On the definition of temperature using time–averages.

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ABSTRACT

This paper is a natural continuation of a previous one by the author, which was concerned with the foundations of statistical thermodynamics far from equilibrium. One of the problems left open in that paper was the correct definition of temperature. In the literature, temperature is in general defined through the mean kinetic energy of the particles of a given system. In this paper, instead, temperature is defined *à la* Carathéodory, the system being coupled to a heat bath, and temperature being singled out as the "right" integrating factor of the exchanged heat. As a byproduct, the "right" expression for the entropy is also obtained. In particular, in the case of a q-distribution the entropy turns out to be that of Tsallis.

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1 Introduction

The problem of defining temperature in non–equilibrium situations is a quite delicate one (see for example ref. (1)). For systems constituted of particles, it is usually assumed that temperature should be defined, up to a constant factor, as the mean kinetic energy. On the other hand, one should take into account that the notion of temperature originates from thermodynamics, where the notion of "the particles of the system" has no sense at all. In thermodynamics (see refs. (2), (3)) temperature is defined using both the second and the zeroth principle. On the one hand, the second principle (e.g. in the Carathéodory formulation) insures that there exists an integrating factor of the exchanged heat. On the other hand, since actually there exist infinitely many such integrating factors, temperature is singled out among them by the zeroth principle, namely by the requirement that if the system is put in thermal contact with another one, at equilibrium the integrating factors of the two systems and that of the compound one should have the same value.

Thus, when the Gibbs distribution $\exp(-\beta H)/Z(\beta)$ is used in statistical mechanics, it is first checked that β^{-1} is an integrating factor of the exchanged heat, but its identification with temperature requires some more work. One has to put the system in contact with another one and to assume that (at equilibrium) the total system too is described by a Gibbs distribution having as Hamiltonian the sum of the Hamiltonians of the two components. From this, with some further considerations, one then shows that the temperature coincides with β^{-1} (see for example (4), chapter three.).

The aim of the present paper is to implement the analogous procedure when the averaging is performed through time–averages rather than through phase–averages with the Gibbs' measure. The way in which the time–averages should be dealt with was already discussed in reference (5), where it was shown that the exchanged heath has an integrating factor, but the problem of selecting the good one through the zeroth principle was left open. The present paper is thus a strict continuation of that one.

In Section 2 the general setup for dealing with time–averages, and the main results of paper (5) are recalled. In Section 3 it will be recalled how temperature is introduced in the standard thermodynamic way; moreover the definition of "thermal equilibrium" between two systems in terms of time-averages will be introduced, and it will be shown that temperature actually exists. Section 4 is devoted to the study of the thermal contact between a generic system and a thermal bath (a notion that will also be defined), while the thermodynamics in the case of the Tsallis q–distribution will be developed in Section 5. Section 6 is devoted to clarifying another point that was left open in paper (5), namely the identification of the quan-

tity α introduced there, which is shown to be strictly related to free energy. This result is also used for discussing the identification of temperature in the case of the Tsallis q–distribution. Finally, the conclusions follow in Section 7.

2 Time–averages

Usually, nonequilibrium statistical mechanics is dealt with in the following way: one assigns a probability density (ensemble) ρ_0 in phase space and considers the corresponding evolved ensemble ρ_t; then this ensemble is used for computing the expectation for any dynamical variable (real function on phase space) A. However, as particularly emphasizes by Von Neumann and Einstein, the quantities of interest are not the dynamical variables themselves, but rather the corresponding time–averages up to any given time, and their expectations with respect to the assigned ensemble. We recall now how the procedure for dealing with such expectations of time–averages of dynamical variables was dealt with in ref. (5).

For a system with phase space $\mathcal{M}$, suppose a sequence $\{x_n\}$, $x_n \in \mathcal{M}$, is given, depending parametrically on its first element x_0. As a particular case, one can think of the orbit generated by the iteration of a map, for example the time–Δt map induced by the flow of an autonomous Hamiltonian system. Suppose we are interested in computing time–averages of a dynamical variable $A(x)$ (a real function on $\mathcal{M}$)

$$\bar{A}(x_0) \stackrel{\text{def}}{=} \frac{1}{N} \sum_{n=1}^{N} A(x_n) \qquad \text{for} \quad N \gg 1 \ ,$$

the number N playing the role of the "final" time, thought of as a fixed parameter. One can divide the space $\mathcal{M}$ into a large number K of disjoint cells $\mathcal{Z}_j$ (such that $\mathcal{M} = \cup \mathcal{Z}_j$), and one has then

$$\bar{A}(x_0) \simeq \sum_{j=1}^{K} A_j \frac{n_j}{N} \ ,$$

where A_j is the value of A at a point $x \in \mathcal{Z}_j$, and n_j is the number of times the sequence $\{x_n\}$ visits $\mathcal{Z}_j$. It is clear that n_j depends on x_0 so that, if a certain probability distribution is assigned for the initial data x_0, correspondingly n_j turns out to be a random variable with a certain distribution function, which will depend both on the dynamics (i.e. the map) and on the distribution of the initial data. So one can speak in general of the "*a priori probability* P that the cell $\mathcal{Z}_j$ will be visited a

number of times $n_j = n$": [1]

$$P(n_j = n) = f_j(n) \ . \tag{1}$$

For the sake of simplicity of the exposition, in paper (5) the following hypothesis was introduced:

Hypotesis 1 *The quantities n_j are independent random variables, conditioned by $\sum n_j = N$.*

This however is not at all necessary, and the computations could have been performed without it, as will be shown below.

From the fact that the occupation numbers n_j are random variables, there follows that also the time–average $\bar{A}(x_0)$ itself is a random variable, so that it is meaningful to consider its expectation. Denoting by $< \cdot >$ expectation with respect to the a priori distribution, one has then

$$< \bar{A} >= \frac{1}{N} \sum_{j=1}^{K} A_j < n_j > \ .$$

Now, in statistical thermodynamics one does not deal directly with the a priori probability, because it is generally assumed that the time–average of a certain macroscopic quantity, typically the energy of the system, has a given value, which should play the role of an independent variable. So we consider the energy of the system, which we denote by ε, and its time–average $\bar{\varepsilon} = \sum_j \varepsilon_j n_j / N$, and we impose on the numbers $n_1, \cdots, n_K$ the condition

$$\frac{1}{N} \sum_{j=1}^{K} \varepsilon_j n_j = U = \text{const} \ .$$

The problem of computing the *a posteriori expectation* $< \bar{A} >_U$ of $\bar{A}$ given U, is solved, in the thermodynamic limit (see reference (5)), by the relation

$$< \bar{A} >_U = -\frac{1}{N} \sum_j A_j \chi_j' \left(\frac{\theta \varepsilon_j}{N} + \alpha \right) \ . \tag{2}$$

where prime denotes derivative, and the function $\chi_j(z)$ is defined through the Laplace transform of the probability distribution function (1) by

$$\exp(\chi_j(z)) \stackrel{\text{def}}{=} \sum_{n=0}^{+\infty} e^{-nz} f_j(n) \ , \tag{3}$$

