\int e^{-\beta H} d\tau} \tag{5.4}
$$

where tha variable τ runs over all the possible microstates compatible with the given macrostate X.

Practically speaking, to perform such averages during the simulation, one needs to

1. Bring the system in a configuration compatible with specified macrostate

2. Calculate the value of the desired quantity in the specific microstate

3. Store the value

4. Move the system to another microstate compatible with the specified macrostate and repeat from point 2 until desired

5. Perform the average

Of course, in order to perform an accurate average, one needs to

1. Guarantee that the system visit every possible microstate compatible with the macroscopical configuration so that all the possible values of the physical quantity are taken into account when performing the average

2. Guarantee that every possible state is visited with a frequency that is equal to the probability of the state itself

This can be accomplished by means of the Monte Carlo method, precisely by means of the Metropolis-Hastings algorithm, which allows to perform a random walk trough the configurations of the system and respect the above states conditions under the correct assumptions.

The main points of the Metropolis-Hastings' algorithm are now briefly reported, inviting the reader to consult more appropriate sources for further information.

Let us suppose that we want to sample from a probability distribution $p(x)$.

The system is initially prepared in a certain configuration x which can be arbitrarilly chosen. Each Monte-Carlo cycle then consists in the following steps

1. A new configuration of the system x^* is proposed sampling from a proposal distribution $J(x^*|x)$. The proposal distribution can be arbitrarilly chosen, provided the fact that is symmetric $J(x^*|x) = J(x|x^*)$ and that in an infinite number of steps, it guarantees that every states is visited.

2. The ratio of the probabilities of the two states of the system is then calculated

$$w = \frac{p(x^*)}{p(x)}$$

3. if $w \geq 1$ the proposal change is accepted and $x_{i+1} = x^*$

4. otherwise a number r is extracted from a uniform distribution in $[0, 1]$. If $w > r$ the proposal change is still accepted and $x_{i+1} = x^*$. Otherwise the proposal moved is refused and $x_{i+1} = x_i$

Figure 5.2

Figure 5.3

The higher the number of Monte-Carlo cycles, the closer is the distribution of the visited states to the probability distribution $p(x)$, the more precise the expectation values calculated as 5.4.

Practically speaking the simplest choice for the proposal distribution $J(x^*|x)$, even if not the most efficient, is the uniform distribution. The distribution $p(x)$, on the other side, is related to the ensemble in which we describe the system: in the canonical ensemble $p(x)$ is given by the Maxwell-Boltzmann distribution given in equation 5.2. [1]

5.3 Single system at negative temperature

The first case I want to study is one single system prepared at temperature T. In order to perform the simulation, the system is initially prepared in a random configuration: then the systems goes under 10^7 Monte Carlo cycles sampling from the probability distribution given by 5.2. The simulations are run for three different values of the temperature, that is $T_1 = 0\,\mathrm{K}, T_2 = 1\,\mathrm{K}, T_3 = 1000\,\mathrm{K}$, and each of them is run both for the ferromagnetic antiferromagnetic cases.

Figure 5.2 reports the final state of a ferromagnetic system, while figure 5.3 reports those of an antiferromagnetic system for the same temperature values.
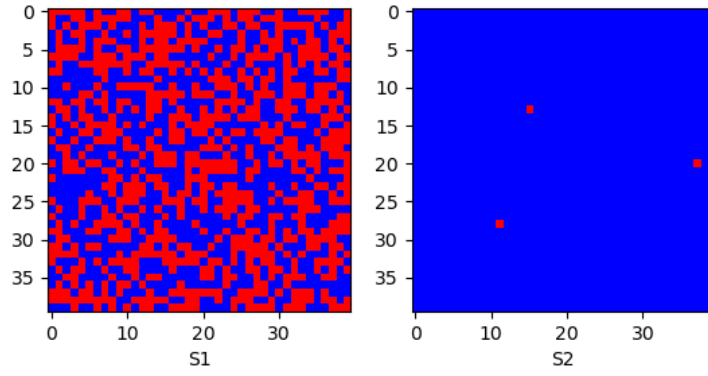
5.4 Two systems into contact

Two systems are prepared at temperature T_1 and T_2. The spin configurations are obtained after 10^4 Monte Carlo cycles in the canonical ensemble.

After that, the two systems are put into contact forming a new system that can be threaded as a microcanonical ensemble. The simulation of the latter was obtained with a demon Monte Carlo method with 10^6 cycles.
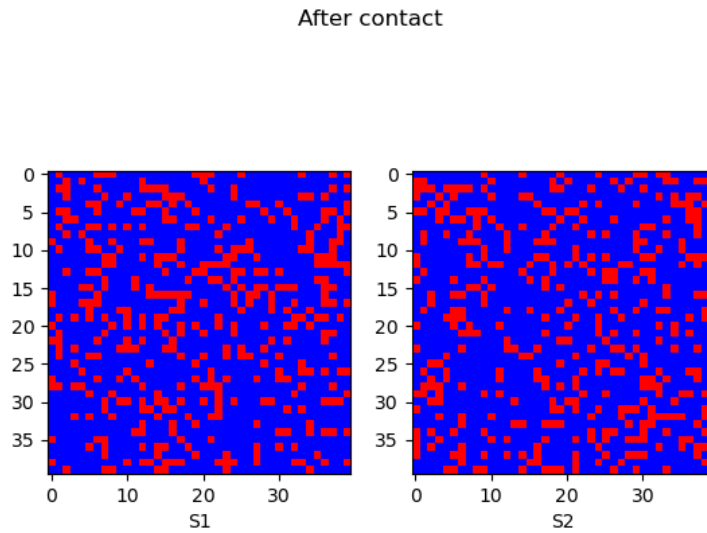
---

[1]Difference between Metropolis and Metropolis-Hastings

Figure 5.4: Before contact
The red tiles indicate the *up* state, while the blue tiles indicate the *down* state. Before beeing put into contact the two systems are prepared respectively at temperature
$$k_B T_1 = -\infty \, (10^8) \text{ and } k_B T_2 = 0^+ \, (10^{-8})$$

After contact

Figure 5.5: After contact

The red tiles indicate the *up* state, while the blue tiles indicate the *down* state. The equilibrium temperature after putting the two systems into contact is in between the two values according to the hierarchy presented at the end of chapter 1. The system at negative temperature get cooled down changing some up states to down states, while the system at positive temperature gets heated changing some down states into up. The resuls is of course an approximately equal concentrarion of up/down in both systems.

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