



UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI FISICA E DI ASTRONOMIA “GALILEO
GALILEI”

CORSO DI LAUREA TRIENNALE IN FISICA

**Symmetries in thermodynamics and
the conundrum of negative
temperature**

Laureando:

Alessio LAPOLLA
Matricola:1054962

Relatore:

Dott. Fulvio BALDOVIN

Anno accademico 2014/2015

Abstract

In recent years the postulate of non negative temperature [1] has been questioned both theoretically and experimentally. In order to address this issue, theoretical physicists are arguing about the use of the Gibbs and Boltzmann entropy; while the latter, under specific circumstances, allows for the existence of negative absolute temperatures, the former one guarantees that temperatures are only positive for thermodynamic systems. In this thesis, after a brief introduction about the role of symmetries in thermodynamics, we contribute to this discussion checking whether these two entropies satisfy self-consistent thermodynamic requirements in systems constrained to preserve not only the energy but also the linear and the angular momenta. Then, we show that the Boltzmann entropy better satisfies the symmetric form of thermodynamics, so we shortly discuss about one of the most important consequences of the existence of negative temperatures, the possibility of Carnot cycles with efficiency larger than one.

Finally we show, in a practical way, how to study the thermodynamic equilibrium of systems of classical noninteracting particles with not only the energy constraint but also the linear momentum and/or the angular one, and we are going to check the validity of the general discussion made before.

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Chapter 1

A symmetric base for thermodynamics

Thermodynamics is a branch of Physics which is characterized by the study of systems with a large number of particles, usually of the order of the Avogadro's number ($\simeq 6.022 \cdot 10^{23}$); because the huge number of variables, it is therefore impracticable to study these kinds of systems using the laws of mechanics .

Thermodynamics was born between the eighteenth and the nineteenth century with the advent of Industrial Revolution, thanks to the work of physicists as Joule, Clausius, lord Kelvin and others. In fact, at the start of its development, it has been characterized by strong technological connotations because it was developed to solve some practical problems which arose from new technological machinery.

Afterwards, a number of physicists contributed to extend thermodynamics to address fundamental problems, even outside the technological realm. In particular an axiomatic form of thermodynamics has been developed by H.B. Callen [1] in order to build a solid theoretical foundation to it.

In his dissertation[1] Callen identifies some minimal postulates which constitute the basis for all empirical observations in thermodynamics. So, in order to do this, he noted that some specific extensive thermodynamics parameters are needed to identify the thermodynamic equilibrium of a given system. For the so-called simple systems they are:

- the volume V ;
- the energy U of the system;
- the number of particles N ¹.

Indeed they are at basis of the equilibrium states which are characterized by the first postulate:

Postulate 1 *There exist equilibrium states, and they are characterized completely by extensive parameters.*

¹In principle there should be more than one parameter N , one for ever component of the system, but, without losing in generality, we only consider a system with one component to make concise notations

The knowledge of the existence of equilibrium states it is not enough; the fundamental problem of thermodynamics is to know the properties of the final equilibrium state of a system after a transformation, which is usually represented by removal of one (or more) internal constraint. This fundamental problem is formally solved by the second postulate:

Postulate 2 *There exist a function that only depends on extensive parameters, called entropy S . It is defined for equilibrium states and the knowledge of entropy is the same as the knowledge of all thermodynamic properties of the system. Moreover, the values assumed by the extensive parameters after the removal of an internal constraint are those that maximize the value of entropy over the manifold of constrained equilibrium states.*

The expression that links the value of the entropy to those extensive parameters is called fundamental equation

$$S = S(U, V, N). \quad (1.1)$$

This postulate is basically equivalent to the second law of thermodynamics.

Other properties of entropy function are defined in the third postulate:

Postulate 3 *The entropy S is an extensive function, continuous, derivable and it is a monotonic increasing function of energy U that is: $(\frac{\partial S}{\partial U})_{V,N} > 0$.*

This postulate has two very important consequences: one is that it implies the possibility of inverting the function $S = S(U, V, N)$ in a function $U = U(S, V, N)$ and the other one, which is going to be discussed later in the text, is connected with the temperature T and its positiveness. Finally, Callen states a fourth postulate which is reported here for completeness, although not relevant in the present work,

Postulate 4 *The entropy of a system vanishes in the states for which $(\frac{\partial U}{\partial S})_{V,N} = 0$.*

As a consequence of the third postulate, there are two equivalent functions, each containing all the thermodynamic information about the system. In other words, there exist two different representations of the system, corresponding to two different choices of thermodynamics coordinates:

$$S = S(U, V, N) \quad \text{entropy representation,} \quad (1.2)$$

$$U = U(S, V, N) \quad \text{energy representation.} \quad (1.3)$$

The differential form in the energy representation is given by

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN. \quad (1.4)$$

These partial derivatives are very practical for the characterization of thermal, mechanical and chemical equilibriums. They correspond to intensive parameters, and they deserve the name of temperature T , pressure P , chemical potential μ because they represent these quantities, easily measured in an experiment. Respectively, we have thus

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \quad (1.5)$$

In view of the equivalence between the energy and entropy representations, also the partial derivatives of the entropy,

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN, \quad (1.6)$$

represent intensive parameters, which are given by:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, \quad -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}. \quad (1.7)$$

Now it can be stressed that as a consequence of the third postulate, $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$, and so $T > 0$; that is to say, according to Callen's postulate, negative absolute temperature can not exist in thermodynamics.

In thermodynamics it is also possible to describe a system in other representations containing both extensive and intensive parameters (of free energy, Gibbs potential, Massieu potentials, etc...), carrying out a Legendre transformation; they are very convenient in a lot of practical situations but thermodynamics is logically complete and self-contained within either the entropy or the energy representations[1].