[1] Notice that in (5) reference was instead made to the corresponding cumulative distribution function $F_j(n) = P(n_j \leq n)$.

while the parameters θ and α are determined by the equations

$$\left\{ \begin{array}{rcl} U & = & -\frac{1}{N}\sum_j \varepsilon_j \chi_j'\Big(\frac{\varepsilon_j\theta}{N}+\alpha\Big) \\ N & = & -\sum_j \chi_j'\Big(\frac{\varepsilon_j\theta}{N}+\alpha\Big)\ . \end{array} \right. \tag{4}$$

In terms of the quantities

$$\bar{\nu}_j \stackrel{\rm def}{=} -\chi_j'\Big(\frac{\varepsilon_j\theta}{N}+\alpha\Big)\ , \tag{5}$$

relations (2) and (4) take the form

$$< \bar{A} >_U = \frac{1}{N}\sum_j A_j\bar{\nu}_j\ , \quad U=\frac{1}{N}\sum_j \varepsilon_j\bar{\nu}_j\ , \quad N=\sum_j \bar{\nu}_j\ , \tag{6}$$

and this shows that $\bar{\nu}_j$ can be interpreted as the mean occupation number of cell $\mathcal{Z}_j$.

In particular if the process of occupation of any cell is a Poisson one, i.e. if the successive visits of a given cell are independent events, then one finds

$$\chi_j(z) = p\exp(-z) - p\ , \tag{7}$$

with a parameter $p>0$. In such a case one easily shows that the system follows a Gibbs statistics. In fact the mean occupation numbers are easily calculated from (5), and turn out to be given by

$$\bar{\nu}_k = N\frac{e^{-\theta\varepsilon_k/N}}{Z(\theta)}\ , \tag{8}$$

where $e^\alpha \stackrel{\rm def}{=} Z(\theta) = \sum_k e^{-\theta\varepsilon_k/N}$ is the usual partition function, so that relations (6) become the usual canonical ones.

Let us now recall how thermodynamics was formulated in reference (5) in terms of time–averages. First of all, following Gibbs and Khinchin (see refs. (4),(6)), one defines the exchanged heat δQ in terms of the work performed by the system. Indeed if one defines the macroscopic work $\delta\mathcal{W}$ performed by the system as $\delta\mathcal{W} =< \partial_\kappa H >_U d\kappa$, i.e. as the expectation of the microscopic work performed when a parameter κ entering the Hamiltonian is changed, then, using the first principle one defines the exchanged heat as $\delta Q \stackrel{\rm def}{=} dU - \delta\mathcal{W}$. It is easily shown (see ref. (5), but also below) that one has

$$\delta Q = \frac{1}{N}\sum_j \varepsilon_j d\bar{\nu}_j\ . \tag{9}$$

This expression shows, recalling (5), that it is convenient to introduce as an independent variable, in place of z, the quantity $\nu_j = -\chi_j'(z)$, and this naturally leads to introducing in place of χ_j its Legendre transform h_j, defined as usual by

$$h_j(\nu_j) = \big(\nu_j z + \chi_j(z)\big)\big|_{\nu_j = -\chi'(z)} \ .$$

Notice that, while $\bar{\nu_j}$ has the meaning of a mean occupation number (conditioned on U), the quantity ν_j just plays the role of a parameter, in the same sense as z does in (3). In particular, the quantities ν_j do not need satisfy any condition related to normalization, or the fixing of an energy value. Now, from the Legendre duality, one has

$$\bar{\nu_j} = -\chi_j'\left(\frac{\theta\varepsilon_j}{N} + \alpha\right) \qquad \Longleftrightarrow \qquad \frac{\theta\varepsilon_j}{N} + \alpha = h_j'(\bar{\nu_j}) \ ,$$

so that, expressing ε_j in terms of h_j' and using $\sum d\bar{\nu_j} = 0$, relation (9) takes the form

$$\delta Q = \frac{1}{\theta}\sum_j h_j'(\bar{\nu_j}) d\bar{\nu_j} = \frac{N}{\theta} d\left(\frac{1}{N}\sum_j h_j(\bar{\nu_j})\right) \ . \tag{10}$$

This shows that the exchanged heat always admits an integrating factor.

The problem left open in reference (5) is that there actually exist infinitely many integrating factors, so that a further requirement is needed in order to single out which one should be identified with the inverse absolute temperature. The aim of this paper is to show that, under suitable hypotheses, θ/N indeed *is* the inverse temperature, and consequently $h = \sum_j h_j(\bar{\nu_j})$ is the thermodynamic entropy.

3 Thermal equilibrium.

As a general fact it is well known that, if the exchanged heat δQ admits an integrating factor θ (i.e. $\theta\delta Q = d\sigma$ for a certain σ), then any function of the form $\theta F(\sigma)$ will be an integrating factor too. The (inverse) temperature β is singled out by the requirement that, if two systems are put in thermal contact, at equilibrium the values of the integrating factors are the same. More precisely, consider systems A and B, with their integrating factors θ_1, θ_2 and related functions σ_1 and σ_2. Put them in thermal contact to form system C, with integrating factor θ_{12} and function σ_{12}. Then one can show (as recalled in the Appendix) that for each of the systems there exists essentially a unique integrating factor, characterized by the property that the values of the three functions β_1, β_2, and β_{12} are equal when A and

B are in mutual equilibrium. By definition, the inverse of this integrating factor is the (absolute) temperature of the system, and the corresponding functions S_1, S_2, S_{12} are the entropies. From the equality of the integrating factors there follows immediately that one also has

$$dS_{12} = dS_1 + dS_2 \ ,$$

i.e., as one usually says, entropy is additive. We want to implement now this thermodynamic approach in order to identify the temperature of our system. So we have to couple our system to another one, define the notion of mutual equilibrium and show that three corresponding integrating factors can be found such that at equilibrium their values are equal.

