Temperature and pressure in nonextensive thermostatistics

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Abstract

The definitions of the temperature in the nonextensive statistical thermodynamics based on Tsallis entropy are analyzed. A definition of pressure is proposed for nonadditive systems by using a nonadditive effective volume. The thermodynamics of nonadditive photon gas is discussed on this basis. We show that the Stefan-Boltzmann law can be preserved within nonextensive thermodynamics.

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1 Introduction

The nonextensive statistical mechanics (NSM)[1] based on Tsallis entropy is believed by many to be a candidate replacing Boltzmann-Gibbs statistics (BGS) for nonextensive or nonadditive systems which may show probability distributions different from that of BGS. So according the common belief, NSM, just as BGS, should be able to address thermodynamic functions and intensive variables like temperature T, pressure P, chemical potential μ etc. Although the Legendre transformation between the thermodynamic functions is preserved in some versions of NSM with sometimes certain deformation, the definition of intensive variables is not obvious if the thermodynamic functions

such as entropy S, energy U or free energy F are nonadditive. There are sometimes misleading calculations using $\beta = 1/T = \left(\frac{\partial S}{\partial U}\right)_V$ (let Boltzmann constant $k = 1$) and $P = -\left(\frac{\partial F}{\partial V}\right)_T$ or $P = \frac{1}{3}\frac{U}{V}$ (for photon gas) without specifying the nonadditivity (or additivity) of each functions or noticing that additive internal energy U and volume V associated with nonadditive S and F will lead to non-intensive temperature or pressure which would make the thermodynamic equilibrium or stationarity impossible in the conventional sense.

On the other hand, within NSM, due to the fact that different formalisms are proposed from different statistics or information considerations, thermodynamic functions do not in general have the same nonadditive nature in different versions of NSM. This has led to different definitions of, among others, a physical or measurable temperature β_p which is sometimes equal to β[2], sometimes equal to β multiplied by a function of the partition function Z^{q-1}[3, 4, 5, 6, 7] or Z^{1-q}[8, 9] which keeps β_p intensive, where q is the nonadditive entropy index[1], or sometimes defined by deformed entropy and energy[9, 10, 11]. This situation often results in confusion and misleading discussions of these temperatures[12] or other intensive variables[13], without knowing or mentioning the validity conditions relevant to them and the risk to have non intensive temperature or pressure.

The present paper tries to make a state of the art on this subject with brief discussions of the specificities of each formalism of NSM and the relevant consequences. It is hoped that this paper may offer to the reader a global view of the situation and of some important questions which are still matters of intense investigation.

2 The first definition of physical temperature of NSM

We look at a composite system containing two subsystems A and B, all having the same q as nonadditive entropy index. The entropy nonadditivity of the total system is given by

$$S(A+B) = S(A) + S(B) + (1-q)S(A)S(B). \tag{1}$$

[1] Tsallis entropy is given by $S = \frac{\sum_i p_i^q - 1}{1-q}, (q \in R)$[1]

This relationship is intrinsically connected with the product joint probability

$$p_{ij}(A+B) = p_i(A)p_j(B), \tag{2}$$

or inversely, where i or j is the index of physical states for A or B. Eq.(2) has been intuitively taken as an argument for the independence of A and B and for the energy additivity of $A+B$. This additivity offers the first possibility to establish zeroth law and to define temperature within NSM[3, 4, 5, 6, 7]. The intensive physical temperature is defined as

$$\beta_p = \frac{1}{T_p} = \frac{1}{\sum_i^w p_i^q} \frac{\partial S}{\partial U} = \frac{1}{\sum_i^w p_i^q} \beta. \tag{3}$$

This definition is an universal model of NSM and not connected to any specific statistical formalism.