The differences between extensive and intensive parameters do not concern only mathematical properties, but they concern also their physical origin. In fact, while intensive parameters correspond to emergent variables not traceable at the microscopical level, the extensive parameters directly arise from the symmetries of the microscopic world. The first one who noted the connection between symmetries and thermodynamic extensive parameters again has been H.B.Callen [3][1], who understood that the parameters U , V , and N reflect some fundamental symmetries. Indeed U reflects the symmetry of the system Hamiltonian under time-translation, N reflects the conservation of baryon number, in low energy limit, that is due to strong interaction symmetries, V is an order parameter that arises from the machinery of spontaneous symmetry breaking[3][1].

Starting from this observation, Callen affirms that if a thermodynamic system involves another extensive parameter X , with the fundamental equation $S = S(U, V, N, X)$, then this parameter has to be related to another fundamental symmetry.

In view of this symmetric construction it appears strange the formulation of the third postulate, which gives to temperature a more peculiar role, because it is the only intensive parameter which is defined positive. Indeed, this postulate has been challenged many times, both theoretically and experimentally, also in recent years [8].

In order to address this problem, in this work we are going to concentrate on symmetries which come from continuous transformation of Hamiltonian coordinates, as the one underlined U . For this kind of symmetries, the Noether's theorem says that if the Hamiltonian of a system is invariant under a continuous transformation then there is a conserved quantity associated to the dynamical evolution of the system.

For instance, since the Hamiltonian of an isolated system is invariant under time-translations the related conserved quantity becomes one of the dependent variables of entropy. Similarly, if an Hamiltonian is invariant under space-translations and space-rotations then also linear momentum (\vec{P}) and angular momentum (\vec{M}) have to be dependent variables for the entropy.

But, even though if U , \vec{P} , \vec{M} arise from the same machinery, there is an important difference between U and the other parameters. Indeed while there exists a postulate which

forces the intensive parameter related to U to be positive, that is $T > 0$, there are not any postulates about the intensive parameters related to \vec{P} and \vec{M} . In fact, defining $\frac{\partial S}{\partial \vec{P}} \equiv \vec{\lambda}$ and $\frac{\partial S}{\partial \vec{M}} \equiv \vec{\nu}$, they can be either positive or negative, and this has got a very strong physical meaning because, as is going to be showed in chapter 2, $T \frac{\partial S}{\partial \vec{P}} = \vec{v}$, that represents a velocity, could be either negative or positive by definition. So one may think that it would be legitimate that T could be also negative, because there is not a true physical reason because it has to be positive; indeed the third postulate was formulated taking in account empirical observations and negative temperatures maybe could be peculiar of some very specific systems, as the one of the experiment [8]. In this thesis work we will try to elucidate this , using methods belonging to statistical mechanics.

Chapter 2

Entropy and the negative temperature problem

Statistical mechanics studies how to connect the microscopic properties of atoms and molecules to the macroscopic ones of the system they belong; so it is the most natural method to study problems that concern connections between fundamental symmetries and thermodynamic parameters.

In statistical mechanics, entropy is the most important function in view of the Boltzmann postulate, which connects the entropy function S with the number of states allowed by the system's dynamics, a number counted starting from the Hamiltonian of the system. Using the approach of classical statistical mechanics, we consider a phase space of $6N$ dimensions where the small volume elements of size h^{3N} around its points represent a microscopic state of the system. Since we are analyzing systems in which energy is conserved, the representative point of the system describes a trajectory that belongs to the hypersurface $U = \mathcal{H}(q, p)$; and this trajectory is going through the hypersurface visiting with equal probability any possible state. This is the content of the equal a priori probability postulate. So if we consider two hypersurfaces U and $U + \epsilon_U$ (with $\epsilon_U \ll U$, allowing for some small but realistic exchange of energy with the environment); the hypervolume within the two, on which is moving the representative point, contains all possible states allowed to the system: the microcanonical ensemble.

So, because of the equal a priori probability postulate, the microcanonical density distribution function is:

$$\rho(q, p) = \begin{cases} \text{const}, & \text{if } U < \mathcal{H}(q, p) < U + \epsilon_U, \\ 0, & \text{elsewhere.} \end{cases}$$

Or an other general way to write it is:

$$\rho(U) = C \epsilon_U \delta(U - \mathcal{H}), \quad (2.1)$$

with the constraint

$$\int d^{3N} q d^{3N} p \rho(q, p) = \frac{C}{N! h^{3N}} \int_{U < \mathcal{H}(q, p) < U + \epsilon_U} d^{3N} q d^{3N} p = 1, \quad (2.2)$$

therefore to normalize the expression $C = \frac{1}{Tr[\delta(U-\mathcal{H})\epsilon_U]}^1$. Now we can define the number of allowed states,

$$\Gamma(E) = \frac{1}{N!h^{3N}} \int_{U < \mathcal{H} < U + \Delta U} d^{3N}q d^{3N}p, \quad (2.3)$$

and because ϵ_U is tiny, we can define, without losing any information, the number of states under the hypersurface U as

$$\Omega(U) = \frac{1}{N!h^{3N}} \int_{\mathcal{H} < U} d^{3N}q d^{3N}p = Tr[\Theta(U - \mathcal{H})], \quad (2.4)$$

and finally the density of states

$$\omega(U) \equiv \frac{\partial \Omega(U)}{\partial U} = Tr[\delta(U - \mathcal{H})]. \quad (2.5)$$

We note that with this definition the microcanonical density distribution can be written

$$\rho(q, p) = \frac{\delta(U - \mathcal{H})}{\omega}, \quad (2.6)$$

and that the mean value of a physical quantity is

$$\langle (\dots) \rangle = Tr[\rho(\dots)]. \quad (2.7)$$

Therefore the entropy definition is

$$S = k_B \ln(\Gamma(U)), \quad (2.8)$$

which for ordinary systems is held to be equivalent [4] to

$$S_G = k_B \ln(\Omega(U)), \quad (2.9)$$

$$S_B = k_B \ln(\epsilon_U \omega(U)). \quad (2.10)$$

where ϵ_U is a constant, that can be easily put to 1 changing the measure system, with dimensions of energy required to make the argument of the logarithm dimensionless.