Consider two systems with phase spaces $\mathcal{M}_1$ and $\mathcal{M}_2$, let $\{\mathcal{Z}_j\}$ and $\{\mathcal{Z}_k\}$ be the corresponding partitions into cells, and $\varepsilon_j^{(1)}$ and $\varepsilon_k^{(2)}$ the corresponding values of the energy. When the systems are isolated, they are supposed to be described as in Section 2. When put in thermal contact, they form a compound system with phase space $\mathcal{M}_{12} = \mathcal{M}_1 \times \mathcal{M}_2$, and $\{\mathcal{Z}_{jk}\} \stackrel{\text{def}}{=} \{\mathcal{Z}_j \times \mathcal{Z}_k\}$ is a partition with corresponding energies $\varepsilon_j^{(1)} + \varepsilon_k^{(2)} + \lambda\varepsilon_{jk}^{int}$; here, the term $\lambda\varepsilon_{jk}^{int}$ corresponds to the interaction due to the thermal contact, which should be thought of as small (one may assume $\lambda \ll 1$). We denote by n_{jk} the numbers of times an orbit $\{(x_n^{(1)}, x_n^{(2)})\}$ in $\mathcal{M}_{12}$ visits the cell $\mathcal{Z}_{jk}$, and correspondingly we denote by n_j and n_k the number of times the corresponding projections $\{x_n^{(1)}\}$, $\{x_n^{(2)}\}$ visit the cell $\mathcal{Z}_j$ and $\mathcal{Z}_k$ respectively. One obviously has the relation [2]

$$n_j = \sum_k n_{jk}$$
$$n_k = \sum_j n_{jk} \ .$$

Concerning the a priori probability distribution for the occupation numbers, this will in general depend not only on the distribution of the initial data in the space $\mathcal{M}_1 \times \mathcal{M}_2$, but also on λ (i.e. on the dynamics). One should however take into account that, if the two systems are at the same temperature, nothing happens when they are put in contact, i.e. the probability distribution for n_j and n_k will not change, or rather will change so little that the changes can be neglected. This in turn implies that the probability distribution on the product phase space cannot be given in

[2] For the sake of notational simplicity, here and in the following we write n_j in place of $n_j^{(1)}$, and n_k in place of $n_k^{(2)}$, with the understanding that index j refers always to system 1 while index k refers to system 2. The same is understood for other objects such as for example $\mathcal{Z}_j$, $\mathcal{Z}_k$.

an arbitrary way, but must have some relation to the case $\lambda = 0$. With this motivation in mind we give the following definition of mutual thermal equilibrium

Definition 1 *Two systems are said to be in* mutual equilibrium *if their a priori probabilities* $f_j^{(1)}(n)$ *and* $f_k^{(2)}(n)$ *do not depend sensibly on* λ *for* $\lambda \simeq 0$.

It can be shown (see the next section) that the notion of thermal equilibrium implies that the mean energies U_1 and U_2 of the two systems cannot be given at will, but (having fixed all external parameters) the value of the energy of any of the two systems fixes the value of the energy of the other one. Thus, in the plane U_1, U_2 there remains defined an *equilibrium curve* which determines the relation that the energies of two systems have to satisfy when they are in mutual equilibrium.

To show that there exist integrating factors which have the same value for the three systems, one needs taking into consideration an apparently obvious relation among the exchanged heats, namely

$$\delta Q_{12} = \delta Q_1 + \delta Q_2 \ ,$$

where δQ_1, δQ_2 and δQ_{12} are the heats exchanged by system 1, system 2 and the compound system respectively. This relation is actually far from trivial, because the single terms δQ_1 and δQ_2 are not a priori the same ones as one would have in the absence of a thermal contact between the systems. The relation is however true when there is a mutual equilibrium, because in such a case one has

$$\begin{aligned}\delta Q_{12} &= \sum_{jk} (\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) d\bar{\nu}_{jk} = \sum_j \varepsilon_j^{(1)} \sum_k d\bar{\nu}_{jk} + \sum_k \varepsilon_k^{(2)} \sum_j d\bar{\nu}_{jk} \\ &= \sum_j \varepsilon_j^{(1)} d\bar{\nu}_j + \sum_k \varepsilon_k^{(2)} d\bar{\nu}_k = \delta Q_1 + \delta Q_2 \ ,\end{aligned}$$

where $\bar{\nu}_{jk}$ is the expectation of n_{jk} conditioned by $\sum n_{jk} = N$ and $\sum(\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) n_{jk} = U$. In the above expression, in virtue of Definition 1 the quantities $\bar{\nu}_j$, $\bar{\nu}_k$ are essentially the same as in the uncoupled case $\lambda = 0$; by the same token the contribution $\lambda \varepsilon_{jk}^{int}$ to ε_{jk} was neglected. From the above expression for δQ_{12} and relation (10) there follows that there exist functions θ_1, θ_2, θ_{12}, and correspondingly σ_1, σ_2, σ_{12}, such that

$$\frac{1}{\theta_{12}} d\sigma_{12} = \frac{1}{\theta_1} d\sigma_1 + \frac{1}{\theta_2} d\sigma_2 \ . \tag{11}$$

From this it can be proved that there exist three integrating factors (the inverse temperatures) β_1, β_2, β_{12}, uniquely defined apart from a multiplicative constant, which have the same common value for the three systems,

and correspondingly three functions (the thermodynamic entropies) S_1, S_2, S_{12} which are additive in the sense that

$$dS_{12} = dS_1 + dS_2 \ .$$

The proof is standard and is recalled in Appendix A.

There remains the problem that, for the coupling of two generic systems, we are presently unable to find an explicit expression for the entropy of the compound system. We are able however to do it when one of the systems is a heat bath. In the next section the coupling of a system with a heat bath is considered, and it is shown how to compute the probability distribution of the occupation numbers n_{jk} and the thermodynamic quantities of interest.

4 A system in contact with a heat bath.

We want to compute the probability distribution of the occupation numbers n_{jk} for the cells $\mathcal{Z}_{jk}$ of the compound system $\mathcal{M}_1 \times \mathcal{M}_2$, when the second system is a heat bath, i.e. follows a Gibbs distribution. For the sake of simplicity notation, we will limit ourselves to the case in which the probability $f_j^{(1)}(n)$ for the occupation number of the cell $\mathcal{Z}_j$ of the first subsystem does not actually depend on j, i.e. one has $f_j^{(1)}(n) = f^{(1)}(n)$. Coherently, the corresponding Laplace transform (3) will be denoted by $\exp(\chi(z))$. In the general case of probability depending on the cell, one has to put $\chi_j(\,)$ in place of $\chi(\,)$ in all the expressions we will find below, in much the same way as the formulas of section 2. As there are already so many indexes in the expressions, we prefer to avoid the ones that are not strictly necessary.

