Physics at negative absolute temperatures

1 Temperature

Thermal equilibrium

Definition of macroscopic variables, equilibrium

Temperature as equivalence class with respect to equilibrium equivalence relation

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

$$Y_1 = g_{AB}(X_1, X_2, \dots, Y_2, \dots)$$
$$Y_1' = g_{BC}(Y_2', \dots, Z_1, Z_2, \dots)$$

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

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

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

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

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 [1], 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

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

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

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

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

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

[1] 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 Θ 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 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 this chapter.

Thermodynamic temperature

Once introducing an entropy as a function of the enrgy $S(E)$ 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 [2]

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

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

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

[2] 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 $N \to +\infty$ 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 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 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

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

2 Two levels system

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

$$E = n_1 E_1 + n_2 E_2 = n_1 \epsilon \tag{6}$$

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

$$\Omega(E, N) = \frac{N!}{N_1! N_2!} = \frac{N!}{N_1!\,(N-1)!}$$

which corresponds to the Boltzmann entropy

$$S(E, N) = k_B \ln\left(\frac{N!}{N_1!\,(N-1)!}\right)$$

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

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

By using relation 6

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

where in the last step I used equation 6 again.