S_G and S_B are called, respectively, Gibbs (or Hertz) entropy and Boltzmann entropy. Usually the two definitions of entropy (2.9) and (2.10) were considered equivalent for practical purposes, but in recent years some physicians are arguing about this equivalence. In fact in 2013 an experiment [8] claimed having measured negative temperatures (in spite of Callen's third postulate). This is consistent with the use of Boltzmann entropy for a system in which the density of states ω is not an increasing function of energy. So, taking in account the thermodynamic postulate, in an article [2] Jörn Dunkel and Stefan Hilbert stated the two definitions of entropy are not equivalent and, in addition, that only Gibbs entropy is a good entropy function while Boltzmann one not. Indeed, they noted that Gibbs entropy depends on the number of states Ω , that is always an increasing function of the energy and so $T_G = \frac{\partial S_G}{\partial U} > 0$ in every cases and they said the authors of the experiment [8] measured the Boltzmann temperature $T_B = \frac{\partial S_B}{\partial U}$ which depends on T_G and on the thermodynamic heat capacity C , which could be a negative quantity.

¹Where $Tr[(\dots)] = \frac{1}{N!h^{3N}} \int d^{3N}q d^{3N}p(\dots)$ for classical systems

2.1 The Gibbs entropy discussion

The core of the article [2] relies on the fact that, according to the authors, only the Gibbs entropy fulfills some formal thermodynamic properties. Namely, taking into account the differential fundamental relation for a system

$$dS = \left(\frac{\partial S}{\partial U}\right) dU + \left(\frac{\partial S}{\partial V}\right) dV + \left(\frac{\partial S}{\partial N}\right) dN + \left(\frac{\partial S}{\partial X}\right) dX, \quad (2.11)$$

if we consider an adiabatic transformation ($dS = 0$), in which the volume and the number of particles do not change, it is easy to show that for a generic variable X we have

$$T \left(\frac{\partial S}{\partial X}\right) = \left(\frac{\partial S}{\partial U}\right)^{-1} \left(\frac{\partial S}{\partial X}\right) = - \left(\frac{\partial U}{\partial X}\right) = - \left\langle \frac{\partial \mathcal{H}}{\partial X} \right\rangle. \quad (2.12)$$

If we use the Gibbs entropy definition and if we take into account the equation (2.6), indeed we obtain

$$\begin{aligned} T_G \left(\frac{\partial S_G}{\partial X}\right) &= \left(\frac{\partial S_G}{\partial U}\right)^{-1} \left(\frac{\partial S_G}{\partial X}\right) = \\ &= \frac{1}{Tr[\delta(U - \mathcal{H})]} \cdot \frac{\partial Tr[\Theta(U - \mathcal{H})]}{\partial X} = \\ &= -Tr\left[\left(\frac{\partial \mathcal{H}}{\partial X}\right) \frac{\delta(U - \mathcal{H})}{\omega}\right] = -Tr\left[\rho \frac{\partial \mathcal{H}}{\partial X}\right] = - \left\langle \frac{\partial \mathcal{H}}{\partial X} \right\rangle \end{aligned} \quad (2.13)$$

and, clearly, if we add the Boltzmann entropy definition in the former equation, we do not obtain the microcanonical density distribution after the differentiation.

Our first concern is to test whether the former calculations can be generalized considering a similar classical system but with also another conserved dynamic quantity, such as the linear momentum \vec{P} which we use in the following calculations. In this system the Hamiltonian is $\mathcal{H}_0 = \mathcal{H}_0(\vec{q}, \vec{p})$, and \vec{P} is a function of (\vec{q}, \vec{p}) and we want that it corresponds to \vec{P} , the extensive thermodynamic parameter from which depends on the entropy function, exactly as the Hamiltonian \mathcal{H}_0 corresponds to the total energy U . So now we have to build a new statistical ensemble where the density distribution has to be constant over a manifold where either $U = \mathcal{H}_0(\vec{q}, \vec{p})$ and $\vec{P} = \vec{P}(\vec{q}, \vec{p})$:

$$\rho(U, \vec{P}) = C \delta(U - \mathcal{H}_0) \delta^3(\vec{P} - \vec{P}). \quad (2.14)$$

But because \mathcal{H}_0 and \vec{P} are both functions depending on (\vec{q}, \vec{p}) , we can find some new coordinates (\vec{q}', \vec{p}') respect to which the Hamiltonian is $\mathcal{H} = \mathcal{H}(\vec{q}', \vec{p}')$ and we choose the transformation doing that the dynamical quantity $\vec{P} = \vec{p}'_i$, so the Hamiltonian depends directly on \vec{P} , that is

$$\mathcal{H} = \mathcal{H}(q'_1 \cdots q'_N, p'_1 \cdots p'_N) = \mathcal{H}(q'_1 \cdots q'_N, p'_1 \cdots p'_{N-1}, \vec{P}). \quad (2.15)$$

So we can write the density distribution as

$$\rho(U, \vec{P}) = C \delta(U - \mathcal{H}) \delta^3(\vec{P} - \vec{P}). \quad (2.16)$$

Taking this in account, following the same ideas of the microcanonical ensemble, we can easily define also the number of states and the density of states as:

$$\omega(U, \vec{P}) = Tr[\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})] \quad (2.17)$$

$$\Omega(U, \vec{P}) = Tr[\Theta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})]. \quad (2.18)$$

and so clearly we always have got $\omega = \frac{\partial\Omega}{\partial U}$.