If this β_p is applied to NSM having typically the power law distribution

$$p_i = \frac{1}{Z}[1 - a\beta_p E_i]^{\frac{1}{a}} \quad with \;\; [\cdot] \geq 0 \tag{4}$$

where E_i is the energy of a system at state i and a is $1-q$ or $q-1$ according to the maximum entropy constraints of the formalism[8, 14], there may be in general a conflict between the product joint probability and the energy additivity condition due to the nonadditive energy $E_i(A+B) = E_i(A) + E_j(B) - a\beta_p E_i(A)E_j(B)$. So the validity of this thermostatistics strongly lies on neglecting $E_i(A)E_j(B)$.

A mathematical proof[3] shown that this was possible, for a N-body system, if and only if $q < 1$ and $N \to \infty$. This is not to be forgotten. For the systems with $q > 1$ or with finite size without thermodynamic limits, this additive energy model is not justified.

Especially, when this model is applied to the formalism of NSM deduced from the normalized expectation given by the escort probability $U = \frac{\sum_i p_i^q E_i}{\sum_i p_i^q}$[14] where p_i is a normalized probability which reads

$$p_i = \frac{1}{Z}[1 - (1-q)\beta_p(E_i - U)]^{\frac{1}{1-q}} = \frac{1}{Z}[1 - (1-q)\frac{\beta}{Z^{1-q}}(E_i - U)]^{\frac{1}{1-q}}, \tag{5}$$

Eq.(3) becomes

$$\beta_p = \frac{1}{Z^{1-q}} \frac{\partial S}{\partial U} = Z^{q-1}\beta. \tag{6}$$

In this case, β_p is not to be confounded with β although we have here $\beta = \frac{\partial S}{\partial U}$ which is evidently non intensive.

3 The first formalism of NSM

The first formalism[1] of NSM maximizes entropy under the constraint $U = \sum_i p_i E_i$ with normalized p_i. The distribution function is given by

$$p_i = \frac{1}{Z}[1-(q-1)\beta_p E_i]^{\frac{1}{q-1}}. \tag{7}$$

The product probability implies the following nonadditivity of energy :

$$E_i(A+B) = E_i(A) + E_j(B) - (q-1)\beta_p E_i(A)E_j(B) \tag{8}$$

and $U(A+B) = U(A) + U(B) - (q-1)\beta_p U(A)U(B)$. The temperature of this formalism is still given by Eq.(6) as briefly discussed in [8].

The thermodynamic relations can be deduced from the basic expression of entropy of this formalism

$$S = \frac{Z^{1-q}-1}{1-q} + \beta_p Z^{1-q} U \tag{9}$$

or $S_p = Z^{q-1}S = \frac{Z^{q-1}-1}{q-1} + \beta_p U$ where S_p is an "auxiliary entropy" introduced to write the generalized heat as $dQ = T_p dS_p$. The first law reads $dU = T_p dS_p - dW$. The free energy F is defined as

$$F = U - T_p S_p = -T_p \frac{Z^{q-1}-1}{q-1}. \tag{10}$$

The first law becomes $dF = -S_p dT_p - dW$ where dW is the work done by the system.

S_p can be calculated by using $S_p = -\left(\frac{\partial F}{\partial T_p}\right)_V$ and Eqs.(5) and (10) with $Z = \sum_i [1-(q-1)\beta_p E_i]^{\frac{1}{q-1}}$ [12]. This leads to

$$S_p = -\sum_i p_i^{2-q} \frac{p_i^{q-1}-1}{q-1} = \frac{1-\sum_i p_i^{2-q}}{1-q}. \tag{11}$$

Notice that this auxiliary entropy is not to be maximized since it is concave only for $q < 2$.

4 The second formalism of NSM with unnormalized expectation

This formalism is deduced from the entropy maximum under the constraint $U = \sum_i p_i^q E_i$ with normalized p_i[15]. The distribution function is given by

$$p_i = \frac{1}{Z}[1 - (1-q)\beta_p E_i]^{\frac{1}{1-q}}. \tag{12}$$

and the nonadditivity of energy by $E_i(A+B) = E_i(A) + E_j(B) - (1-q)\beta_p E_i(A)E_j(B)$ and

$$U(A+B) = U(A)Z^{1-q}(B) + U(B)Z^{1-q}(A) + (q-1)\beta_p U(A)U(B). \tag{13}$$

As discussed in [2], this is the only formalism of NSM in which the mathematical framework of the thermodynamic relationships is strictly identical to that of BGS with $\beta_p = \beta$. The heat is given by $dQ = TdS$, the first law by $dU = TdS - dW$ and the free energy by

$$F = U - TS = -T\frac{Z^{1-q} - 1}{1-q}. \tag{14}$$

Heat and work are interpreted as $dQ = \sum_i E_i dp_i^q$ and $dW = \sum_i p_i^q dE_i$, which is not so simple within other formalisms[2].

