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What are the numbers that experiments provide?

···One who brings
A mind not to be changed by place or time.
The mind is its own place, and in itself
Can make a heaven of hell, a hell of heaven.

Paradise Lost (1658-1665), John Milton.

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ABSTRACT

On the basis of a recently proposed generalization of Boltzmann-Gibbs Statistical Mechanics and Thermodynamics, we argue that the numbers provided by experimental measurements are to be interpreted as q-expectation values $\langle\hat{O}\rangle_q \equiv Tr\hat{\rho}^q\hat{O}$, where $\hat{O}$ is the observable, $\hat{\rho}$ is the density operator and the real index q characterizes the corresponding (generically nonextensive) entropy and depends on some general characteristics of the system. The familiar association with the mean value $\langle\hat{O}\rangle_1 \equiv Tr\hat{\rho}\hat{O}$ as well as the extensivity of standard additive observables are recovered only for the Boltzmann-Gibbs particular case $(q=1), \forall\hat{\rho}$, or for pure states, $\forall q$. This interpretation leaves untouched the standard additivity and conservation of energy for *pure states*, but, unless $q=1$, modifies the definition and additivity of internal energies for *statistical mixtures*.

Key-words: *Measure; Entropy; Emsembles; Generalized Statistical Mechanics and Thermodynamics.*

The fundamental connection between the experiment and the theory in any quantitative Science relies (always did and always will!) on the *mathematical object* to which is to be associated the *number provided by the experiment.* Our purpose here is to show that this central question is – curiously enough! – related to Ludwig Boltzmann's thermostatistics, its subsequent formalization by Josiah Willard Gibbs, and a recently proposed [1] generalization of Boltzmann-Gibbs (BG) Statistical Mechanics and Thermodynamics.

Let us briefly recall that the (Hilbert space) full description of an arbitrary quantum system can be done (see, for instance, [2]) by giving its *density operator* $\hat{\rho}$ which satisfies

$$Tr\hat{\rho} = 1 \tag{1}$$

If and only if the system is in a *pure state* (which is the typical situation in Quantum Mechanics) we verify that $\hat{\rho}^2 = \hat{\rho}$, i.e., $\hat{\rho}$ is a projector (hence, if diagonalized, $\hat{\rho}$ presents zeros everywhere excepting *one* diagonal value which equals *unity*); in other words, the system is in a *perfectly known* vector of the Hilbert space (this vector might or not be an eigenvector of a particular observable, say the Hamiltonian $\hat{\mathcal{H}}$). If the state is not a pure one, then we have a *statistical mixture* (if diagonalized, $\hat{\rho}$ presents in its diagonal the probabilities $\{p_i\}$ which satisfy $\sum_{i=1} p_i = 1$). In this sense, the pure state is that particular instance of statistical mixture where all but one probability vanish (say $p_\ell = 1$, and $p_i = 0, \forall i \neq \ell$).

A typical quantum experiment consists in an apparatus devised for measuring an observable $\hat{O}$ of a given physical system. If the system state is a pure one (for simplicity we shall assume it to be an *eigenvector* of the observable $\hat{O}$), then, as convincingly argued in any good Quantum Mechanics textbook, the number provided by the experiment is to be interpreted as one of the *eigenvalues* of $\hat{O}$. The situation is more subttle when the system state is a statistical mixture characterized by $\hat{\rho}$ (e.g., for a typical calorimetric experiment, where the system is thermalized at temperature T). In this complex case (which is that of Gibbs-like ensembles, for instance,) textbooks normally associate the number provided by the experiment with the mean value $Tr\hat{\rho}\hat{O}$. We shall argue here that this is only a *particular* (though extremely ubiquitous, hence important) case. We propose instead to generically interpret the experimental result as the *q-expectation value*

$$\langle \hat{O} \rangle_q \equiv Tr\hat{\rho}^q \hat{O} \tag{2}$$

where the index q is a real number which depends on some generic characteristics of the system we shall discuss later on. This new interpretation

(i) is irrelevant for pure states since then $p_\ell = 1$, hence $p_\ell = p_\ell^q = 1$, $\forall q$;

(ii) recovers the usual interpretation for all systems whose index $q = 1$.

