An ideal mixture of parahydrogen (with nuclear spin $K = 0$) and orthohydrogen (with $K = 1$), in statistical weights $1/4$ and $3/4$, respectively, is used as a test ground for the existence of non-extensivity in chemical physics. We report on a new bound on the non extensivity parameter $q - 1$ that characterizes generalized thermostatistics à la Tsallis. This bound is obtained on the basis of laboratory measurements of the specific heat of hydrogen. Suggestions are advanced for the performance of improved measurements.

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In the last twelve years a considerable amount of effort has been expended investigating systems for which the traditional Boltzmann-Gibbs-Shannon (BGS) statistical treatment, for a variety of circumstances, seems to fail, at least in some respects. The so-called Tsallis non-extensive thermostatistics (TT) has played a prominent role in these endeavors. TT is characterized by a real parameter $q$, such that $q = 1$ yields the standard BGS treatment. The first successful applications of such formalism was the finding of a non-divergent, physical distribution function for stellar polytropes. A significant TT step was that of Boghosian. His analysis of the specific heat of hydrogen. Suggestions are advanced for the relaxation of a two dimensional pure electron plasma yielded a $q$-value quite different from unity.

Many subsequent advances, both on the basic theory and in different applications, have transformed this non-extensive treatment into a new paradigm for statistical mechanics. TT is based upon Jaynes’ MaxEnt approach to statistical mechanics. Its main feature is that of replacing the conventional Shannon logarithmic information measure $S$ (subject to appropriate constraints derived from the available a priori knowledge) by Tsallis’ non-extensive measure (we normalize all quantities to $k = 1$)

$$S_q = (q - 1)^{-1} \sum_{i=1}^{W} (p_i - p_i^q), \quad q \in \mathbb{R}, \quad (1)$$

where the set $\{p_i\}$, to be obtained by recourse to Jaynes’ variational procedure, yields the probability distribution associated to the relevant $W$ microstates. Notice that for $q = 1$ one has $S_q \equiv S$.

$S_q$ is non-extensive on account of the fact that, for a system composed of two noninteracting subsystems $(A, B)$

$$S_q(A + B) = S_q(A) + S_q(B) + (1 - q)S_q(A)S_q(B), \quad (2)$$

so that $q$ measures the degree of non-extensivity. During almost 10 years, the concomitant non extensive thermostatistical considerations were based upon the theoretical framework of Curado and Tsallis. Nowadays, it is believed that this framework has been superseded by a new one, called “the normalized one”, advanced in and formalized in great detail by Tsallis, Mendes and Plastino, which seems to exhibit important advantages.

This normalized treatment, in turn, has been considerably improved by the so-called “Optimal Lagrange Multipliers” (OLM) approach. The OLM treatment seems to provide one with a natural bridge that connects Tsallis’ thermostatistics with thermodynamics. The main difference between the Curado-Tsallis approach and the “normalized-OLM” one is to be found in the manner of computing expectation values.

One has, for a given observable $A$ that takes the value $a_i$ for the microstate $i$

$$\langle A \rangle_q = \sum_{i=1}^{W} p_i^q a_i, \quad (\text{Curado-Tsallis}), \quad (3)$$

and

$$\langle A \rangle_q = \frac{\sum_{i=1}^{W} p_i^q a_i}{\sum_{i=1}^{W} p_i^q}, \quad (\text{normalized-OLM}). \quad (4)$$

Differences in some details of the variational procedure distinguish the approach of Ref. from the one of [11], that is to be the focus of attention in this work.

It is quite clear that $S_q$ provides us with an exceedingly useful information theory tool. Can we identify it with a thermodynamic entropy as well? For an appropriate answer an experimental determination of the $q$-value within a purely thermodynamics setting becomes necessary. One such a test was reported in Refs., where bounds on $|q - 1|$ were established using the cosmic black-body radiation. Also, present-day determinations of the Stefan-Boltzmann constant $\sigma$ put a similar constraint, for which the order of magnitude is $|q - 1| < 10^{-4}$. Finally, bounds on the non extensivity of fermion systems have been reported, namely $|q - 1| < 2 \times 10^{-5}$. All these works refer to the Curado-Tsallis formalism.