5 The formalism with incomplete probability distribution

If the probability distribution is incomplete in such a way that $\sum_i p_i^q = 1$[17, 18] where the sum is calculated only over an incomplete set of states or of random variables as discussed in [16] and if we suppose $U = \sum_i p_i^q E_i$, the maximum entropy leads to the following distribution function

$$p_i = \frac{1}{Z}[1 - (1-q)\beta_p E_i]^{\frac{1}{1-q}}. \tag{15}$$

where $Z^q = \sum_i [1 - (1-q)\beta_p E_i]^{\frac{1}{1-q}}$.

The nonadditivity of energy is given by

$$U(A+B) = U(A) + U(B) + (q-1)\beta_p U(A)U(B).$$

The definition of the physical temperature β_p in this formalism is discussed in [8, 9] and reads

$$\beta_p = Z^{1-q}\frac{\partial S}{\partial U} = Z^{1-q}\beta. \tag{16}$$

The introduction of the distribution Eq.(15) into Tsallis entropy gives

$$S = \frac{Z^{q-1}-1}{q-1} + \beta_p Z^{q-1}U \tag{17}$$

or $S_p = Z^{1-q}S = \frac{Z^{1-q}-1}{1-q} + \beta_p U$ where still S_p is the "entropy" introduced to write $dQ = T_p dS_p$. The first law reads $dU = T_p dS_p - dW$ or, with the help of the free energy

$$F = U - T_p S_p = -T_p \frac{Z^{1-q}-1}{1-q}, \tag{18}$$

$dF = -S_p dT_p - dW$ where dW is the work done by the system. S_p is given by[12]

$$S_p = -\sum_i p_i^q \frac{p_i^{q-1}-1}{q-1} = \frac{1-\sum_i p_i^{2q-1}}{q-1}. \tag{19}$$

which is concave only for $q > 1/2$ so that not to be maximized to get distribution functions although its maximum formally leads to $p_i \propto [1-(q-1)\beta_p E_i]^{\frac{1}{q-1}}$. Notice that this latter is not the original distribution function of incomplete statistics.

The above calculation of S_p cannot be carried out for S by using β or T because $S \neq -\frac{\partial F}{\partial T}$ although we can write $F = U - T_p S_p = U - TS$. In addition, Z is not derivable with respect to β since it is a self-referential function when written as a function of β. This calculation can be done for S only in the second formalism with unnormalized expectation and normalized probability associated to $\beta = 1/T = \frac{\partial S}{\partial U}$.

An additive form of this formalism of a nonadditive statistical thermodynamics is proposed by using some deformed entropy s and energy e_i[9], where $s = \sum_i p_i^q \ln\frac{1}{p_i}$ and $e_i = \frac{\ln[1+(q-1)\beta_p E_i]}{(q-1)\beta_p}$ both being additive, i.e., $s(A+B) = s(A)+s(B)$ and $e_{ij}(A+B) = e_i(A)+e_j(B)$. The maximization of s under the constraint $u = \sum_i p_i^q e_i$ and $\sum_i p_i^q = 1$ leads to $p_i = \frac{1}{Z}e^{-\beta_p e_i}$ which is identical to Eq.(15). Within this framework, the temperature is $\beta = \frac{\partial s}{\partial u}$, the deformed first law is $du = T_p ds - dw$ (dw is a deformed work), the deformed free energy is

$$f = u - T_p s = -T_p \ln Z = \frac{\ln[1+(q-1)\beta_p F]}{(q-1)\beta_p}. \tag{20}$$

In this deformed formalism, everything is just as in BGS. This mathematical framework has been used for the equilibrium problem of the systems having different q's[10, 11].

