



University of Trento, Department of Physics
Bachelor Degree in Physics

Negative absolute temperatures

Candidate: Matteo Zortea

Supervisor: Raffaello Potestio

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Introduction

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

Since temperature is a physical quantity, an adequate measure requires a physical unit. The most common temperature unit is the degree Celsius: this scale of values is normally established by fixing the values of temperature of two well known physical phenomena and assuming a linear relation between temperature and the physical property of 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.

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 criteria that make the calibration process reproducible.

A roughly good calibration of a thermometer in the Celsius scale can be done by assigning a thermometer 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. 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 temperatures. 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 a simulation of a system at negative temperature will be presented in the last chapter.

1 Formal definition of 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.

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 $\{Z_1, Z_2, \dots\}$ respectively.

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

$$f_{AB}(X_1, X_2, \dots, Y_1, Y_2, \dots) = 0 \quad (1)$$

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

$$f_{BC}(Y'_1, Y'_2, \dots, Z_1, Z_2, \dots) = 0 \quad (2)$$

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

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

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

$$g_{AB}(X_1, X_2, \dots, X_N, Y_2, \dots) = g_{BC}(Y_2, \dots, Y_N, Z_1, Z_2, \dots) \quad (3)$$

or

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

One can use this relation to express X_1 as

$$X_1 = h_{ABC}(X_2, \dots, X_N, Y_2, \dots, Z_1, Z_2) \quad (4)$$

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 equilibrium¹. This means that the constrains 1, 2, lead to a new constrain between A and C 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

$$X_1 = g_{AC}(X_2, \dots, X_N, Z_1, Z_2, \dots) \quad (5)$$

and imposing the equality between 4 and 5

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

The term on the lefts does not depend on the coordinates of B . This means that both g functions in equation 3 must be of the type

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

¹or, alternatively, equilibrium is an equivalence relation

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

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

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 $\{Y_1, Y_2, \dots\}$. 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

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

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

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

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

$$\mathcal{H}(\mathbf{x}) = E \tag{6}$$

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 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 6.

We also assume the Boltzmann definition of entropy ²

$$S(E, \mathbf{x}) = k_B \log(\Omega(E, \mathbf{x})) \tag{7}$$

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

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

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

By using now equation 7 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 the previous section 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

$$\frac{1}{T} = \frac{\partial S(E)}{\partial E} \quad (8)$$

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 8 sometimes is also called *absolute temperature*.

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.

A rather counterintuitive result at negative absolute temperatures concerns the direction of heat flow. Consider two systems S_1 and S_2 isolated and individually in thermal equilibrium at temperatures T_1 and T_2 respectively. We say that S_1 is *hotter* and S_2 is *colder* if, when S_1 and S_2 are put into contact, the heat flows from S_1 to S_2 , and viceversa. When S_1 and S_2 are put into contact the change in S_1 's entropy is $\delta S_1 = \frac{\delta Q}{T_1}$ and in S_2 's is $\delta S_2 = -\frac{\delta Q}{T_2}$. If the process happens keeping the system $S = S_1 + S_2$ 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 δQ , condition 2. 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 3. 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](#)

2 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

$$E = n_1 E_1 + n_2 E_2 = n_1 \epsilon \quad (9)$$

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

$$S(E, N) = k_B \ln \left(\frac{N!}{n_1! (N - n_1)!} \right) \quad (10)$$

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

$$S(E, N) \approx N \ln \left(\frac{N}{N - n_1} \right) + n_1 \ln \left(\frac{N - n_1}{n_1} \right) \quad (11)$$

By using relation 9

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

where in the last step I used equation 9 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 11. The whole expressions as a function of the energy can be easily obtained by 10 by multiplying and dividing by ϵ both inside and outside the logarithm

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

and is reported in figure 2.

Let us formalize this insight in the next section.