Now testing the same thermodynamic property, explained in equation (2.12), we find that:

$$\vec{v} \equiv T_G \left(\frac{\partial S_G}{\partial \vec{P}} \right) = \left(\frac{\partial S_G}{\partial U} \right)^{-1} \left(\frac{\partial S_G}{\partial \vec{P}} \right) = \quad (2.19)$$

$$\frac{Tr[\Theta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})]}{Tr[\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})]} \cdot \frac{Tr[\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})]}{Tr[\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})]}, \quad (2.20)$$

now using the Dirac's Delta we have that $\mathcal{H}(\vec{q}, \vec{p}, \vec{P}) = \mathcal{H}(\vec{q}, \vec{p}, \vec{P})$, and remembering the derivation property of Dirac's Delta², that can be used because the Heaviside function is a good test function near the point that we are interested in; we can write:

$$\vec{v} = \frac{Tr[-\frac{\partial \mathcal{H}}{\partial \vec{P}} \delta(U - \mathcal{H})]}{Tr[\delta(U - \mathcal{H})]} = - \left\langle \frac{\partial \mathcal{H}}{\partial \vec{P}} \right\rangle, \quad (2.21)$$

that confirms the rightness of the Gibbs entropy for this extended ensemble.

2.2 Boltzmann entropy discussion

In reply to the article [2] other two physicists Daan Frenkel and Patrick B. Warren wrote an article [5] in 2014 in which they demonstrate some inconsistencies of Gibbs entropy and moreover they showed in the thermodynamic limit that also the Boltzmann entropy satisfies thermodynamic requests. Thus only the Boltzmann entropy is a good entropy function and, in addition, negative temperatures are inevitable in systems in which their density of states is not an increasing function of the energy; indeed the system of the experiment is one with a bounded energy spectrum.

The core of their reasoning is that thermodynamics studies systems with an huge number of bodies so also the canonical ensemble is a good choice in order to study them, in fact they show that the Boltzmann entropy satisfies criterion in ref. [2]: $-T(\frac{\partial S}{\partial X}) = \langle \frac{\partial \mathcal{H}}{\partial X} \rangle$, using a method which shows the equivalence between the microcanonical and the canonical ensemble averages $\langle (\dots) \rangle_U = \langle (\dots) \rangle_T$. We are going to show, in an similar way to ref. [5], that the Boltzmann entropy fulfills thermodynamic requirements also in systems with more constraints. We study a system with linear momentum conserved, but the demonstration for systems with similar constraint is quite similar.

The canonical ensemble is built considering an other system, in thermal equilibrium with

² $\int dx \phi(x) \frac{d\delta(x-x_0)}{dx} = - \int dx \frac{d\phi(x)}{dx} \delta(x-x_0)$, where $\phi(x)$ is a test function

the one we are studying, which works as thermal reservoir. We analyze a system 1 smaller than a system 2 such that $U_2 \gg U_1$, with total energy U , so the probability to find a state of 1 is proportional to the number of states the second system allowed: $\Omega_2(U - U_1, \vec{P}) = Tr[\Theta(U - U_1)\delta^3(\vec{P} - \vec{\mathcal{P}})]$, that is:

$$\rho(q_1, p_1) \propto \Omega(U - U_1). \quad (2.22)$$

Because we think that all information is contained around the value of U_1 and because $U \gg U_1$ we can expand around U_1 and so we have:

$$\Omega(U - U_1) \approx e^{\frac{U_1}{k_B T}}, \quad (2.23)$$

and because $U_1 = \mathcal{H}(q_1, p_1)$ we can assume that the normalized canonical density is:

$$\rho_{can} = \frac{e^{-\beta \mathcal{H}} \delta^3(\vec{P} - \vec{\mathcal{P}})}{Tr[e^{-\beta \mathcal{H}} \delta^3(\vec{P} - \vec{\mathcal{P}})]}. \quad (2.24)$$

Therefore we can define the Helmholtz free energy $F = U - TS$ as:

$$e^{-\beta F} = Tr[e^{-\beta \mathcal{H}} \delta^3(\vec{P} - \vec{\mathcal{P}})]. \quad (2.25)$$

Now we show that in the canonical ensemble the thermodynamic property

$$\left(\frac{\partial F}{\partial \vec{P}} \right)_T = \left(\frac{\partial \mathcal{H}}{\partial \vec{P}} \right)_T \quad (2.26)$$

is true: in fact differentiating (2.25) we obtain

$$-\beta e^{-\beta F} \frac{\partial F}{\partial \vec{P}} = Tr[e^{-\beta \mathcal{H}} \delta^3(\vec{P} - \vec{\mathcal{P}})], \quad (2.27)$$

and because $e^{-\beta \mathcal{H}}$ is usually a good test function we have:

$$-\beta e^{-\beta F} \frac{\partial F}{\partial \vec{P}} = Tr[-\beta e^{-\beta \mathcal{H}} \frac{\partial \mathcal{H}'}{\partial \vec{P}}], \quad (2.28)$$

and dividing by (2.25), we show (2.26) is true.

So the Boltzmann entropy satisfies thermodynamic requests also in an ensemble with both the energy and the linear momentum conserved.

We want to recover the equation (2.12), so we have first to demonstrate the equivalence between the canonical ensemble and the ensemble in which are conserved either energy and an other dynamical constant (\vec{P}); where the ensemble average is (2.16).

Now with these in hand we can write

$$\langle (\dots) \rangle_{T, \vec{P}} \equiv Tr[(\dots) e^{-\beta \mathcal{H}} \delta(\vec{P} - \vec{\mathcal{P}})] = \int_0^\infty dE e^{-\beta E} (\dots) Tr[\delta(U - \mathcal{H}) \delta(\vec{P} - \vec{\mathcal{P}})] \quad (2.29)$$

where the two Dirac's deltas select only the states allowed by the constraints.

Bearing in mind the Boltzmann entropy definition (inverted)

$$Tr[\delta(E - \mathcal{H}) \delta(\vec{P} - \vec{\mathcal{P}})] = e^{\frac{S_B}{k_B}}, \quad (2.30)$$

we can add this definition in equation (2.29), and so also using the equation (2.25)

$$\langle\langle \dots \rangle\rangle_{T, \vec{P}} e^{-\beta F} = \int_0^\infty dE e^{-\beta E + \frac{S_B}{k}} \langle \dots \rangle_{E, \vec{P}}. \quad (2.31)$$

At this point it is important to stress that only the Boltzmann entropy fulfills the mathematical requirements to make passage between the two former equations; because the inverted Gibbs entropy definition: $\Omega = \text{Tr}[\Theta(U - \mathcal{H})\delta^{(3)}(\vec{P} - \vec{\mathcal{P}})] = e^{\frac{S_G}{k_B}}$ can not be inserted in the equation (2.29).