6 Systems having different q's

The reader should have noticed that all the above discussions are based on the entropy nonadditivity given by Eq.(1) which is valid only for systems having the same index q. For systems A, B and $A+B$ each having its own q, this relationship breaks down even if the product joint probability holds. So for establishing the zeroth law, we need more general nonadditivity for entropy. A possible one is proposed as follows[10] :

$$\begin{aligned}(1-q_{A+B})S(A+B) &= (1-q_A)S(A)+(1-q_B)S(B) \\ &+ (1-q_A)(1-q_B)S(A)S(B)\end{aligned} \tag{21}$$

which recovers Eq.(1) whenever $q_{A+B}=q_A=q_B$.

The establishment of zeroth law for this case has been discussed by using the unnormalized expectations just as in the second formalism of NSM, i.e., $u=\sum_i p_i^q e_i$ with $\sum_i p_i = 1$[10], or $u=\sum_i p_i e_i$ with $\sum_i p_i^q = 1$[11]. The reason for this is that these unnormalized expectations allow one to split the thermodynamics of the composite systems into those of the subsystems through the generalized product joint probability $p_{ij}^{q_{A+B}}(A+B) = p_i^{q_A}(A)p_i^{q_B}(B)$ if $\sum_i p_i = 1$ [or $p_{ij}(A+B)=p_i(A)p_i(B)$ if $\sum_i p_i^q = 1$]. This thermodynamic splitting is just a necessary condition for the statistical interpretation of the zeroth law.

In this case, the deformed entropy s and energy u are not necessarily additive as in the case of an unique q. In fact, when $u=\sum_i p_i^q e_i$ with $\sum_i p_i = 1$ is used, their nonadditivities are given as follows

$$\frac{q_{A+B}s(A+B)}{\sum_{ij} p_{ij}^{q_{A+B}}(A+B)} = \frac{q_A s(A)}{\sum_i p_i^{q_A}(A)} + \frac{q_B s(B)}{\sum_j p_j^{q_B}(B)} \tag{22}$$

and

$$\frac{q_{A+B}u(A+B)}{\sum_{ij} p_{ij}^{q_{A+B}}(A+B)} = \frac{q_A u(A)}{\sum_i p_i^{q_A}(A)} + \frac{q_B u(B)}{\sum_j p_j^{q_B}(B)}. \tag{23}$$

The temperature is given by $\beta_p = \beta = \frac{\partial s}{\partial u} = \frac{\partial S}{\partial U}$ here $U = \sum_i p_i^q E_i$. The thermodynamic relations are the same as in the second formalism of NSM or in BGS.

This definition of temperature can be discussed in another way. From Eq.(21), for a stationary state of $(A+B)$ extremizing $R(A+B)$, we have

$$\frac{(q_A-1)dS(A)}{\sum_i p_i(A)} + \frac{(q_B-1)dS(B)}{\sum_i p_i(B)} = 0. \tag{24}$$

Now using the above mentioned product joint probability and the relationship $\sum_i p_i^q = Z^{1-q} + (1-q)\beta U$, we get $\frac{(1-q_A)\beta(A)dU(A)}{\sum_i p_i(A)} + \frac{(1-q_B)\beta(B)dU(B)}{\sum_i p_i(B)} = 0$ which suggests following energy nonadditivity

$$\frac{(1-q_A)dU(A)}{\sum_i p_i(A)} + \frac{(1-q_B)dU(B)}{\sum_i p_i(B)} = 0 \tag{25}$$

as the analogue of the additive energy $dU(A) + dU(B) = 0$ of Boltzmann-Gibbs thermodynamics. Eq.(27) and Eq.(28) lead to $\beta(A) = \beta(B)$.