Remark (i) implies, for instance, that concepts such as the conservation of the total energy of an isolated system, as well as the additivity of its parts, *remain untouched if the state is a pure one. But, unless $q = 1$, this is not true anymore if we are facing a generic statistical mixture.* Although we shall come back onto this problem later on, we can already advance that, if we have a composite system $\Sigma \cup \Sigma'$, the subsystems Σ and Σ' being *independent* (i.e., $\hat{\rho}_{\Sigma\cup\Sigma'} = \hat{\rho}_\Sigma \otimes \hat{\rho}_{\Sigma'}$, hence $p_{ij}^{\Sigma\cup\Sigma'} = p_i^\Sigma p_j^{\Sigma'}, \forall (i,j)$) and *energetically noninteracting* (i.e., $\hat{\mathcal{H}}_{\Sigma\cup\Sigma'} = \hat{\mathcal{H}}_\Sigma + \hat{\mathcal{H}}_{\Sigma'}$, hence $\varepsilon_{ij}^{\Sigma\cup\Sigma'} = \varepsilon_i^\Sigma + \varepsilon_j^{\Sigma'}$, where the ε's are the eigenvalues of the respective Hamiltonians), then

$$\begin{aligned}
\langle \hat{\mathcal{H}}_{\Sigma\cup\Sigma'} \rangle_1 &= Tr\hat{\rho}_{\Sigma\cup\Sigma'}\hat{\mathcal{H}}_{\Sigma\cup\Sigma'} \\
&= Tr(\hat{\rho}_\Sigma \otimes \hat{\rho}_{\Sigma'})(\hat{\mathcal{H}}_\Sigma + \hat{\mathcal{H}}_{\Sigma'}) \\
&= Tr[(\hat{\rho}_\Sigma \otimes \hat{\rho}_{\Sigma'})\hat{\mathcal{H}}_\Sigma] + Tr[(\hat{\rho}_\Sigma \otimes \hat{\rho}_{\Sigma'})\hat{\mathcal{H}}_{\Sigma'}] \\
&= (Tr\hat{\rho}_\Sigma\hat{\mathcal{H}}_\Sigma)(Tr\hat{\rho}_{\Sigma'}) + (Tr\hat{\rho}_{\Sigma'}\hat{\mathcal{H}}_{\Sigma'})(Tr\hat{\rho}_\Sigma) \\
&= Tr\hat{\rho}_\Sigma\hat{\mathcal{H}}_\Sigma + Tr\hat{\rho}_{\Sigma'}\hat{\mathcal{H}}_{\Sigma'} \\
&\equiv \langle \hat{\mathcal{H}}_\Sigma \rangle_1 + \langle \hat{\mathcal{H}}_{\Sigma'} \rangle_1
\end{aligned} \tag{3}$$

whereas generically

$$\begin{aligned}\langle\hat{\mathcal{H}}_{\Sigma\cup\Sigma'}\rangle_q &\equiv Tr\hat{\rho}^q_{\Sigma\cup\Sigma'}\hat{\mathcal{H}}_{\Sigma\cup\Sigma'}\\ &= (Tr\hat{\rho}^q_\Sigma\hat{\mathcal{H}}_\Sigma)(Tr\hat{\rho}^q_{\Sigma'}) + (Tr\hat{\rho}^q_{\Sigma'})(Tr\hat{\rho}^q_\Sigma)\\ &= \langle\hat{\mathcal{H}}_\Sigma\rangle_q(Tr\hat{\rho}^q_{\Sigma'}) + \langle\hat{\mathcal{H}}_{\Sigma'}\rangle_q(Tr\hat{\rho}^q_\Sigma)\\ &\neq \langle\hat{\mathcal{H}}_\Sigma\rangle_q + \langle\hat{\mathcal{H}}_{\Sigma'}\rangle_q \end{aligned} \tag{4}$$

(Remark that $Tr\hat{\rho}^{\,q}$ equals unity *only* if we have a pure state $(\forall q)$ or if $q = 1(\forall\hat{\rho})$). Eq. (2) can be rewritten as follows

$$\langle\hat{O}\rangle_q = Tr\hat{\rho}\rho^{q-1}\hat{O} = \langle\hat{\rho}^{q-1}\hat{O}\rangle_1 \tag{5}$$