From Definition 1 one can limit oneself to consider the uncoupled case $\lambda = 0$. As recalled above, in the case of a system described by a Gibbs distribution the visiting of the cells are independent events having a common probability p to happen. Our aim is now to compute $P(\{n_{jk}\})$, namely the probability of a given set $\{n_{jk}\}$ of occupation numbers. The main difference with respect to the case considered in ref. (5), is that now the random variables n_{jk} cannot be assumed to be independent, so that now $P(\{n_{jk}\})$ is not factorized. One can proceed in the following way. For a given set $\{n_{jk}\}$ let $l_j = \sum_k n_{jk}$ be the corresponding number of visits of cell $\mathcal{Z}_j$ in the first system. As the visits of the cells of the second system are independent events, the probability distribution conditioned by fixing l_j will be multinomial, i.e. will be giving by

$$P\Big(\{n_{jk}\}|l_j = \sum_k n_{jk}\Big) = \frac{l_j!}{n_{j1}! \cdots n_{jK_2}!} p^{l_j} \ .$$

On the other hand, if $f^{(1)}(l_j)$ is the probability that the cell $\mathcal{Z}_j$ of the first system is visited l_j times, as the occupation numbers of the first system have been assumed to be independent (Hypothesis 1), one finally has

$$P(\{n_{jk}\}) = \prod_j \frac{l_j! p^{l_j}}{n_{j1}! \cdots n_{jK_2}!} f^{(1)}(l_j) \ . \tag{12}$$

In computing the conditional expectations, it will be seen in the next pages that an essential role is played by the Laplace transform of distribution (12). A simple computation shows that

$$\sum_{\{n_{jk}\}} e^{-\sum_{jk} n_{jk} z_{jk}} P(\{n_{jk}\}) = \exp\Big[\sum_j \chi\big(-\log(p \sum_k e^{-z_{jk}})\big)\Big] \ , \tag{13}$$

where by $\sum_{\{n_{jk}\}}$ we mean a sum over all possible sets $\{n_{jk}\}$. In fact, (13) follows from the chain of identities:

$$\begin{aligned}
\sum_{\{n_{jk}\}} e^{-\sum_{jk} n_{jk} z_{jk}} P(\{n_{jk}\}) &= \sum_{\{l_j \geq 0\}} \sum_{\{\sum_k n_{jk} = l_j\}} \prod_j \frac{l_j! p^{l_j} e^{-\sum_{jk} n_{jk} z_{jk}}}{n_{j1}! \cdots n_{jK_2}!} f(l_j) \\
&= \prod_j \sum_{l_j \geq 0} f(l_j) \sum_{\sum_k n_{jk} = l_j} \frac{l_j! (p e^{-z_{j1}})^{n_{j1}} \cdots (p e^{-z_{jK_2}})^{n_{jK_2}}}{n_{j1}! \cdots n_{jK_2}!} \\
&= \prod_j \sum_{l_j \geq 0} f(l_j) \big(\sum_k p e^{-z_{jk}} \big)^{l_j} \\
&= \exp\Big[\sum_j \chi\big(-\log(p \sum_k e^{-z_{jk}})\big)\Big] \ .
\end{aligned}$$

One has now to compute the expectation of the time–average of a generic dynamical variable A, conditioned by $1/N \sum (\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) n_{jk} = U$ and $\sum n_{jk} = N$, namely the quantity

$$< \bar{A} >_U = \frac{1}{N} \sum_{\{n_{jk}\}}{}' \sum_{jk} A_{jk} n_{jk} \, P(\{n_{jk}\}) \quad \Big/ \sum_{\{n_{jk}\}}{}' P(\{n_{jk}\}) \ ,$$

where $\sum'$ denotes a sum over the possible sequences $\{n_{jk}\}$ constrained by $1/N \sum n_{jk} = N$ and $\sum (\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) n_{jk} = U$. This can be reduced to the computation of the "generating function"

$$Z(A, \mu) \stackrel{\text{def}}{=} \sum_{\{n_{jk}\}}{}' \exp(-\mu \sum A_{jk} n_{jk}) P(\{n_{jk}\}) \ , \tag{14}$$

through the relation

$$< \bar{A} >_U = -\frac{1}{N}\frac{\partial}{\partial \mu}\log Z(A,\mu)\Big|_{\mu=0} \quad . \tag{15}$$

It turns out that, as in reference (5), the asymptotic expansion of the generating function $Z(A,\mu)$ is very simply computed in the limit of very "large" systems (the ones of interest for thermodynamics), by using the steepest descent method. This indeed is commonly done in statistical mechanics, following Fowler and Darwin (see ref. (7)). Such an expansion will be performed below up to the leading term, neglecting the remainder (an explicit expression of which could however be given). As the remainder depends both on the form of the energy of the total system, and on the function $\chi(z)$ (i.e. on the probability distribution) characterizing the first system, the validity of the procedure should be checked for any particular system. In paper (5) it was shown that such a procedure is indeed correct, for example, for systems described by the Gibbs measure. So, we suppose that our systems too are well described by the leading order term of the asymptotic expansion, and we presently show how the expansion is actually performed.

This goes as follows. The expression (14) can be rewritten as

$$\begin{aligned}
Z(A,\mu) = & \sum_{\{n_{jk}\geq 0\}} \delta\Big(\frac{1}{N}\sum(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})n_{jk} - U\Big)\delta\Big(\sum n_{jk} - N\Big) \\
& \exp(-\mu\sum A_{jk}n_{jk})P\Big(\{n_{jk}\}\Big) \\
= & \lim_{L\to+\infty}\iint_{-L}^{L} d\kappa_1 d\kappa_2 \exp(-i\kappa_1 U - i\kappa_2 N) \\
& \sum_{\{n_{jk}\geq 0\}} \exp\Big(-\sum n_{jk}[\mu A_{jk} + \frac{i\kappa_1}{N}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)}) + i\kappa_2]\Big) P\Big(\{n_{jk}\}\Big) \\
= & \lim_{L\to+\infty}\iint_{-L}^{L} d\kappa_1 d\kappa_2 \exp(-i\kappa_1 U - i\kappa_2 N) \\
& \exp\Big[\sum_j \chi\Big(-\log\big(p\sum e^{\mu A_{jk} + i\kappa_1(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})/N + i\kappa_2}\big)\Big)\Big] \ ,
\end{aligned}$$

where in the second line the familiar representation of the Dirac delta function $\delta(x) = \int d\kappa \exp(i\kappa x)$ was used, while in the third line use was made of formula (13) for the Laplace transform of the probability $P(\{n_{jk}\})$.