Summarizing the definitions of temperature, we have $\beta_p = Z^{q-1}\beta = Z^{q-1}\frac{\partial S}{\partial U}$ for the normalized expectations $U = \sum_i p_i E_i$ or $U = \sum_i p_i^q E_i / \sum_i p_i^q$ with $\sum_i p_i = 1$, and $\beta_p = Z^{1-q}\beta = Z^{1-q}\frac{\partial S}{\partial U}$ for the normalized expectations $U = \sum_i p_i^q E_i$ with $\sum_i p_i^q = 1$. On the other hand, $\beta_p = \beta = \frac{\partial S}{\partial U}$ can be preserved if and only if unnormalized expectations $U = \sum_i p_i^q E_i$ with $\sum_i p_i = 1$ (or $U = \sum_i p_i E_i$ with $\sum_i p_i^q = 1$) are used. The additive energy model of the nonextensive thermostatistics is justified for $q < 1$ and with the thermodynamic limits.

7 What about the pressure?

If the work in the first law is $dW = PdV$, where P is the pressure and V a certain volume, then the pressure can be calculated through $P = -\left(\frac{\partial F}{\partial V}\right)_T$. If we want the pressure to be intensive, V will be nonadditive. This is a delicate choice to make since nonadditive volume is nontrivial and not so easy to be understood as nonadditive energy or entropy. For a standard system, we tend to suppose additive volume as well as additive particle number. However, in view of the fact that the work dW is in general nonadditive, additive volume implies non intensive pressure P, which is impossible if the equilibrium or stationary state is established in the conventional sense for, e.g. a gas of

photons or of other particles. So, first of all, for the following discussion, let us suppose an intensive pressure P, i.e., $P(A) = P(B)$ at equilibrium or stationarity.

Intensive P implies nonadditive V. If one wants to suppose additive volume (the real one) and particle number N, V must be regarded as an effective volume, as a function of the real volume V_p supposed additive.

In this case, a question arises about the nature of the work dW which is no more proportional to the real volume dV_p. Is it a real work? Our answer is Yes because dW is supposed to contribute to the energy variation dU or dF according to the first law. A possibility to account for this work is that, for a nonextensive or nonadditive system, e.g., a small system or a heterogeneous system, the surface/interface effects on the total energy, compared with the volume effect, are not negligible. When the pressure makes a small volume variation dV_p, the work may be $dW = PdV_p + dW_\sigma$ where dW_σ is the part of work related to the surface/interface variation $d\sigma$. In general, the relationship $dW_\sigma \sim d\sigma$ should depend on the nature and the geometry of the system of interest. If we suppose a simple case where $dW_\sigma = \alpha P d(\sigma^\theta)$ and $\sigma = \gamma V_p^\eta$ (α, γ, η and θ are certain constants), the work can be written as $dW = PdV_p + \alpha\gamma P d(V_p^{\eta\theta}) = Pd[V_p + \alpha\gamma V_p^{\eta\theta}]$ which means $V = V_p + \alpha\gamma V_p^{\eta\theta}$. This example shows that a nonadditive effective volume can be used for nonextensive systems to write the nonadditive work in the form $dW = PdV$, just as in the conventional additive thermodynamics.

7.1 A definition of pressure for NSM

Now let us come back to NSM. To determine the nonadditivity of the effective volume V with additive real volume V_p, one has to choose a given version of NSM with given nonadditivity of entropy and energy. Without lose of generality, the following discussion will be made within the second formalism of NSM. From the entropy definition and nonadditivity Eq.(1) and the energy nonadditivity Eq.(13), we can write, at equilibrium or stationarity,

$$\begin{aligned} dS(A+B) &= [1+(1-q)S(B)]dS(A) + [1+(1-q)S(A)]dS(B) \quad (26) \\ &= \sum_i p_i^q(B)\left[\left(\frac{\partial S(A)}{\partial U(A)}\right)_V dU(A) + \left(\frac{\partial S(A)}{\partial V(A)}\right)_U dV(A)\right] \\ &+ \sum_i p_i^q(A)\left[\left(\frac{\partial S(B)}{\partial U(B)}\right)_V dU(B) + \left(\frac{\partial S(B)}{\partial V(B)}\right)_U dV(B)\right] \end{aligned}$$

