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*Bachelor Degree in Physics*

# Negative absolute temperatures

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# 1 Introduction

## 2 Formal definition of temperature

### Temperature as an equilibrium property

Temperature can be more systematically 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 equilibrium* 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  $\{X_1, X_2, \dots\}$ ,  $\{Y_1, Y_2, \dots\}$  and  $\{Z_1, Z_2, \dots\}$ .

If  $A$  and  $B$  are in equilibrium for some values  $\{X_1, X_2, \dots\}$  and  $\{Y_1, Y_2, \dots\}$  of the coordinates, then there must be a relation between  $\{X_1, X_2, \dots\}$  and  $\{Y_1, Y_2, \dots\}$  which can be expressed as

$$f_{AB}(X_1, X_2, \dots, Y_1, Y_2, \dots) = 0$$

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

$$f_{BC}(Y'_1, Y'_2, \dots, Z_1, Z_2, \dots) = 0$$

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

$$\begin{aligned} Y_1 &= g_{AB}(X_1, X_2, \dots, Y_2, \dots) \\ Y'_1 &= g_{BC}(Y'_2, \dots, Z_1, Z_2, \dots) \end{aligned}$$

Now let us bring the system  $B$  in the same state in both cases, which means imposing  $Y_1 = Y'_1$  and  $Y_2 = Y'_2$ . The last two equations implies that

$$g_{AB}(X_1, X_2, \dots, Y_2, \dots) = g_{BC}(Y_2, \dots, Z_1, Z_2, \dots) \quad (1)$$

or

$$G_{ABC}(X_1, X_2, \dots, Y_2, \dots, Z_1, Z_2, \dots) = 0$$

One can use this relation to express  $X_1$  as

$$X_1 = h_{ABC}(X_2, \dots, Y_2, \dots, Z_1, Z_2) \quad (2)$$

According to the zeroth principle of thermodynamics, which states that if  $A$  and  $B$  are in equilibrium and  $B$  and  $C$  are in equilibrium then  $A$  and  $C$  are in equilibrium <sup>1</sup>, then there must be a constrain on the values  $X_1, X_2, \dots, Z_1, Z_2, \dots$  which can be expressed as

$$f_{AC}(X_1, X_2, \dots, Z_1, Z_2, \dots) = 0$$

which means that  $X_1$  can be expressed as

$$X_1 = g_{AC}(X_2, \dots, Z_1, Z_2, \dots) \quad (3)$$

imposing the equality between 2 and 3

$$g_{AC}(X_2, \dots, Z_1, Z_2, \dots) = h_{ABC}(X_2, \dots, Y_2, \dots, Z_1, Z_2)$$

The term on the left does not depend on the coordinates of  $B$ . This means that both  $g$  functions in equation 1 must be of the type

$$\begin{aligned} g_{AB}(X_1, X_2, \dots, Y_2, \dots) &= \Theta(X_1, X_2, \dots) + \phi(Y_2, \dots) \\ g_{BC}(Y_2, \dots, Z_1, Z_2, \dots) &= \Theta(Z_1, Z_2, \dots) + \phi(Y_2, \dots) \end{aligned}$$

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

$$\Theta_A(X_1, X_2, \dots) = \Theta_B(Y_1, Y_2, \dots)$$

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<sup>1</sup>or, alternatively, that equilibrium is an equivalence relation

We started this reasoning by assuming equilibrium between  $A - B$  and  $B - C$ , but one could repeat this reasoning by assuming equilibrium between  $A - C$  and  $B - C$  obtaining the same result in terms of  $\{Z_1, Z_2, \dots\}$ . But also, 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  $\Theta$  such that

$$\Theta_A(X_1, X_2, \dots) = \Theta_B(Y_1, Y_2, \dots) = \Theta_C(Z_1, Z_2, \dots) = \dots$$

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  $\Theta$ . 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

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

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

Another possible definition of the function  $\Theta$ , the one relevant for what follows, will be presented later in this chapter.