The (double) integral in the last line can be evaluated using the steepest descent method, and to leading order one finds

$$\log Z(A,\mu) = -\frac{\theta}{N}U - \alpha N + \sum_j \chi\Big(-\log\big(p\sum e^{\mu A_{jk}+\theta(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})/N+\alpha}\big)\Big) \ ,$$

where θ and α are the solution of the system

$$U = -\frac{1}{N}\sum_{jk}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\chi'\left(-\log\left(p\sum_k e^{\mu A_{jk}+\theta(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})/N+\alpha}\right)\right)\cdot \frac{\exp\left(\mu A_{jk}+\frac{\theta}{N}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\right)}{\sum_k \exp\left(\mu A_{jk}+\frac{\theta}{N}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\right)}$$

$$N = -\sum_{jk}\chi'\left(-\log\left(p\sum_k e^{\mu A_{jk}+\theta(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})/N+\alpha}\right)\right)\cdot \frac{\exp\left(\mu A_{jk}+\frac{\theta}{N}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\right)}{\sum_k \exp\left(\mu A_{jk}+\frac{\theta}{N}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\right)} \ .$$

Now, taking the derivative of $\log Z(A,\mu)$ and putting $\mu = 0$, after some simple algebra one finds

$$< \bar{A} >_U = -\frac{1}{N}\sum_{jk} A_{jk}\chi'\left(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log(pZ_2)\right)\frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \ , \qquad (16)$$

where we have defined $Z_2(\theta) \stackrel{\text{def}}{=} \sum \exp(-\theta\varepsilon_k^{(2)}/N)$, whereas the constants θ and α are the solution of the previous system with $\mu = 0$, i.e. are solution of

$$\begin{aligned} U &= -\frac{1}{N}\sum_{jk}(\varepsilon_j^{(1)}+\varepsilon_k^{(2)})\chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2)\frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \\ N &= -\sum_{jk}\chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2)\frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \ . \end{aligned} \qquad (17)$$

The formulæ (16) and (17) solve the problem of computing the conditional expectation of a dynamical variable of the compound system, when the second one is a heat bath.

Now, it is very interesting to consider two limit cases: that in which the observable A depends only on the variables of the first system (so that $A_{jk} = A_j$), and that in which A depends only on the variables of the second one ($A_{jk} = A_k$). In the first case it is meaningful to consider a situation in which the energy conditioning is given not on the total energy of the compound system, but on the energy U_1 of the first one. This essentially amounts to considering the first system as isolated from the second one. Now, if one computes the generating function with the conditioning $\sum \varepsilon_j^{(1)} n_{jk}/N = U_1$, one finds

$$< A >_{U_1} = -\frac{1}{N} \sum_j A_j \chi'(\frac{\theta_1}{N} \varepsilon_j^{(1)} + \alpha_1) \ , \tag{18}$$

with θ_1 and α_1 solution of

$$\begin{aligned} U_1 &= -\frac{1}{N} \sum_j \varepsilon_j^{(1)} \chi'(\frac{\theta_1}{N} \varepsilon_j^{(1)} + \alpha_1) \\ N &= -\sum_j \chi'(\frac{\theta_1}{N} \varepsilon_j^{(1)} + \alpha_1) \ . \end{aligned} \tag{19}$$

These relations are the same as (2) and (4) of Section 2, as it should be.

Instead, if the dynamical variable A depends only on the variables of the heat bath, and the conditioning is done only on the energy U_2 of the latter, one finds

$$< A >_{U_2} = -\frac{1}{N} \sum_k A_k \frac{\exp(-\theta_2 \varepsilon_k^{(2)}/N)}{Z_2(\theta_2)} \ , \tag{20}$$

where Z_2 is the canonical partition function defined above, while θ_2 is defined by

$$\sum_k \varepsilon_k^{(2)} \frac{\exp(-\theta_2 \varepsilon_k^{(2)}/N)}{Z_2(\theta_2)} = U_2 \ . \tag{21}$$

These are the standard Gibbs relations.

It is interesting to compare these results with the computation of the mean energy of any of the two systems, when *the total energy* U is fixed.

One finds (using in the second line the definition of Z_2)

$$\begin{aligned} < \bar{\varepsilon}^{(1)} >_U &= -\frac{1}{N}\sum_{jk} \varepsilon_j^{(1)} \chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2) \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \\ &= -\frac{1}{N}\sum_{j} \varepsilon_j^{(1)} \chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2) \sum_k \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \qquad (22) \\ &= -\frac{1}{N}\sum_{j} \varepsilon_j^{(1)} \chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2) \ , \end{aligned}$$

which is the same as (19) with $U_1 = U_1(\theta) \stackrel{\rm def}{=} < \bar{\varepsilon}^{(1)} >_U$. For what concerns U_2 one finds instead (using now, in the second line, the second of (19))

$$\begin{aligned} < \bar{\varepsilon}^{(2)} >_U &= -\frac{1}{N}\sum_{jk} \varepsilon_k^{(2)} \chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2) \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \\ &= -\frac{1}{N}\sum_{j} \chi'(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2) \sum_k \varepsilon_k^{(2)} \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \qquad (23) \\ &= \sum_{k} \varepsilon_k^{(2)} \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} \ , \end{aligned}$$

namely again the same as (21), with $U_2 = U_2(\theta) \stackrel{\rm def}{=} < \bar{\varepsilon}^{(2)} >_U$. These computations show first of all that

$$U(\theta) = U_1(\theta) + U_2(\theta) \ , \qquad (24)$$

but also, as mentioned in Section 3, that the equilibrium energies U_1 and U_2 lie on a curve, i.e. the curve $(U_1(\theta), U_2(\theta))$ parametrized by θ.

5 The thermodynamics.

We turn now to formulæ (16) and (17), in order to write them in a more transparent way. In fact, defining in perfect analogy with (5) the mean occupation numbers $\bar{\nu}_{jk}$ by

$$\bar{\nu}_{jk} \stackrel{\rm def}{=} -\chi'\left(\frac{\theta}{N}\varepsilon_j^{(1)} + \alpha + \log pZ_2\right) \frac{\exp(-\theta\varepsilon_k^{(2)}/N)}{Z_2(\theta)} \ , \qquad (25)$$

such formulæ take the form

$$< \bar{A} >_U = \frac{1}{N}\sum_{jk} A_{jk}\bar{\nu}_{jk} \ , \qquad U = \frac{1}{N}\sum_{jk}(\varepsilon_j^{(1)} + \varepsilon_k^{(2)})\bar{\nu}_{jk} \ , \qquad N = \sum_{jk}\bar{\nu}_{jk} \ .$$

As in the case of (5), one has now

$$\bar{\nu}_{jk} = -\frac{\partial}{\partial z_{jk}} \sum_{l'} \chi\left(-\log p \sum_{l} \exp(-z_{l'l})\right)\Big|_{z_{l'l}=(\theta/N)(\varepsilon^{(1)}_{l'}+\varepsilon^{(2)}_{l})+\alpha} .$$