Let us then stress that the q-expectation value $\langle\hat{O}\rangle_q$ ***is not a mean value of*** $\hat{O}$ (unless $q = 1$ or the state is a pure one), but it is *always* the mean value of $\hat{\rho}^{q-1}\hat{O}$. Consequently, if we consider a real number λ and the operator $\hat{O} \equiv \lambda\hat{1}$ where $\hat{1}$ is the identity, we have that $\langle\lambda\hat{1}\rangle_q$ *generically differs from* λ (it coincides only if $\lambda = 0, \pm\infty$ or if $q = 1$ or if the state is a pure one). A trivial though unfamiliar corollary is that generically $\langle\hat{1}\rangle_q \neq 1$. Let us now address the following questions: where q comes from?, why proposing the q-expectation values as the right connection with experimental values?, what are the physical systems having $q \neq 1$?

We proposed in 1988 [1] the following generalization for the entropy:

$$S_q \equiv k\frac{1-\sum_i p_i^q}{q-1} \qquad (q \in I\!R) \tag{6}$$

where k is a conventional positive constant. Eq. (6) can be written as follows in terms of $\hat{\rho}$:

$$S_q = k\frac{1-Tr\hat{\rho}^{\,q}}{q-1} = \langle\hat{S}_q\rangle_q \tag{7}$$

with

$$\hat{S}_q \equiv -k\frac{\hat{\rho}^{\,1-q}-1}{1-q} \tag{8}$$

In the $q \to 1$ limit we recover the standard Boltzmann-Gibbs-Shannon entropy $S_1 = -k_B \sum_i p_i \ln p_i = -k_B Tr\hat{\rho}\ln\hat{\rho}$, and the entropy operator $\hat{S}_1 = -k_B \ln\hat{\rho}$.

If we define the following *generalized logarithmic function* (which naturally appears, for instance, in the replica trick used in the discussion of spin-glasses)

$$\ln_q x \equiv \frac{x^{1-q}-1}{1-q} \qquad (\forall x) \tag{9}$$

we verify that

$$\ln_1 x \equiv \lim_{q\to 1} \ln_q x = \ln x \tag{10}$$

and that Eqs. (6) and (8) can be respectively rewritten as follows:

$$S_q = -k \sum_i p_i^q \ln_q p_i \tag{11}$$

and

$$\hat{S}_q = -k \ln_q \hat{\rho} \tag{12}$$

S_q vanishes for any pure state and is positive for any other statistical mixture; it is concave (convex) if $q > 0$ ($q < 0$), $\forall\hat{\rho}$ (this is an important property since it guarantees the thermodynamic stability of the system). But, in contrast with the standard entropy, S_q is generically not additive (*nonextensive*). Indeed, it is straightforward to show that, for the system $\Sigma \cup \Sigma'$ mentioned before, the assumption $\hat{\rho}_{\Sigma\cup\Sigma'} = \hat{\rho}_\Sigma \otimes \hat{\rho}_{\Sigma'}$ implies

$$\frac{S_q^{\Sigma\cup\Sigma'}}{k} = \frac{S_q^\Sigma}{k} + \frac{S_q^{\Sigma'}}{k} + (1-q)\frac{S_q^\Sigma}{k}\frac{S_q^{\Sigma'}}{k} \tag{13}$$

and

$$\frac{\hat{S}_q^{\Sigma\cup\Sigma'}}{k} = \frac{\hat{S}_q^\Sigma}{k} + \frac{\hat{S}_q^{\Sigma'}}{k} + (q-1)\frac{\hat{S}_q^\Sigma}{k}\frac{\hat{S}_q^{\Sigma'}}{k} \tag{14}$$