### Thermodynamic temperature

Once introducing an entropy as a function of the energy  $S(E)$  it is possible to define a so called *thermodynamic temperature* via the relation  $\frac{1}{T} = \frac{\partial S}{\partial E}$ . To see why this makes sense it is convenient to 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  $\mathbf{x} = (q_1, \dots, q_n, p_1, \dots, p_n)$  where  $(q_i, p_i)$  is a pair of canonical coordinates. If  $\mathcal{H}(\mathbf{x})$  denotes the hamiltonian of the system, the condition

$$\mathcal{H}(\mathbf{x}) = E \tag{4}$$

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 4 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 4.

We also assume the Boltzmann definition of entropy <sup>2</sup>

$$S(E, \mathbf{x}) = k_B \log(\Omega(E, \mathbf{x})) \tag{5}$$

Let us now consider two systems with fixed energies  $E_1, E_2$  when separated. By putting them into contact and allowing them exchanging 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  $E_2 = E - E_1$  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 of the volumes at fixed  $E_1$

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

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<sup>2</sup>This assumption is non trivial and will be deeply discussed in section SECTION

By using now equation 5 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  $N \rightarrow +\infty$  the integral 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 maximizes  $\Omega(E, \mathbf{x})$  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 section (ADD SECTION REFERENCE), the function  $\frac{\partial S}{\partial E}$  must be an empirical temperature or, better, because 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

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E} \quad (6)$$

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 6 sometimes is also called *absolute 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  $\mathcal{S}_2$ , and viceversa. 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

$$\delta Q \left( \frac{1}{T_1} - \frac{1}{T_2} \right) > 0$$

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 absorbs a heat  $\delta Q$ , condition 1) 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 gives heat to the one at higher temperature. 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 section 3.

## Intuitive interpretation of 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 amount 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.

## 3 Two-levels system

### 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  $|2\rangle$ .

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

$$E = n_1 E_1 + n_2 E_2 = n_1 \epsilon \quad (7)$$

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

$$S(E, N) = k_B \ln \left( \frac{N!}{N_1! (N - n_1)!} \right) \quad (8)$$

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

$$S(E, N) \approx N \ln \left( \frac{N}{N - n_1} \right) + n_1 \ln \left( \frac{N - n_1}{n_1} \right) \quad (9)$$

By using relation 7

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

where in the last step I used equation 7 again.

A plot of the temperature as a function of the system's energy is reported in figure 1. Negative temperatures occur 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. Let us recall what we mentioned at the end of 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 9. The whole expressions as a function of the energy can be easily obtained by 8 by multiplying and dividing by  $\epsilon$  both inside and outside the logarithm

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

and is reported in figure 2.

Let us formalize this insight in the next section.