One can then introduce the Legendre transform $h^{(12)}(\nu_{11}, \cdots)$ of the function $\sum_{l'} \chi(\cdots)$ occurring above, by

$$h^{(12)}(\nu_{11}, \cdots) = \sum_{jk} z_{jk}\nu_{jk} + \sum_{l'} \chi\left(-\log p \sum_{l} \exp(-z_{l'l})\right) , \qquad (26)$$

where as usual the dependence of z_{jk} on ν_{jk} is obtained by solving

$$\nu_{jk} = \partial_{z_{jk}} \sum_{l'} \chi\left(-\log p \sum_{l} \exp(-z_{l'l})\right) . \qquad (27)$$

Now, the Legendre duality gives

$$\frac{\theta}{N}(\varepsilon^{(1)}_j + \varepsilon^{(2)}_k) + \alpha = \frac{\partial}{\partial \nu_{jk}} h^{(12)}(\bar{\nu}_{11}, \cdots) ,$$

so that for the exchanged heat δQ_{12} one finds

$$\delta Q_{12} = \frac{1}{N}\sum_{jk}(\varepsilon^{(1)}_j + \varepsilon^{(2)}_k) d\bar{\nu}_{jk} = \frac{N}{\theta}\frac{1}{N}\sum_{jk}\left(\frac{\partial h^{(12)}}{\partial \nu_{jk}} - \alpha\right) d\bar{\nu}_{jk} = \frac{N}{\theta} dh^{(12)} .$$

This shows that the exchanged heat does indeed have an integrating factor.

But there is more. Indeed, from the definitions (5) and (25) of the quantities $\bar{\nu}_j$ and $\bar{\nu}_{jk}$ respectively one checks that

$$\bar{\nu}_j = \sum_k \bar{\nu}_{jk} ,$$

so that

$$\frac{1}{N}\sum_{jk} \varepsilon^{(1)}_j d\bar{\nu}_{jk} = \sum_j \varepsilon^{(1)}_j d\bar{\nu}_j = \delta Q_1 = \frac{N}{\theta} dh^{(1)} ,$$

where the last equality comes from (10). In the same way one can check that

$$\frac{1}{N}\sum_{jk} \varepsilon^{(2)}_k d\bar{\nu}_{jk} = \sum_k \varepsilon^{(2)}_k d\bar{\nu}_k = \delta Q_2 = \frac{N}{\theta} dh^{(2)} .$$

Here $h^{(2)}$ is the standard Gibbs entropy $h^{(2)} = \sum n_k \log n_k - n_k \log p$, while $\bar{\nu}_k$ is given by (8).

Finally, we find that

$$\frac{N}{\theta} dh^{(12)} = \delta Q_{12} = \delta Q_1 + \delta Q_2 = \frac{N}{\theta} dh^{(1)} + \frac{N}{\theta} dh^{(2)} \ .$$

This shows that θ/N is indeed the absolute temperature, while the thermodynamic entropies can be identified[3] as

$$S_1(U_1, \kappa) \stackrel{\text{def}}{=} h^{(1)}(\bar{\nu}_j) \ , \quad S_2(U_2, \kappa) \stackrel{\text{def}}{=} h^{(1)}(\bar{\nu}_k) \ , \quad S_{12}(U, \kappa) \stackrel{\text{def}}{=} h^{(12)}(\bar{\nu}_{jk}) \ .$$

Moreover the thermodynamic entropies are additive, in the sense that

$$dS_1 + dS_2 = dS_{12} \ .$$

6 The case of the q–distribution.

If system 1 is described by a Gibbs statistics, the function χ is an exponential, and the usual formulæ are recovered. In fact in such a case one gets

$$\sum_j \chi\Big(-\log p \, \big(\sum_k \frac{\theta}{N}(\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) + \alpha\big)\Big) = \sum_{jk} p \exp\Big(-\frac{\theta}{N}(\varepsilon_j^{(1)} + \varepsilon_k^{(2)}) - \alpha\Big) \ ,$$

so that formula (26) gives

$$h^{(12)} = -\sum_{jk} \bar{\nu}_{jk} \log \bar{\nu}_{jk} + p\bar{\nu}_{jk} \ .$$

From this, the additivity of the entropy easily follows, using

$$\bar{\nu}_{jk} = \frac{1}{N} \bar{\nu}_j \bar{\nu}_k \ ,$$

which follows from definition (25). In fact, one has

$$\bar{\nu}_{jk} = p e^{-\alpha} e^{-\theta \varepsilon_j^{(1)}/N} e^{-\theta \varepsilon_k^{(2)}/N} \ .$$

On the other hand, computing α by the second of (17), one finds

$$p e^{-\alpha} \sum_{jk} e^{-\theta \varepsilon_j^{(1)}/N} e^{-\theta \varepsilon_k^{(2)}/N} = \frac{N}{Z_1(\theta) Z_2(\theta)} \ ,$$

[3]Notice that in paper (5) the thermodynamic entropy was denoted by S^{th}, while the quantity h was denoted by S.

so that for $\bar{\nu}_{jk}$ one gets

$$\bar{\nu}_{jk} = N \frac{e^{-\theta\varepsilon_j^{(1)}/N}}{Z_1(\theta)} \frac{e^{-\theta\varepsilon_k^{(2)}/N}}{Z_2(\theta)} = \frac{1}{N}\bar{\nu}_j\bar{\nu}_k \ ,$$

the second equality following from the known expression (8) which holds both for $\bar{\nu}_j$ and $\bar{\nu}_k$.

A comment is now in order before discussing the expression of the entropy in the case system 1 follows the Tsallis q–distribution. The relation $\bar{\nu}_{jk} = \frac{1}{N}\bar{\nu}_j\bar{\nu}_k$, which can be rewritten in the more expressive form

$$< n_{jk} >_{U(\theta)} = \frac{1}{N} < n_j >_{U_1(\theta)} < n_k >_{U_2(\theta)} \ , \tag{28}$$

holds always true, as one can check from the definition (25) of $\bar{\nu}_{jk}$ and from the definitions (5) and (8) of $\bar{\nu}_j$ and $\bar{\nu}_k$. But the important point is that a relation of this kind holds neither for the occupation numbers n_{jk}, n_j, n_k, nor for the parameters ν_{jk}, ν_j, ν_k. In particular, concerning the two functions $h^{(12)}(\nu_{jk})$ and $h^{(1)}(\nu_j) + h^{(2)}(\nu_k)$ (the values of which obviously cannot be compared unless some relation is assumed between the corresponding arguments), we will find that their values coincide when they are computed at equilibrium, i.e. when their arguments satisfy relation (28).

If system 1 follows the Tsallis q–distribution, then one has

$$\chi(z) = p_1(1 - (1-q)z)^{1/(1-q)} - p_1 \tag{29}$$

with a constant $p_1 > 0$, so that (from 25) one gets

$$\nu_{jk} = p_1 \left(1 + (1-q)\log pZ_j\right)^{q/(1-q)} \frac{e^{-z_{jk}}}{Z_j} \tag{30}$$

with $Z_j = \sum_k e^{-z_{jk}}$. The aim is now to compute the explicit expression of the function $h^{(12)}$, the entropy of the compound system, and make a comparison with the sum $h^{(1)} + h^{(2)}$.