Let us establish now an interesting property which follows along the lines of Eq. (4). If we go back to the system $\Sigma\cup\Sigma'$ and consider any observable satisfying $\hat{O}_{\Sigma\cup\Sigma'} = \hat{O}_\Sigma + \hat{O}_{\Sigma'}$, we straightforwardly obtain

$$\begin{aligned} \langle \hat{O}_{\Sigma\cup\Sigma'}\rangle_q &= \langle \hat{O}_\Sigma\rangle_q (Tr\hat{\rho}^q_{\Sigma'}) + \langle \hat{O}_{\Sigma'}\rangle_q (Tr\hat{\rho}^q_{\Sigma}) \\ &= \langle \hat{O}_\Sigma\rangle_q + \langle \hat{O}_{\Sigma'}\rangle_q + (1-q)\left[\langle \hat{O}_\Sigma\rangle_q S_q^{\Sigma'}/k + \langle \hat{O}_{\Sigma'}\rangle_q S_q^{\Sigma}/k\right] \end{aligned} \tag{15}$$

where we have used definition (6). This relation once again exhibits that, for arbitrary observables, extensivity is obtained only if $q = 1$ (for any states), or for pures states ($\forall q$) since, for them, the entropy vanishes.

Following along the lines of Gibbs (see also [3, 4]) let us deduce now the equilibrium distribution associated with appropriately generalized canonical and grand-canonical ensembles. We shall optimize S_q given by (6) under the constraints given by Eq. (1) as well as by

$$\langle \hat{O} \rangle_q \equiv Tr \hat{\rho}^q \hat{O}_m = O_q^{(m)} \qquad (m = 0, 1, 2, \cdots, M) \tag{16}$$

where $O_q^{(m)}$ are *finite* fixed quantities ($\hat{O}_0 \equiv \hat{\mathcal{H}}$ and $O_q^{(0)} \equiv U_q \equiv$*generalized internal energy*). $M = 0$ corresponds to the canonical ensemble, and $M \geq 1$ to the grand-canonical one. We straightforwardly obtain the following generalized equilibrium distribution

$$\hat{\rho}_{eq} = \frac{\left[1 - (1-q)\beta(\hat{\mathcal{H}} - \sum_{m=1}^{M} \mu_m \hat{O}_m)\right]^{\frac{1}{1-q}}}{Z_q} \tag{17}$$

with

$$Z_q \equiv Tr \left[1 - (1-q)\beta(\hat{\mathcal{H}} + \sum_{m=1}^{M} \mu_m \hat{O}_m)\right]^{\frac{1}{1-q}} \tag{18}$$

In the limit $q \to 1$ we recover the well known BG equilibrium distribution

$$\hat{\rho}_{eq} = \frac{e^{-\beta(\hat{\mathcal{H}} - \sum_{m=1}^{M} \mu_m \hat{O}_m)}}{Z_1} \tag{19}$$

with

$$Z_1 \equiv Tr \; e^{-\beta(\hat{\mathcal{H}} - \sum_{m=1}^{M} \mu_m \hat{O}_m)} \tag{20}$$

If we define the following *generalized exponential function*

$$e_q^x \equiv [1 + (1-q)x]^{\frac{1}{1-q}} \qquad (\forall x) \tag{21}$$

we verify that

$$e_1^x \equiv lim_{q \to 1} e_q^x = e^x \tag{22}$$

and that Eqs. (17) and (18) can be respectively rewritten as follows:

$$\hat{\rho}_{eq} = \frac{e_q^{-\beta(\hat{\mathcal{H}}-\sum_{m=1}^{M}\mu_m\hat{O}_m)}}{Z_q} \tag{23}$$

with

$$Z_q \equiv Tr\; e_q^{-\beta(\hat{\mathcal{H}}-\sum_{m=1}^{M}\mu_m\hat{O}_m)} \tag{24}$$

It is worthy to stress that, $\forall q$,

$$\ln_q e_q^x = e_q^{\ln_q x} = x \qquad (\forall x) \tag{25}$$

Following along the lines of standard Statistical Mechanics, it can be quite straightforwardly shown (by introducing $\beta \equiv 1/kT$) that, $\forall q$,

$$\frac{1}{T} = \frac{\partial S_q}{\partial U_q} \tag{26}$$

$$\frac{\mu_m}{T} = -\frac{\partial S_q}{\partial O_q^{(m)}} \qquad (m = 1, 2, \cdots, M) \tag{27}$$

$$U_q = -\frac{\partial}{\partial\beta}\frac{Z_q^{1-q}-1}{1-q} = -\frac{\partial}{\partial\beta}\ln_q Z_q \tag{28}$$

$$O_q^{(m)} = \frac{1}{\beta}\frac{\partial}{\partial\mu_m}\frac{Z_q^{1-q}-1}{1-q} = \frac{1}{\beta}\frac{\partial}{\partial\mu_m}\ln_q Z_q \qquad (m = 1, 2, \cdots, M) \tag{29}$$

$$F_q \equiv U_q - TS_q - \sum_{m=1}^{M}\mu_m O_q^{(m)} = -\frac{1}{\beta}\frac{Z_q^{1-q}-1}{1-q} = -\frac{1}{\beta}\ln_q Z_q \tag{30}$$

