Canonical equilibrium distribution derived from Helmholtz potential

Thomas Oikonomou\textsuperscript{a,b}, G. Baris Bagci\textsuperscript{c} and Ugur Tirnakli\textsuperscript{c}

\textsuperscript{a}Department of Physics, University of Crete, 71003 Heraklion, Hellas

\textsuperscript{b}Institute of Physical Chemistry, National Center for Scientific Research “Demokritos”, 15310 Athens, Hellas

\textsuperscript{c}Department of Physics, Faculty of Science, Ege University, 35100 Izmir, Turkey

Abstract

Plastino and Curado [Phys. Rev. E 72, 047103 (2005)] recently determined the equilibrium probability distribution for the canonical ensemble using only phenomenological thermodynamical laws as an alternative to the entropy maximization procedure of Jaynes. In the current paper we present another alternative derivation of the canonical equilibrium probability distribution, which is based on the definition of the Helmholtz free energy (and its being constant at the equilibrium) and the assumption of the uniqueness of the equilibrium probability distribution. Noting that this particular derivation is applicable for all trace-form entropies, we also apply it to the Tsallis entropy showing that the Tsallis entropy yields genuine inverse power laws.

Key words: Helmholtz free energy, Canonical Equilibrium distribution, Tsallis entropy

1 Introduction

The statistical mechanics tries to explain the thermodynamic behavior of macroscopic systems by relying on the microscopic constituents of the physical system. In this context, it is of utmost importance to obtain the equilibrium distribution associated with a particular entropy structure corresponding to...
the thermodynamic properties of the system. A well-known approach to obtain the equilibrium distribution in statistical mechanics is the entropy maximization procedure of Jaynes (JF) [1]. This maximization procedure in turn stems from the second law of thermodynamics, since entropy attains its maximum value only at equilibrium.

On the other hand, it is necessary to be able to obtain the equilibrium distributions purely on thermodynamic grounds by also including some microscopic ingredients such as microstates in order to have a comparison with the entropy maximization of Jaynes. This necessity is twofold: First of all, it is not straightforward to conclude the validity of second law for generalized entropies [2,3]. Second, it is apparent that even ordinary statistical second law requires a deep and detailed study [4].

The generalized entropies do not change the inherent dynamics so that the first law of thermodynamics (FLT) and its solutions must be certainly preserved i.e., they must be form invariant independent of the entropy structure one adopts [5]. This is also required, since the first law of thermodynamics is the conservation of energy [6]. The second law of thermodynamics too must be preserved in these generalized schemes in order to construct a link between information-theoretic entropy measures and the statistical mechanics. In short, then, the generalized entropy measures must conform to the thermodynamical laws in order to be considered useful in statistical mechanics, instead of being solely useful for information theoretical approaches.

The paper is organized as follows. The next section outlines how to obtain canonical equilibrium probability distributions through the requirement of a constant Helmholtz potential \( F \) and the assumption of the uniqueness of the aforementioned distribution. This approach is then extended to all trace-form entropies and applied to the Tsallis entropy measure [7]. Conclusions are presented in the last section.

2 Thermodynamics and Equilibrium Distributions

The first law of thermodynamics for reversible processes reads

\[
dU = T \, dS - P \, dV + \mu \, dN ,
\]

(1)

where \( U \) is the internal energy, \( S \) is the entropy and \( T \) is the temperature, while \( P \) and \( V \) denote pressure and volume, respectively. The term \( \mu \) is the chemical potential associated with the change in the number of particles \( N \).

A particular case of great interest in thermodynamics is when \( U = U(S, V, N) \) is a homogeneous function of first degree [6]. In this case, Eq. (1) can be
explicitly solved, independent from the analytical expressions of $T$, $P$ and $\mu$, yielding
\[ U = TS - PV + \mu N. \] (2)

The equation above is referred to as the Euler equation of thermodynamics. In terms of the free energy $F = F(S, V, N)$ (also called the Helmholtz potential), the above equation can simply be rewritten as
\[ F = U - TS. \] (3)

Keeping in mind that $F = -PV + \mu N$, Eq. (3) is equivalent to Eq. (2). This definition of Helmholtz potential $F$ is also in accordance with the rest of the thermodynamical potentials. For example, the Gibbs potential $G$ is equal to $F + PV$ so that one obtains the well known relation $G = \mu N$. We can further rewrite Eq. (3) as
\[ S = \beta U - \beta F. \] (4)

where $1/\beta \equiv T$.