Now doing the Laplace transformation to (2.31), with (E, β) the transform variables; and because we are supposing to be in the thermodynamics limit, it is possible to evaluate the integral using the saddle-point method, so the integral value coincide with the value of the integrand's maximum, that is when $E = U$; with this method we obtain two conditions:

$$F = U - TS_B \quad \text{and} \quad \frac{1}{T} = \frac{\partial S_B}{\partial U} \quad (2.32)$$

where the first is the thermodynamic definition of free energy and the second is the maximum condition for the integrand. Thus the saddle-point method has converted the Laplace transformation in a Legendre transformation because now we are passed in the free energy representation.

Now using these two conditions in the equation (2.31) we find $\langle\langle \dots \rangle\rangle_{T, \vec{P}} = \langle\langle \dots \rangle\rangle_{U, \vec{P}}$ that demonstrate the ensembles equivalence also if density of states dependent on both energy and one (or more) other dynamic quantity in the thermodynamic limit.

The thermodynamic connection between the derivatives of F and S can be obtained differentiating respect to \vec{P} the equation $F = U - TS$

$$\left(\frac{\partial F}{\partial \vec{P}}\right)_T = \frac{\partial U}{\partial \vec{P}} - T \frac{\partial S}{\partial \vec{P}} \frac{\partial U}{\partial \vec{P}} - T \left(\frac{\partial S}{\partial \vec{P}}\right)_U \quad (2.33)$$

and so

$$\left(\frac{\partial F}{\partial \vec{P}}\right)_T = -T \left(\frac{\partial S}{\partial \vec{P}}\right)_U, \quad (2.34)$$

remembering equivalence between ensembles and the equation (2.26) we finally recover the consistency criterion of [2]:

$$-T \left(\frac{\partial S}{\partial \vec{P}}\right)_U = \left\langle \frac{\partial \mathcal{H}}{\partial \vec{P}} \right\rangle_U. \quad (2.35)$$

2.3 Symmetries and entropies

Formally both entropies are good entropy functions to study classical systems, but already at this point we can support the Boltzmann entropy instead of the Gibbs entropy: since the former treats symmetrically all the dynamical parameters selecting them with Dirac's Deltas, while the latter gives to the energy a peculiar role picking the possible states using the Heaviside function for the energy and Dirac's Deltas for the others. Indeed there is not any favorite role among the dynamic fundamental symmetries, as also stated by Callen himself [1][3], and the Boltzmann entropy reflects this idea.

In classical systems, the single particle energy has not an upper bound, so if we add energy to the system the number of allowed states will always increase and so $T = \frac{\partial S}{\partial U} > 0$. But in some unusual quantum systems single particle energy is bounded from above, so if we put in a lot of energy to a system of this kind, all particles will have to populate the state of maximum energy; but, doing this, the number of microstates of the system will decrease so at a certain point $T = \frac{\partial S}{\partial U} < 0$.

Taking this in account we could affirm that the Callen's third postulate has to be modified, for these kind of quantum systems.

2.4 Carnot cycles with efficiency larger than 1

We have brought a discussion in favor of the Boltzmann entropy, which allows negative temperatures. The existence of them rises several questions, but one of the most important among them is the possibility of creating engines performing Carnot cycles with efficiency larger than one.

We can imagine a Carnot engine working between two heat reservoirs: the reservoir 1 operates at temperature $T_1 > 0$ while the reservoir 2 operates at temperature $T_2 < 0$. Moreover we assume that heat flowing out of reservoir 1 has a positive sign while heat flowing out of 2 has a negative sign.

The first law of thermodynamics states the work W done by the cycle has to be equal to the heat $Q_1 - Q_2$, and usually the efficiency η is defined as

$$\eta = -\frac{W}{Q_1} \quad (2.36)$$

because it is expected that the engine absorbs heat only from the reservoir 1. Assuming an isentropic cycle (maximum possible W), the total entropy variation has to be equal to zero, and because it is an extensive function we can consider separately the entropy variations:

$$\Delta S = \Delta S_1 + \Delta S_2 = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad (2.37)$$

and so

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \quad (2.38)$$

But because T_1 and Q_1 are positive and T_2 is negative, then the sign of Q_2 has to be negative, that means the heat flows out the reservoir 2, so the engine absorbs heat also from the reservoir 2. So as consequence of (2.38) we have:

$$\eta = 1 + \frac{|Q_2|}{Q_1} = 1 - \frac{T_2}{T_1} > 1. \quad (2.39)$$

Thought, if we do not define the efficiency with the definition (2.36), but as the ratio of the work done to the heat extracted from both reservoirs, that is more logical because we are interested in how much work we can obtain from a given quantity of heat, and in effect the engine take heat from both the reservoirs, we can define the efficiency as

$$\eta = -\frac{W}{Q_1 + |Q_2|}; \quad (2.40)$$

therefore with this definition efficiency cannot be larger than one saving impossibility of the perpetual motion also with negative temperatures.

Chapter 3

Study of some classical systems with not only the energy conserved

After having talked in general about systems with more than the energy constraint, we are going to apply, in a practical way, the methods explained before to systems the linear and/or the angular momentum conserved. Our aim is to show the calculations and the ideas explained before can be really applied, at least to some simple systems. Though, in these cases, we have to underline that the Boltzmann entropy and the Gibbs entropy perfectly overlap in the thermodynamic limit; but this is due to the Hamiltonians of the systems which do not have an upper bound. Hence, the densities of states are increasing functions of the energy and in these cases both entropies are equals in the thermodynamic limit. In order to make these calculations we inspired to two articles written by A.Børns [7][6].