First one has to express z_{jk} as a function of ν_{jk}. To this end, note that from (30), taking the logarithm of both sides, one gets

$$z_{jk} = -\log\nu_{jk} - \log\left(\left(1 - (1-q)\log pZ_j\right)^{q/(1-q)}\right) + \log p_1 - \log Z_j \ .$$

In turn, the expression of the function Z_j in terms of ν_{jk} is obtained from (30) by summing over the index k, which gives

$$\sum_k \nu_{jk} = p_1 \left(1 + (1-q)\log pZ_j\right)^{q/(1-q)} \ ,$$

so that

$$\log pZ_j = \frac{1}{1-q}\left[\Big(\frac{\sum_k \nu_{jk}}{p_1}\Big)^{\frac{1-q}{q}} - 1\right] .$$

Inserting this relation into the expression for z_{jk} one finds

$$z_{jk} = -\log \nu_{jk} + \log\Big(\sum_k \nu_{jk}\Big) + \frac{1}{1-q}\left[1 - \Big(\frac{\sum_k \nu_{jk}}{p_1}\Big)^{\frac{1-q}{q}}\right] + \log p \ .$$

It is now immediate to perform the Legendre transform $h^{(12)}$ of the function $\sum_j \chi(..) = \sum_j p_1(1-(1-q)\log(pZ_j)/q)^{1/(1-q)} - p_1$, and one obtains

$$h^{(12)} = -\sum_{jk}(-\nu_{jk}\log\nu_{jk} + \nu_{jk}\log p) + \sum_j \big(\sum_k \nu_{jk}\big)\log\big(\sum_k \nu_{jk}\big) + \frac{1}{1-q}\sum_{jk}\nu_{jk} - \frac{p_1 q}{1-q}\sum_j \Big(\frac{\sum_k \nu_{jk}}{p_1}\Big)^{\frac{1}{q}} .$$

This expression reduces at equilibrium, i.e for $\bar\nu_{jk} = \bar\nu_j\,\bar\nu_k/N$, to the simpler one

$$h^{(12)} = \sum_k(-\bar\nu_k\log\bar\nu_k + \bar\nu_k\log p) + p_1\frac{q\sum_j\Big(\frac{\bar\nu_j}{p_1}\Big)^{\frac{1}{q}} - \sum_j\Big(\frac{\bar\nu_j}{p_1}\Big)}{1-q} \ .$$

The first term coincides with the familiar expression of the Boltzmann entropy of the heat bath, whereas the second one coincides with the expression of the Tsallis entropy for the first system (see refs. (5),(8)), written however in terms of the mean occupation numbers, rather than in terms of the escort probabilities. It is then apparent that

$$dh^{(12)} = dh^{(1)} + dh^{(2)} \ .$$

7 The meaning of the parameter α.

We now come back to another problem concerning the case of a single system, which was left open in paper (5), namely the identification of the quantity α entering formula (2). To this end we remark that, according to formula (5), the mean occupation number is given by

$$\bar\nu_j \stackrel{\text{def}}{=} -\chi_j'\Big(\frac{\varepsilon_j\theta}{N} + \alpha\Big) \ ,$$

whereas the parameter θ/N was shown to be the temperature of the system. It is thus convenient to choose as independent variables $\beta \stackrel{\text{def}}{=} \theta/N$ and N in place of U and N. In fact if we define

$$f(\beta) \stackrel{\text{def}}{=} \frac{1}{N} \sum_j \chi_j(\beta\varepsilon_j + \alpha) \ ,$$

taking the derivative of both sides with respect to β and using (6) one finds (we denote $\frac{\partial}{\partial\beta} = \partial_\beta$)

$$\partial_\beta(-\alpha - f) = U \ .$$

Now we recall that the free energy $F = U - \beta^{-1}S$ satisfies the relation

$$\partial_\beta(\beta F) = U \ ,$$

so that one has, apart from an additive constant (possibly depending on the external parameters entering the Hamiltonian), the important relation

$$\alpha = -\beta F - f \ .$$

In particular, if the system follows a Gibbs statistics, f is a constant and one has

$$\alpha = -\beta F \ .$$

This coincides with the familiar relation $\beta F = -\log Z$, where Z is the canonical partition function, because in such a case one has $\alpha = \log Z$ (see formula (8)).

If instead the system follows a Tsallis distribution of index q, then the expression of $\chi(z)$ is given by (29), so that f is given by

$$\begin{aligned} f(\beta) &= \frac{1}{N} \sum_j \Big[p_1 \big(1 - (1-q)(\beta\varepsilon_j + \alpha)\big)^{\frac{1}{1-q}} - p_1 \Big] \\ &= \frac{1}{N} \sum_j p_1 \big(1 - (1-q)(\beta\varepsilon_j + \alpha)\big) \big(1 - (1-q)(\beta\varepsilon_j + \alpha)\big)^{\frac{q}{1-q}} - 1 \\ &= 1 - (1-q)(\beta U + \alpha) - 1 = (q-1)(\beta U + \alpha) \ , \end{aligned}$$

where, in the second line, use was made of the second and the third of (6). We find in this way

$$\alpha = -\frac{1}{q}\, \beta \big[F - (1-q)U \big] \ ,$$

which gives the relation between α and the thermodynamic functions F and U.

At this point, it is worth noting that usually the Tsallis distribution is written in the form (see ref. (8))

$$\bar{\nu}_j = C(\beta_q)\big(1 - \beta_q \varepsilon_j\big)^{\frac{q}{1-q}} \ ,$$

where the function $C(\beta_q)$ is a normalization factor, and β_q is determined by somehow fixing the mean energy. But in terms of our β, i.e. of inverse temperature, one has

$$\beta_q = \frac{(1-q)\beta}{1-(1-q)\alpha} \ .$$

This shows that β_q is *not* the inverse temperature, but a complicated function of it, which could be obtained by expressing α as a function of β.

8 Conclusions.

So we have shown, that the parameter $\beta \stackrel{\text{def}}{=} \theta/N$ is the inverse temperature, in the sense that it has the same value for every system which is in thermal equilibrium with a heat bath at (inverse) temperature β. Such an identification also enables one to find out the thermodynamic entropy S. In particular, in the case of the Tsallis q–distribution, the entropy just coincides with its q–entropy (as one could have imagined). A relevant point is however that in such a case the entropy turns out to be additive, at least for what concerns its differential, i. e. in the sense that one has $dS_{12} = dS_1 + dS_2$. Whether such a relation can be integrated to give $S_{12} = S_1 + S_2$ is a non trivial point which we are unable to discuss at the moment.