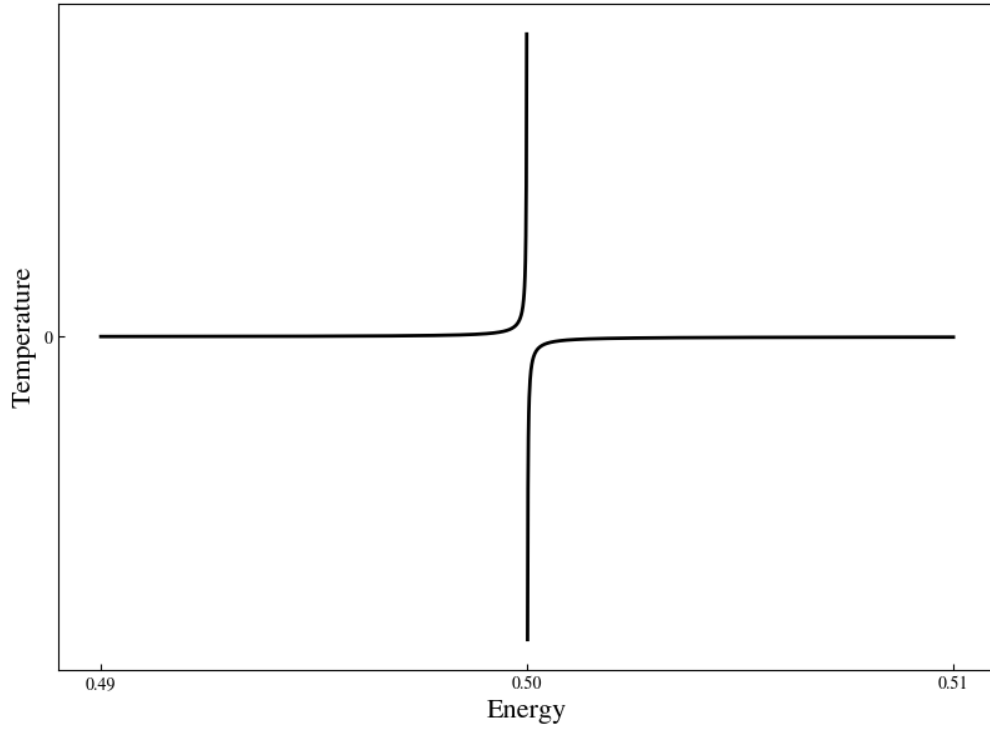


Figure 1: The plot reports the temperature as a function of the energy in a two-level system. When there are more excited particles than those in the lower state (Energy  $> 0.5$ ), the system exhibits negative absolute temperatures.

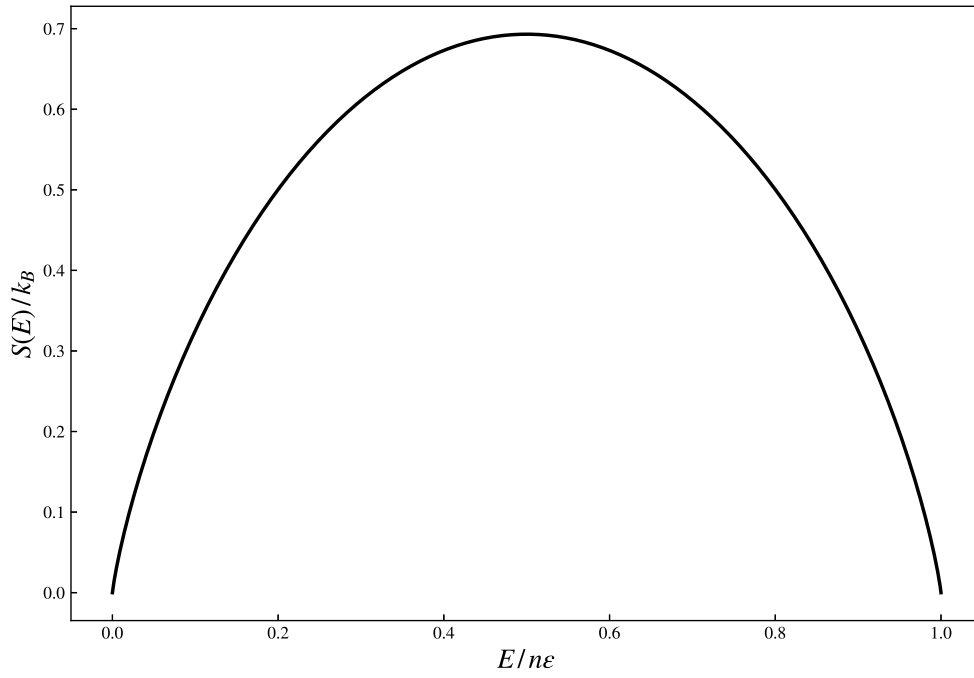


Figure 2: Entropy of a TLS as a function of the energy.

## Ramsey's criteria

Ramsey 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

$$p(E) \propto e^{-\beta E} \quad (10)$$

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 10 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. Clearly, an infinite amount of energy cannot be put into the system, meaning that such a system cannot exist.

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.