Up to this point, all these equations contain nothing related to the statistical nature of the physical system under investigation. In order to introduce in Eq. (4) statistics, one needs some statistical ingredients. We then consider the very definition of Boltzmann-Gibbs (BG) statistical entropy, which reads (setting $k_B = 1$)
\[ S_{\text{BG}} = \sum_i p_i \ln(1/p_i), \] (5)

and the definition of the internal energy in terms of the microscopic probabilities i.e., $U = \sum_i p_i \varepsilon_i$, where $p_i$ is the probability of the corresponding $i$th microstate and $\varepsilon_i$ is the microstate energies.

Then, when the Helmholtz potential is constant, Eq. (4) can be rewritten as
\[ \sum_i p_i \ln(1/p_i) = \beta \sum_i p_i \varepsilon_i - \beta \sum_i p_i F, \] (6)

where we also assumed probability normalization as usual. Eq. (6) naturally yields to the relation below
\[ \sum_i p_i \left[ \ln(1/p_i) - \beta \varepsilon_i + \beta F \right] = 0. \] (7)

However, it is not trivial to obtain the equilibrium probability distribution $p_i^*$ from the equation above, since whole summation might be equal to zero, and not only one singled out term within the summation. On the other hand, assuming the existence of the thermodynamic state of the stationary equilibrium, we can invoke the uniqueness of the aforementioned state and therefore of the corresponding equilibrium distribution. Due to the former assumption i.e., the existence of the equilibrium state, we have $p_i^* \neq 0$, since the condition
$p^*_i = 0$ contradicts with the existence of an equilibrium state. The uniqueness of the thermodynamic state of equilibrium and hence of the equilibrium distribution implies the trivial solution to Eq. (7), equating the term in the brackets to zero i.e.,

$$\ln \left( \frac{1}{p^*_i} \right) - \beta \varepsilon_i + \beta F = 0. \tag{8}$$

It is then obvious that the equation above yields an equilibrium distribution and this is all one needs, since the equilibrium distribution (and the state of equilibrium) is unique, so that having one solution of Eq. (7) is tantamount to obtaining the only solution indeed. Therefore, we finally have the following equilibrium distribution

$$p^*_i = \exp \left( -\beta (\varepsilon_i - F) \right), \tag{9}$$

which is the canonical equilibrium distribution. Moreover, note that identifying $e^{-\beta F}$ as the canonical partition function $Z$, one obtains another well known relation i.e., $F = -T \ln Z$ (remember that we set Boltzmann constant $k_B$ to unity). We observe that the canonical distribution $p^*_i$ satisfies Eq. (1) and the FLT in Eq. (1).

Some remarks are in order: although mathematically simple, the above calculations are novel in the sense that it does not make use of ordinary entropy maximization procedure put forth by Jaynes. Apart from the definitions of entropy and internal energy in terms of microscopic constituents, it relies solely on the definition of Helmholtz free energy and the existence and the uniqueness of the thermodynamic equilibrium state. Moreover, obtained in this manner, one sees that the canonical BG-equilibrium distribution, apart from the multiplicative factor $\beta$, is of exponential form, where the exponent is formed by shifting the microstate energies $\varepsilon_i$ by the constant (and minimum at the canonical equilibrium state) Helmholtz free energy $F$.

The above calculation can easily be extended to generalized entropy measures, since these definitions are information-theoretic and not supposed to violate any of the ingredients used in the above derivation. In order to extend the formalism above to generalized trace-form entropies, we study the following statistical representation of the thermodynamic entropy i.e., $S = \langle \Lambda(1/p_i) \rangle_{\text{lin}}$, where $\langle (\cdots) \rangle_{\text{lin}} = \sum_i p_i (\cdots)_i$ is the arithmetic expectation value of the quantity $(\cdots)_i$, $p_i$ are the microstate probabilities, and assuming that the internal energy is given statistically as $U = \langle \varepsilon_i \rangle_{\text{lin}}$, where $\varepsilon_i$ are the microstate energies. Similar to Eq. (5), we now write

$$\langle \Lambda(1/p_i) \rangle_{\text{lin}} = \langle \beta \varepsilon_i \rangle_{\text{lin}} - \langle \beta F \rangle_{\text{lin}} \quad \Longrightarrow \quad \langle \Lambda(1/p_i) - \beta \varepsilon_i + \beta F \rangle_{\text{lin}} = 0. \tag{10}$$