Although we have not attempted a proof, the Gibbs-Duhem relation is hopefully generalized as follows:

$$U_q - TS_q - \sum_{m=1}^{\bar{M}}\mu_m O_q^{(m)} = 0 \tag{31}$$

where $\bar{M}$ corresponds to the number of observables which completely *exhausts* the thermodynamic description of the system (hence $\bar{M} > M$).

Let us now briefly list our arguments in favour of the q-expectation values being the mathematical objects to be associated with the experimental data.

(i) We have seen above a *very remarkable* fact: the entire formalism of Thermodynamics can be extended to be nonextensive *without loosing its Legendre-transform structure.*

This transformation seems to play in Thermodynamics the crucial role that the Lorentz transformation plays in Relativity. E.M.F. Curado (private communication) made a variety of heuristic trials with large classes of entropic forms: the present formalism seems to be the *unique* which preserves the standard Legendre-transform structure.

(ii) The Ehrenfest theorem remains *form-invariant*, $\forall q$, as follows [4]:

$$\frac{d\langle\hat{O}\rangle_q}{dt} = \frac{i}{\hbar}\langle[\hat{\mathcal{H}},\hat{O}]\rangle_q \tag{32}$$

Consequently, as first pointed to me by A.R. Plastino (private communication), if $[\hat{\mathcal{H}},\hat{O}] = 0$, it is precisely the q-expectation value $\langle\hat{O}\rangle_q$ which is a *constant of the motion*, and not $\langle\hat{O}\rangle_1$.

(iii) The Shannon theorem can be simply generalized [3], and its form makes naturally appear prefactors of the type (probability)^q (see also [5]).

(iv) The generalized entropy S_q, together with the q-expectation values, satisfies Jaynes *Information Theory duality relations*[4]; these relations are necessary for an entropy to be considered a measure of the (lack of) information. In fact this point is related with the above point (i).

(v) The *fluctuation-dissipation theorem* can be naturally generalized [6], and the *Onsager reciprocity theorem* can be shown to remain *form-invariant* [7], $\forall q$, if the q-expectation values are assumed to be the relevant quantities.

(vi) The q-expectation values enable the retrieval, from a variational principle, of *Lévy distributions* [8] as well as of the Student's-distribution and the r-distribution [9].

(vii) Barlow [10] and Toulouse [11] have emphasized the necessity, in the theoretical approach of the *physiology of perceptions*, of enhancing the weight of the events that are *rare*. More specifically, they argue about the necessity of having weights proportional to $-\ln p_i$. We can easily see that a weight p_i^q enhances the rare (frequent) events if $q < 1$ ($q > 1$). In the $q \to 0$ limit we verify, for W possible microscopic configurations, that [5]

$$\frac{S_q}{k} = \frac{1 - \sum_{i=1}^{W} p_i^q}{q-1} \sim (W-1) - q\sum_{i=1}^{W}(-\ln p_i) \tag{33}$$

and

$$\langle \hat{O} \rangle_q \equiv \sum_{i=1}^{W} p_i^q O_i \sim \sum_{i=1}^{W} O_i - q\sum_{i=1}^{W} O_i(-ln p_i) \tag{34}$$

We remark that, excepting for constant terms, the weights precisely are $-\ln p_i$ as desired.

(viii) The q-expectation values enable satisfactory discussion for a paradox (*"The envelope game"*) in the Theory of Statistical Inference [12] and the theoretical approach of *dilemmas* in the Theory of Financial Decisions [5].