3.1 System with the linear momentum conserved

Starting from an Hamiltonian of ideal gas $\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$, contained in a box of volume V , with the bond of the linear momentum conserved, $\vec{P} = \sum_{i=1}^N \vec{p}_i$; the density of states, the number of states and the microcanonical statistical distribution, as explained in chapter 2, become:

$$\omega(U, \vec{P}, V, N) = Tr[\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})], \quad (3.1)$$

$$\Omega(U, \vec{P}, V, N) = Tr[\Theta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})], \quad (3.2)$$

$$\rho(U, \vec{P}, V, N) = \frac{\delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P})}{\omega(U, \vec{P}, V, N)}. \quad (3.3)$$

To calculate the entropy functions we can start from equation (3.1) that we can write making explicit the integral

$$\omega(U, \vec{P}, V, N) = \frac{1}{N!h^{3N}} \int dq^{3N} dp^{3N} \delta(U - \mathcal{H})\delta^3(\vec{P} - \vec{P}), \quad (3.4)$$

now using the canonical transformation with determinant of Jacobian equals to 1

$$\begin{aligned}
\vec{p}'_1 &= \frac{\vec{p}_1 - \vec{p}_2}{\sqrt{2}} \\
&\vdots \\
\vec{p}'_j &= \frac{(\vec{p}_1 + \vec{p}_2 + \dots + \vec{p}_j - j\vec{p}_{j+1})}{\sqrt{j(j+1)}} \\
&\vdots \\
\vec{p}'_N &= \frac{\sum_{i=1}^N \vec{p}_i}{\sqrt{N}}
\end{aligned} \tag{3.5}$$

the Hamiltonian become

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{\vec{p}'_i{}^2}{2m} + \frac{p_N^2}{2m}, \tag{3.6}$$

and so the integral (3.4) becomes

$$\omega(U, \vec{P}, V, N) = \frac{V^N}{N!h^{3N}} \int dp'^{3N} \delta(U - \mathcal{H}) \delta^3(\vec{P} - \sqrt{N}\vec{p}'_N), \tag{3.7}$$

then using the Dirac's delta properties

$$\omega(U, \vec{P}, V, N) = \frac{V^N}{N^{3/2}N!h^{3N}} \int dp'^{3N-3} \delta\left(U - \sum_{i=1}^{N-1} \frac{\vec{p}'_i{}^2}{2m} - \frac{\vec{P}^2}{2Nm}\right), \tag{3.8}$$

now changing coordinates with this canonical transformation, that does not change the Hamiltonian form

$$\vec{p}''_i = \sqrt{\frac{\vec{p}'_i{}^2}{2m}} \tag{3.9}$$

and using properties of Dirac's delta with diffeomorphisms and taking in account of the integral domain, it becomes

$$\begin{aligned}
\omega(U, \vec{P}, V, N) &= \frac{V^N}{N^{3/2}N!h^{3N}} (2m)^{\frac{3(N-1)}{2}} \int_{\mathcal{H}=U} (dp'')^{3N-3} \frac{1}{2 \left(U - \frac{\vec{P}^2}{2Nm}\right)^{\frac{1}{2}}} \\
&\quad \cdot \delta\left(\left(U - \frac{\vec{P}^2}{2Nm}\right)^{\frac{1}{2}} - \sqrt{\sum_{i=1}^{N-1} (p'')_i^2}\right)
\end{aligned} \tag{3.10}$$

that is the surface of an hypersphere in $3N - 3$ dimensions because of (2.5), in fact Ω is clearly the volume of an hypersphere

$$\Omega(U, \vec{P}, V, N) = \frac{V^N}{N!h^{3N}} \int dp'^{3N} \Theta(U - \mathcal{H}). \tag{3.11}$$

So finally ω and Ω are:

$$\omega(U, \vec{P}, V, N) = \frac{V^N}{N^{3/2} N! h^{3N}} \frac{(2m\pi)^{\frac{3(N-1)}{2}}}{\Gamma(\frac{3}{2}(N-1))} \left(U - \frac{\vec{P}^2}{2Nm} \right)^{\frac{3N}{2} - \frac{5}{2}}, \quad (3.12)$$

$$\Omega(U, \vec{P}, V, N) = \frac{V^N}{N^{3/2} N! h^{3N}} \frac{(2m\pi)^{\frac{3(N-1)}{2}}}{\Gamma(\frac{3N}{2} - \frac{1}{2})} \left(U - \frac{\vec{P}^2}{2Nm} \right)^{\frac{3(N-1)}{2}}. \quad (3.13)$$

So the entropies (putting $k_B = 1$) are:

$$\begin{aligned} S_B(U, \vec{P}, V, N) &= \ln[\omega(U, \vec{P}, V, N) \epsilon_U \epsilon_P^3] = \frac{3}{2} N \ln \left[\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - \frac{5}{2} \ln \left(\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \epsilon_U \epsilon_P^3 \right) \\ &+ O(\ln(N)), \end{aligned} \quad (3.14)$$

$$\begin{aligned} S_G(U, \vec{P}, V, N) &= \ln[\Omega(U, \vec{P}, V, N)] = \frac{3}{2} N \ln \left[\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - \frac{3}{2} \ln \left(\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \epsilon_U \epsilon_P^3 \right) \\ &+ O(\ln(N)); \end{aligned} \quad (3.15)$$

and in the thermodynamics limit ($N \rightarrow \infty$) the addenda $-\frac{3}{2} \ln \left(\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \right)$ and $-\frac{5}{2} \ln \left(\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \right)$ are negligible, so the entropies are identical.