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

$$p(E) \propto e^{-\beta E} \quad (12)$$

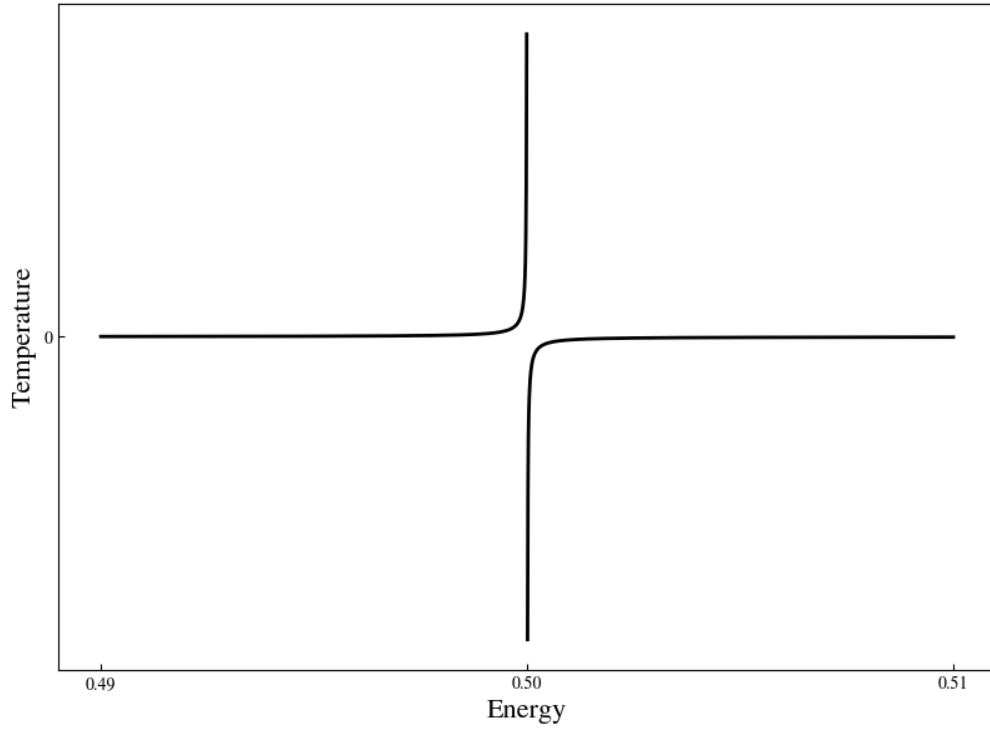


Figure 1: The plot reports the temperature as a function of the energy in a two-level system. When there are more excited particles than those in the lower state (Energy > 0.5), the system exhibits negative absolute temperatures.

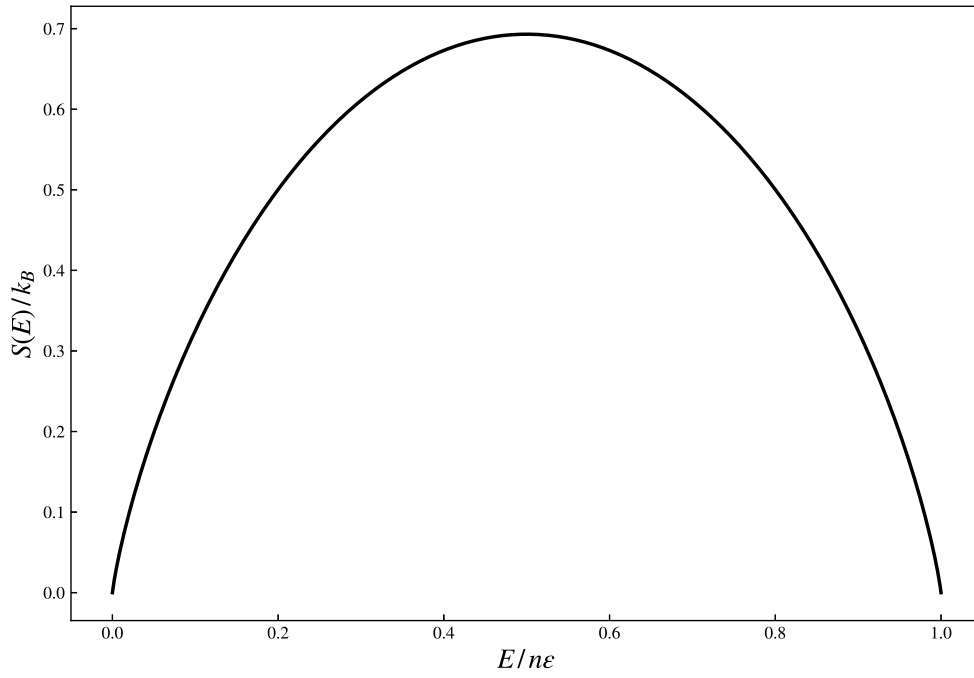


Figure 2: Entropy of a TLS as a function of the energy.

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 12 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.

3 Purcell and Pound experiment

4 Criticism against Boltzmann's 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 section 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 (ADD REFERENCES) since they have direct consequences on the existence of negative temperatures.

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 $q_1, \dots, q_{3N}, p_1, \dots, p_{3N}$ and let us consider also the μ -space associated to each particle in the system.

Let us partition each μ -space into m disjoint rectangular cells of volume $\Delta\omega$ so that $\mu = \omega_1 \cup \dots \cup \omega_m$ and each cell ω_i is characterized 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. 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 $Z = (n_1, \dots, n_m)$ where n_i is the number of particles in the cell ω_i .

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

$$S = k_B \ln(\text{Vol}(\Gamma_Z))$$

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 by 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

$$\begin{aligned} \frac{dp_i}{dt} &= -\frac{\partial \mathcal{H}}{\partial q_i} \\ \frac{dq_i}{dt} &= \frac{\partial \mathcal{H}}{\partial p_i} \end{aligned}$$

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

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial p_i} \dot{p}_i + \frac{\partial \rho}{\partial q_i} \dot{q}_i \right) = 0 \quad (13)$$

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 [1] Gibbs derived a relation in the canonical ensemble that is

$$d\langle H \rangle = \theta d\sigma - \sum_i \langle A \rangle da_i \quad (14)$$

which is formally analogue to the fundamental equation of thermodynamics

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

where $\langle H \rangle$ in equation 14 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 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 14 can be obtained in the microcanonical ensemble. Gibbs proposed (see [1] 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

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

is called *integrated density of states*.

References

- [1] Josiah Willard Gibbs. *Elementary Principles in Statistical Mechanics: Developed with Especial Reference to the Rational Foundation of Thermodynamics*. Cambridge Library Collection - Mathematics. Cambridge University Press, 2010. DOI: [10.1017/CB09780511686948](https://doi.org/10.1017/CB09780511686948).