Let us finally briefly address what kind of systems correspond to $q \neq 1$. The crucial point is whether the range of the relevant interactions is small compared with the size of the system, and whether the range of the microscopic memory is small compared with the time of observation. If *both* conditions are satisfied, then $q = 1$. If one or both of them are violated, then one expects $q \neq 1$. Consistently, one expects $q \neq 1$ if the space-time of the system is (multi) fractal-like. Typical $q \neq 1$ situations are:

(i) d-dimensional gravitational-like systems [13, 14] (two-body attractive interactions with a potential which behaves, at long distances, as $r^{-\alpha}$). The relevant BG integrals *diverge* if $0 < \alpha < d$ [13, 15]; the difficulties hopefully disappear if $q < q_c(d, \alpha)$ where $q_c(d, \alpha) < 1$. For $(d, \alpha) = (3, 1)$ (Newtonian gravitation), it is [14, 15] $q_c(3, 1) = 7/9$.

(ii) d-dimensional long-range magnetism (e.g., spin 1/2 Ising ferromagnet) with $J_{ij} = J r_{ij}^{-(d+\delta)} (d + \delta \geq 0)$. The relevant sums *diverge* if $\delta \leq 0$ (hence the BG critical point

k_BT_c/J *diverges*) [15, 16]. In analogy with the gravitational case, one expects [15] all difficulties to disappear if $q < q_c(d,\delta)$ with $q_c(d,\delta) < 1$ (obviously, it is $q_c(d+\delta) = 1$ if $\delta \geq 0$).

(iii) Nonionized Hydrogen atom. Its BG partition function *diverges*; consistently, no prescription exists for calculating its specific heat. To the best of our knowledge, this very relevant (at least theoretically) point has never been satisfactorily focused in the available Statistical Mechanics textbooks (in fact, generally it is not even mentioned!). It has been recently shown that, if $q < 1$, the specific heat becomes a *computable* quantity, being finite almost everywhere.

(iv) Anomalous diffusion phenomena *(superdiffusion)* following Lévy-like distributions. It is impossible [18] to derive Lévy distributions from a BG entropic variational principle using simple (i.e., acceptable *a priori*) constraints. In contrast, this becomes possible [8, 19], as already mentioned, for $q > q_c(d)$ where $q_c(d) > 1$ (e.g., $q_c(1) = 5/3$). More precisely, whenever the visiting probability behaves, at long distances, as $r^{-(d+\gamma)}$ with $0 < \gamma < 2$, a strict relationship can be established between q, d and γ (e.g., for $d = 1$ and $q > 5/3$, $q = (3+\gamma)(1+\gamma)$ [8]). This fact yields a statistical-mechanical foundation of a variety of Lévy-like phenomena occurring in Nature, such as superdiffusion of CTAB micelles dissolved in salted water (where $1.5 < \gamma < 2$) [20], heartbeat histograms (where $\gamma = 1.7$) [21], and others [22].

(v) Line tension phenomena at wetting. If the range of the forces is long enough, relevant thermodynamic quantities such as the boundary tension *diverge* [23]. Once more, in analogy with the gravitational case, one expects the problem to be overcome if q is sufficiently below unity.

Summarizing, we have presented here a variety of mathematical and physico-chemical arguments which support the need and convenience for generalizing Boltzmann-Gibbs

Statistical Mechanics and Thermodynamics. Special attention has been given to the mathematical object which is to be identified with experimental data; it has been argued (convincingly, we hope!) that this is $\langle \hat{O} \rangle_q \equiv Tr \hat{\rho}^q \hat{\rho}$. This proposal recovers the usual concept ($\langle \hat{O} \rangle_1 \equiv Tr \hat{\rho} \hat{O}$) for $q = 1$ (for *both* pure and statistical mixtures) as well as for pure states (for *all* values of q). But it differs from the usual concept if $q \neq 1$ *and* the state is not a pure one. As an important corollary we have that, for pure states and all values of q, the standard conservation of the energy as well as the additivity of its parts remain unchanged; but, if $q \neq 1$ *and* we have a statistical mixture, the quantity which is conserved is a conveniently redefined internal energy and the standard additivity of its parts is violated.

The present attempt to enlarge the frontiers of the magnificent work of Ludwig Boltzmann is, at the occasion of the 150^{th} anniversary of his birth, my homage to his geniality.

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