Note that $\Lambda(1/p_i)$ is a generic function, which can be any monotonic increasing function compatible with the linear averaging scheme, be it ordinary or generalized logarithm. From the relation above, we can obtain the equilibrium
probability distribution \( p_i \), which is compatible with FLT, namely

\[
p_i^\star = \frac{1}{\Lambda^{-1}(\beta(\varepsilon_i - F))} = \frac{[\Lambda^{-1}(\beta \varepsilon_i)]^{-1}}{Z},
\]

\[
S = \beta(U - F) = \sum_i p_i^\star [\beta \varepsilon_i \oplus \Lambda \Lambda(Z)],
\]

where \( x \oplus \Lambda y := \Lambda(\Lambda^{-1}(x)\Lambda^{-1}(y)) \) (\( x, y \geq 0 \)) and \( \oplus_{\Lambda \rightarrow \ln} \rightarrow + \) is the ordinary addition operation. \( Z \) in Eq. (11a) represents the partition function, defined implicitly through Eq. (11b). As can be seen, its analytical expression depends on the function set \{\Lambda, \Lambda^{-1}\}. If we now substitute the probability distribution given by Eq. (11a) into the left hand side of Eq. (4), it reproduces indeed the Euler equation.

2.1 Tsallis entropy

An entropy measure of current interest is the Tsallis entropy [7,9]. This entropy can be constructed by choosing

\[
\Lambda(q, x) \equiv \ln_q(x) = \frac{x^{1-q} - 1}{1-q}, \quad \Lambda^{-1}(q, x) \equiv \exp_q(x) = \left[1 + (1-q)x\right]_+^{1/q} (12)
\]

where \([x]_+ = \max\{0, x\}\), so that the structure \( S \) tends to the following \( q \)-entropy

\[
S_q = \sum_i p_i \ln_q(1/p_i) = \sum_i p_i^q - 1
\]

The equilibrium probability distribution, according to Eqs. (11a) and (11b), takes the form

\[
\frac{1}{p_i^\star} = \exp_q \left( \beta(\varepsilon_i - F) \right) = Z_q \exp_q(\beta \varepsilon_i), \quad \text{with} \quad Z_q = \exp_q \left( -\frac{\beta F}{1 + (1-q)\beta U} \right).
\]

We note that this equilibrium distribution structure is exactly the one obtained through the entropy maximization procedure of the Tsallis entropy with linear constraints [7,10]. It is also worth noting that this method apparently does not apply to non-trace form entropies.

3 Conclusions

In this work, we derived the well-known canonical equilibrium probability distribution by using the microscopic definitions of entropy and internal energy.
together with the definition of the Helmholtz free energy (and its being constant at the equilibrium) and the existence/uniqueness of the state of equilibrium. Providing a generalization of this derivation to all trace-form entropies, we also obtained the stationary equilibrium probability distribution of the Tsallis entropy which is found to be an inverse power law distribution. This work can be considered as an alternative to both the entropy maximization procedure of Jaynes [1] and recently proposed procedure of Plastino et al. [11,12,13,14,15] based on the phenomenological laws of thermodynamics.

Acknowledgments

We thank an anonymous reviewer for his/her very explanatory remarks. T.O. acknowledges partial support by the THALES Project MACOMSYS, funded by the ESPA Program of the Ministry of Education of Hellas.

References

[1] Jaynes E.T., Phys. Rev. 106 (1957) 620; 108 (1957) 171.
[2] Abe S. and Rajagopal A. K., Phys. Rev. Lett. 91 (2003) 120601.
[3] Bashkirov A. G., Theor. Math. Phys. 149 (2006) 1559.
[4] d’Abramo G., Phys. Lett. A 374 (2010) 1801.
[5] Tsallis C., Mendes R. S. and Plastino A. R., Physica A 261 (1998) 534.
[6] Callen H. B., Thermodynamics and an Introduction to Thermostatistics, (Wiley and Sons, New York, 1985) pp.59-60.
[7] Tsallis C., Introduction to nonextensive statistical mechanics: approaching a complex world, (Springer, New York, 2009) pp. 66-84.
[8] Note that in this case the functions \( T = T(S, V, N) \), \( P = P(S, V, N) \) and \( \mu = \mu(S, V, N) \) are homogeneous of degree zero, as a consequence of the degree of homogeneity of \( U = U(S, V, N) \) being one.
[9] Bagci G. B. and Tirnakli U., Chaos 19 (2009) 033113.
[10] Oikonomou T. and Bagci G. B., Phys. Lett. A 374 (2010) 2225.
[11] Plastino A. and Curado E. M. F., Phys. Rev. E 72 (2005) 047103.
[12] Plastino A. and Curado E. M. F., Physica A 365 (2006) 24.
[13] Curado E. M. F. and Plastino A., Physica A 386 (2007) 155.
[14] Plastino A., Plastino A. R., Curado E. M. F. and Casas M., Entropy 10 (2008) 124.

[15] Curado E. M. F., Nobre F. D. and Plastino A., Physica A 389 (2010) 970.