$$
\begin{aligned}
&= \sum_i p_i^q(B)\left[\left(\frac{\partial S(A)}{\partial U(A)}\right)_V - \left(\frac{\partial S(B)}{\partial U(B)}\right)_V\right] dU(B) \\
&+ \sum_i p_i^q(B)\left(\frac{\partial S(A)}{\partial U(A)}\right)_V \left(\frac{\partial U(A)}{\partial V(A)}\right)_S dV(A) \\
&+ \sum_i p_i^q(A)\left(\frac{\partial S(B)}{\partial U(B)}\right)_V \left(\frac{\partial U(B)}{\partial V(B)}\right)_S dV(B) \\
&= \beta\left[P(A)\sum_i p_i^q(B)dV(A) + P(B)\sum_i p_i^q(A)dV(B)\right] = 0.
\end{aligned}
$$

Here we have used $\frac{dS(A)}{\sum_i p_i^q(A)} + \frac{dS(B)}{\sum_i p_i^q(B)} = 0$, $\frac{dU(A)}{\sum_i p_i^q(A)} + \frac{dU(B)}{\sum_i p_i^q(B)} = 0$[2], and $\left(\frac{\partial S}{\partial V}\right)_U = \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V$. Then $P(A) = P(B)$ leads to $\frac{dV(A)}{\sum_i p_i^q(A)} + \frac{dV(B)}{\sum_i p_i^q(B)} = 0$, which implies that the quantity $\frac{dV}{\sum_i p_i^q}$ is additive, just as $\frac{dS}{\sum_i p_i^q}$ and $\frac{dU}{\sum_i p_i^q}$.

It can be checked that this kind of calculation is also possible within other versions of NSM as long as the energy nonadditivity is determined by the product joint probability which is in turn a consequence of the entropy nonadditivity Eq.(1) or Eq.(21) postulated for Tsallis entropy.

7.2 About nonadditive photon gas

Now let us suppose a nonadditive photon gas, which is possible when emission body is small. For example, the emission of nanoparticles or of small optical cavity whose surface/interface effect may be important. We have seen in the above paragraph that dU, dS and dV should be proportional to each other. This can be satisfied by $U = f(T)V$ and $S = g(T)V$. In addition, we admit the photon pressure given by $P = \frac{U}{3V} = \frac{1}{3}f(T)$. From the first law $dU = TdS - PdV$, we obtain

$$
V\frac{\partial f}{\partial T}dT + fdV = T(V\frac{\partial g}{\partial T}dT + gdV) - \frac{1}{3}fdV, \tag{27}
$$

which means $\frac{\partial f}{\partial T} = T\frac{\partial g}{\partial T}$ and $\frac{4}{3}f = Tg$ leading to $\frac{1}{3}\frac{\partial f}{\partial T} = \frac{4f}{3T}$ implying

$$
f(T) = cT^4 \tag{28}
$$

where c is a constant. This is the Stefan-Boltzmann law. On the other hand, from the relationship $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$, we obtain $g = \frac{1}{3}\frac{\partial f}{\partial T}$ and $g(T) = bT^3$ where b is a constant. Notice that the above calculation is similar to that

in the conventional thermodynamics. This is because the thermodynamic functions here, though nonadditive, are nevertheless "extensive" with respect to the effective volume. This result contradicts what has been claimed for blackbody radiation on the basis of non intensive pressure[13], and is valid as far as the pressure is intensive.

Is intensive pressure always true? The final answer of course depends on experimental proofs which are still missing as far as we know. If pressure may be non intensive for nonadditive or nonextensive systems, the whole theory of thermodynamics must be reviewed.

8 Conclusion

In summery, we have analyzed all the temperature definitions of NSM we can actually find in the literature. A definition of intensive pressure is proposed for nonextensive thermodynamics by using a nonadditive effective volume. The thermodynamics of a nonadditive photon gas is discussed on that basis. It is shown from purely thermodynamic point of view that the Stefan-Boltzmann law can be valid within NSM in this case.

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