In the literature there is a long debate about this point; in particular it is often pointed out that, if entropy is assumed to be additive (for independent systems), then the Boltzmann–Gibbs expression should follow. This is usually based on a uniqueness theorem of Khinchin (see ref. (9)) in the information theory framework, in which additivity plays a key role. The q–entropy, being characterized instead (see refs. (10)) by a requirement of pseudo–additivity in term of conditional probability, seems at first sight that it could not be additive. However, also in this framework, (see for example the paper (11)) the q–entropy can be shown to be extensive, if the indipendence ipothesis is given up (as one expectes if the dynamic of the system is weakly chaotic) and replaced by a requirement of suitable correlations.

Without entering these very interesting questions, we only want to point out that, in our definition (26) of the entropy, the independent variables are the parameters ν_j, which are *not* the probabilities of the occupation of the

cells in the space phase. So the functional dependence of the entropy on the quantities ν_j may be out of the reach of Khinchin's theorem, in which the role of the independent variables is played by the probabilities. In any case, it is true that one ought to understand in a deeper way the connection of the present approach with Kinchin's theorem, and more generally with information entropy.

In this connection, we want to point out that it is very difficult to give an a priori expression of the entropy of a compound sistem, unless the dynamic is very chaotic (in this case the occupation numbers are Poisson distribuited and the entropy turns out to be given by the Boltzmann–Gibbs expression). For example, in our case, the entropy of the compound system could not be guessed by the expressions for the components entropy, but one had to compute it using some (strong) information about the dynamic. In the general case, at the moment, I have no clear ideas about how to proceed.

Appendix: proof of the existence of temperature.

In the following, for the sake of completeness, the familiar deduction of the existence of absolute temperature is recalled. The only difference with respect to the treatments of most textbooks, is that we make use not of the concept of "empirical temperature", but rather of the concept, recalled above, of the "equilibrium curve" in the plane (U_1, U_2).

So let us assume there exist θ_1, σ_1 such that for the exchanged heat δQ_1 of system A one has $\delta Q_1 = \theta_1 d\sigma_1$, and analogously for system B and the compound system A∪B, i.e. $\delta Q_2 = \theta_2 d\sigma_2$, $\delta Q_{12} = \theta_{12} d\sigma_{12}$. From $\delta Q_{12} = \delta Q_1 + \delta Q_2$, one has

$$\theta_{12} d\sigma_{12} = \theta_1 d\sigma_1 + \theta_2 d\sigma_2 \ , \tag{31}$$

i.e.

$$d\sigma_{12} = \frac{\theta_1}{\theta_{12}} d\sigma_1 + \frac{\theta_2}{\theta_{12}} d\sigma_2 \ .$$

This shows that σ_{12} depends only on the values of σ_1 and σ_2, and not on any other external parameters entering the energies of system A or system B, i.e one has

$$\sigma_{12} = G(\sigma_1, \sigma_2) \ .$$

So there follows that the ratio of θ_i by θ_{12} is equal to the partial derivative $\partial_{\sigma_i} G$, i.e. one has

$$\theta_1 = \frac{\partial G}{\partial \sigma_1} \theta_{12} \ , \quad \theta_2 = \frac{\partial G}{\partial \sigma_2} \theta_{12} \ . \tag{32}$$

Use now the condition that systems A and B are in mutual equilibrium. This means that, if one fixes all the parameters but the energies U_1, U_2 of the two systems, then they lie on a curve $(U_1(\rho), U_2(\rho)$ in the plane (U_1, U_2). For example, in the case of two gases, one can fix the volumes and think of changing the internal energies of the gases through an isocoric transformation, i.e. by heating or cooling the gases. In our case, instead, one can think of fixing the entropy and changing U by adiabatic transformations. In other terms, one uses as independent variables the entropies and the internal energies (and, perhaps, some further parameters if the former are not sufficient to the complete thermodynamic description of the systems).

Now, taking the logarithmic derivative of the expressions (32) with respect to ρ, i.e. the variable which parameterizes the equilibrium curve, one finds

$$\partial_\rho \log \theta_1 = \partial_\rho \log \theta_{12} = \partial_\rho \log \theta_2 \ .$$

In principle, here, $\partial_\rho \log \theta_1$ depends only on ρ and on the other parameters of the first system, while $\partial_\rho \log \theta_2$ depends only on ρ and the parameters of the second one. This implies that actually all the three expressions have to be equal to a function depending only on ρ (as can be seen, for example, by the fact that the derivatives with respect to the parameters other then ρ vanish). One has thus

$$\partial_\rho \log \theta_1 = \partial_\rho \log \theta_{12} = \partial_\rho \log \theta_2 = f(\rho) \ ,$$

which on integration gives

$$\theta_1 = e^{F(\rho)} \Sigma_1(\sigma_1) \ , \ \theta_2 = e^{F(\rho)} \Sigma_1(\sigma_2) \ , \ \theta_{12} = e^{F(\rho)} \Sigma_{12}(\sigma_1, \sigma_2) \ , \qquad (33)$$

where $F(\rho)$ is a primitive of $f(\rho)$ and Σ_i are integration constants. One can wonder why Σ_i depends only on σ_i. This too follows from (32), which shows that the ratio θ_1/θ_2 depends only on σ_1, σ_2, and not on any other external parameters needed to describe the system.

The last step is to show that $T^{-1} \stackrel{\text{def}}{=} \exp(F(\rho))$ is the integrating factor one is looking for. By construction, T^{-1} has the same value for all the three systems. It is uniquely defined apart from a multiplicative constant depending on the choice of the primitive F. To show that it is an integrating factor, one has to consider relation (31), which, after simplifying T, reads

$$\Sigma_{12} d\sigma_{12} = \Sigma_1 d\sigma_1 + \Sigma_2 d\sigma_2 \ .$$

Thus one can define the entropy of the two systems as $dS_1 = \Sigma_1(\sigma_1) d\sigma_1$ and $dS_2 = \Sigma_2(\sigma_1) d\sigma_2$ respectively. Moreover, as one has

$$\Sigma_{12} d\sigma_{12} = dS_1 + dS_2 = d(S_1 + S_2) \ ,$$

one finds in the first place that $\Sigma_{12} d\sigma_{12}$ too is a total differential dS_{12}, and furthermore that the entropies are additive in the sense that

$$dS_{12} = dS_1 + dS_2 \ .$$

This also shows that T^{-1} is an integrating factor, because one has

$$\delta Q_1 = T dS_1 \ , \ \delta Q_2 = T dS_2 \ , \ \delta Q_{12} = T dS_{12} \ .$$

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