3.2 System with angular momentum conserved

If the Hamiltonian is the same of the former section but we add the conservation of the angular momentum (instead of the linear one) around the z-axis, to make easy calculations we are bearing in mind a cylindrical box of volume $V = h\pi R^2$ filled with an ideal gas rotating around its axis, represented by the bond $\mathcal{M}_z = \sum_{i=1}^N m_{zi}$ ($m_z = xp_y - yp_x$). The density of states, the number of states and the microcanonical statistical distribution become:

$$\omega(U, M_z, V, N) = Tr[\delta(U - \mathcal{H})\delta(M_z - \mathcal{M}_z)], \quad (3.16)$$

$$\Omega(U, M_z, V, N) = Tr[\theta(U - \mathcal{H})\delta(M_z - \mathcal{M}_z)], \quad (3.17)$$

$$\rho(U, M_z, V, N) = \frac{\delta(U - \mathcal{H})\delta(M_z - \mathcal{M}_z)}{\omega(U, M_z, V, N)}; \quad (3.18)$$

using cylindrical coordinates the Hamiltonian becomes $\mathcal{H}_c = \sum_{i=1}^N \frac{1}{2m} (p_r^2 + p_z^2 + \frac{p_\phi^2}{r^2})$ and using (3.5) only on the ϕ -coordinates the Hamiltonian becomes:

$$\mathcal{H}'_c = \sum_{i=1}^N \frac{1}{2m} p_{ri}^2 + \sum_{i=1}^N \frac{1}{2m} p_{zi}^2 + \sum_{i=1}^{N-1} \frac{1}{2mr^2} p_{\phi i}^2 + \frac{p_{\phi N}^2}{2mr^2}, \quad (3.19)$$

and after some mathematical passages [7] we obtain that the density is:

$$\omega(U, M_z, V, N) = \frac{V^N}{N! \sqrt{\frac{N}{2}} Rh^{3N}} \int dp_r^N dp_\phi^{N-1} dp_z^N \delta(U - H'_c), \quad (3.20)$$

and remembering (2.5)

$$\omega(U, M_z, V, N) = \frac{3V^N}{N! \sqrt{2N} Rh^{3N}} \frac{(2m\pi)^{\frac{3N-2}{2}}}{\Gamma(\frac{3N-2}{2})} \left(U - \frac{M_z^2}{2NI} \right)^{\frac{3N}{2}-2}, \quad (3.21)$$

$$\Omega(U, M_z, V, N) = \frac{V^N}{N! \sqrt{\frac{N}{2}} Rh^{3N}} \frac{(2m\pi)^{\frac{3N-2}{2}}}{\Gamma(\frac{3N-2}{2} + 1)} \left(U - \frac{M_z^2}{2NI} \right)^{\frac{3N}{2}-1}. \quad (3.22)$$

And the entropies are:

$$\begin{aligned} S_B(U, M_z, V, N) &= \frac{3}{2} N \ln \left[\frac{U - \frac{M_z^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - 2 \ln \left(\frac{U - \frac{M_z^2}{2Nm}}{N} \right) \\ &+ O(\ln(N)), \end{aligned} \quad (3.23)$$

$$\begin{aligned} S_G(U, M_z, V, N) &= \frac{3}{2} N \ln \left[\frac{U - \frac{M_z^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - \ln \left(\frac{U - \frac{M_z^2}{2Nm}}{N} \right) \\ &+ O(\ln(N)) \end{aligned} \quad (3.24)$$

and in the thermodynamics limit ($N \rightarrow \infty$) they are identical.

3.3 System with both linear and angular momentum conserved

Finally if we adds both the bonds thinking to the previous system that is moving along and rotating around its z-axis, hypothesis that are needed to make possible calculations, the density of states, the number of states and the microcanonical statistical distribution

become:

$$\omega(U, P_z, M_z, V, N) = Tr[\delta(U - \mathcal{H})\delta(P_z - \mathcal{P}_z)\delta(M_z - \mathcal{M}_z)], \quad (3.25)$$

$$\Omega(U, P_z, M_z, V, N) = Tr[\theta(U - \mathcal{H})\delta(P_z - \mathcal{P}_z)\delta(M_z - \mathcal{M}_z)], \quad (3.26)$$

$$\rho(U, P_z, M_z, V, N) = \frac{\delta(U - \mathcal{H})\delta(P_z - \mathcal{P}_z)\delta(M_z - \mathcal{M}_z)}{\omega(U, P_z, M_z, V, N)}. \quad (3.27)$$

Using the cylindrical coordinates and applying the (3.5) only on p_ϕ and p_z the Hamiltonian becomes:

$$\mathcal{H}'_c = \sum_{i=1}^N \frac{1}{2m} p_{ri}^2 + \sum_{i=1}^{N-1} \frac{1}{2m} p_{zi}'^2 + \sum_{i=1}^{N-1} \frac{1}{2mr^2} p_{\phi i}'^2 + \frac{p_{zN}'^2}{2m} + \frac{p_{\phi N}'^2}{2mr^2} \quad (3.28)$$

so the density becomes after some mathematical calculations:

$$\omega(U, P_z, M_z, V, N) = \frac{V^N}{N! \frac{N}{\sqrt{2}} Rh^{3N}} \int dp_r^N dp_\phi'^{N-1} dp_z'^{N-1} \delta(U - \mathcal{H}'_c) \quad (3.29)$$

and therefore

$$\omega(U, P_z, M_z, V, N) = \frac{3V^N}{\sqrt{2} N! N R h^{3N}} \frac{(2m\pi)^{\frac{3N-2}{2}}}{\Gamma(\frac{3N-2}{2})} \left(U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2NI} \right)^{\frac{3N}{2}-2}, \quad (3.30)$$

$$\Omega(U, P_z, M_z, V, N) = \frac{V^N}{\frac{N}{\sqrt{2}} N! R h^{3N}} \frac{(2m\pi)^{\frac{3N-2}{2}}}{\Gamma(\frac{3N-2}{2} + 1)} \left(U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2NI} \right)^{\frac{3N}{2}-1}. \quad (3.31)$$

And the entropies are:

$$\begin{aligned} S_B(U, P_z, M_z, V, N) &= \frac{3}{2} N \ln \left[\frac{U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - 2 \ln \left(\frac{U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2Nm}}{N} \right) \\ &+ O(\ln(N)), \end{aligned} \quad (3.32)$$

$$\begin{aligned} S_G(U, P_z, M_z, V, N) &= \frac{3}{2} N \ln \left[\frac{U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2Nm}}{N} \right] + \\ &+ N \ln \left(\frac{V}{N} \right) + \frac{5N}{2} + \frac{3N}{2} \ln \left(\frac{2m\pi}{h^2} \right) - \ln \left(\frac{U - \frac{P_z^2}{2Nm} - \frac{M_z^2}{2Nm}}{N} \right) \\ &+ O(\ln(N)); \end{aligned} \quad (3.33)$$

and in the thermodynamics limit ($N \rightarrow \infty$) they are identical.

3.4 Check of the thermodynamic requirements for a sistem with the linear momentum conserved

Taking into account the system with linear momentum conserved and the equations (3.15)(3.16) it is trivial understood $S_B = S_G \equiv S$ in this case (it could be said the same for the other systems discussed), so we verify below that thermodynamic requirements are satisfied by this system. In fact, making explicit calculations, entropy can be written

$$S(U, \vec{P}, V, N) = N \ln \left[A \left(\frac{U - \frac{\vec{P}^2}{2Nm}}{N} \right)^{\frac{3}{2}} \right] \quad (3.34)$$

where $A(V, N)$ contains all addictions from V and N , while the Hamiltonian (expressed in favourable coordinates) is:

$$\mathcal{H} = \sum_{i=1}^{N-1} \frac{\vec{p}_i^2}{2m} + \frac{\vec{P}^2}{2Nm} \quad (3.35)$$

and calculations in section 2.1 lead to:

$$T \frac{\partial S}{\partial \vec{P}} = \left(\frac{\partial S}{\partial U} \right)^{-1} \frac{\partial S}{\partial \vec{P}} = - \left\langle \frac{\partial \mathcal{H}}{\partial \vec{P}} \right\rangle. \quad (3.36)$$

The analysis in section 2.2 follows in a bit more complicated way: doing the Legendre transformation to switch to the representation of free energy. Inverting (3.34):

$$U(S, \vec{P}, V, N) = N \left(\frac{e^{\frac{S}{N}}}{A} \right)^{\frac{2}{3}} + \frac{\vec{P}^2}{2Nm} \quad (3.37)$$

temperature will be:

$$T(S, \vec{P}, V, N) = \frac{\partial U}{\partial S} = \frac{2}{3} \left(\frac{e^{\frac{S}{N}}}{A} \right)^{\frac{2}{3}} \quad (3.38)$$

Inverting (3.38)

$$e^{\frac{S}{N}} = A \left(\frac{3}{2} T \right)^{\frac{3}{2}} \quad (3.39)$$

and replacing in (3.37) and (3.34)

$$U(T, \vec{P}, V, N) = \frac{3}{2} NT + \frac{\vec{P}^2}{2Nm} \quad (3.40)$$

$$S(T, \vec{P}, V, N) = N \ln [A \left(\frac{3}{2} T \right)^{\frac{3}{2}}] \quad (3.41)$$

and so the free energy will be:

$$F(T, \vec{P}, V, N) = U - TS = \frac{3}{2} NT + \frac{\vec{P}^2}{2Nm} - NT \ln [A \left(\frac{3}{2} T \right)^{\frac{3}{2}}], \quad (3.42)$$

therefore it is easy to verify that the model confirms the theory, in fact because either U and S depend on \vec{P} therefore:

$$\left(\frac{\partial F}{\partial \vec{P}}\right)_T = \frac{\partial U}{\partial \vec{P}} - T \frac{\partial S}{\partial U} \frac{\partial U}{\partial \vec{P}} - T \left(\frac{\partial S}{\partial \vec{P}}\right)_U, \quad (3.43)$$

and so we can find the Dunkel and Hilbert's consistency criterion, considering the previous calculations and the ensemble equivalence:

$$\left(\frac{\partial F}{\partial \vec{P}}\right)_T = \left\langle \frac{\partial \mathcal{H}}{\partial \vec{P}} \right\rangle_T = -T \left(\frac{\partial S}{\partial \vec{P}}\right)_U = \left\langle \frac{\partial \mathcal{H}}{\partial \vec{P}} \right\rangle_U = \frac{\vec{P}}{Nm}. \quad (3.44)$$

Chapter 4

Conclusions

Callen's axiomatic description of thermodynamics has the existence of fundamental symmetries at its basis. Since every macroscopic parameter is connected to a symmetry of the microscopic world, and each parameter has to be an independent variable of the entropy; which is the function containing all the informations about the equilibrium system. Furthermore, through the derivatives of the entropy function we can obtain informations about the intensive parameters of the system, that can be easily measured in an experiment and that characterize the equilibrium states of a system.

The temperature is one of them, it is related to the energy extensive parameter which derives from the symmetry under time-translation. In classic and Callen's thermodynamics, the temperature is the only parameter which is defined positive although the symmetry under time-translation has not any favorite role in the thermodynamics construction. Bearing this in mind, we have analyzed the behavior of the two different statistical mechanic definitions of entropy: the Gibbs entropy and the Boltzmann entropy, in systems with not only the energy conserved, but also with the linear and the angular momentum conserved. Even if both entropies provide formally a self-consistent thermodynamics, the Boltzmann one has a more symmetric construction. In fact, it treats alike all the thermodynamic parameters, coherently with the Callen's formulation of thermodynamics, while the Gibbs one not.

This difference is very important in some unusual quantum systems in which the density of microscopic states is not a monotonic increasing function of the energy; indeed in these systems the Boltzmann entropy provide for negative temperatures while the Gibbs one not.

So the possibility of negative temperatures could open some very interesting scenarios in Physics but at the cost of slightly modify the Callen's third postulate.

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