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With respect to this treatment, the OLM reformulation of the theory [11] entails a sensible physical difference: in the latter, non-extensivity is restricted just to $S_q$, while the energy behaves as an extensive quantity (it is non-extensive in the Curado-Tsallis instance). To our knowledge, no comparison of predictions arising from this OLM scenario with experiment has been carried out yet.

Now, except for the measurement of Stefan-Boltzmann constant, all the above reported bounds on $q - 1$ have been based on observational rather than on experimental, chemical physics data. The advantage of laboratory measurements in the comparison of a new theory with nature lies in the possibility of varying and controlling the conditions in which the data is acquired, thus ensuring a thorough validity test. With regards to the observational tests, mostly of cosmological nature [15][18], it has been forcefully argued [19] that they can not test the degree of non extensivity of a system, as the application of thermodynamic arguments is of a strictly local character. This entails that limits on the non-extensivity, in a large, cosmological scale, can not be thereby obtained.

In order to test non extensivity, a (laboratory) physical system composed of two different weakly interacting subsystems should be used. It is well known that $H_2$ gas is a mixture of two different substances [21][24]: parahydrogen (with nuclear spin $K = 0$) and orthohydrogen (with $K = 1$), in statistical weights 1/4 and 3/4, respectively. Since there exist accurate (about 1%) measurements of both its specific heat and relevant spectroscopic data, this ideal mixture is a very good test ground for the existence non-extensivity in chemical physics. In this communication a new bound on the non extensivity parameter $q - 1$, based on laboratory measurements of the specific heat of hydrogen, is reported, and suggestions are advanced for the performance of improved measurements.

Since the proposal of Giauque [24], it has been customary to compute the thermodynamic properties of simple substances, such as hydrogen, from spectroscopic data. Indeed, when accurate spectroscopic data are available, this method gives much greater precision than direct thermal measurements. On the other hand, the method rests on the validity of BGS statistics as the correct description of nature. Giauque himself computed the thermodynamic properties of the $H_2$ molecule [23] and found very good agreement with the measured data [24][26]. The Giauque proposal has been very successful, to the point that no new direct measurement of the specific heat of $H_2$ molecule has been reported since 1930!

At this point we start our non-extensive considerations. Since the experimental thermodynamic value of $q$ can not be expected to appreciably differ from unity (otherwise, non-extensivity would have been discovered decades ago!), a perturbative treatment around $q = 1$ will be undertaken. In order to compute the specific heat of a substance in the standard Curado-Tsallis (CT) formalism, the point of departure is given by the Tsallis partition function

$$Z_q^{(CT)} = \sum_j e^{-\beta x_j},$$

where $e^x_q \equiv [1 + (1 - q)x_j]^{1/(1-q)}$, $\beta = 1/T$ with $T$ the temperature and $\{\epsilon_j\}$ is the set of energy levels. We compute then the Tsallis free energy

$$F_q^{(CT)} = -\frac{1}{\beta} \ln_q Z_q^{(CT)},$$

where $\ln_q x \equiv (x^{1-q} - 1)/(1-q)$, and finally, apply the usual thermodynamic relations

$$S_q^{(CT)} = -\frac{\partial F_q^{(CT)}}{\partial T}, \quad C_q^{(CT)} = T \frac{\partial S_q^{(CT)}}{\partial T}.$$  

An straightforward expansion of equations (5) and (6) around $q = 1$ yields

$$F_q^{(CT)} = F - \frac{1}{2}(q - 1) \left[ \frac{C_q}{\beta} + \beta (U^2 - F^2) \right].$$

where $U$ and $F$ are the BGS ($q = 1$) internal and free energies respectively and $C$ is the BGS specific heat.

Additionally, for an out of equilibrium ($f, 1 - f$) mixture of two substances ($A, B$), the specific heat satisfies the analog of equation (1)

$$C_q^{(CT)}(A + B) = C_q^{(CT)}(A) + C_q^{(CT)}(B) + (1-q)C_{AB}, \quad (9)$$

$$C_{AB} = [C_q^{(CT)}(A)S_q^{(CT)}(B) + C_q^{(CT)}(B)S_q^{(CT)}(A)] \cdot (10)$$

The calculation of the specific heat according to the OLM treatment is of a somewhat more subtle nature because the thermodynamic relations does not keep the usual form in terms of Tsallis’ entropy [11]. One starts from the definition

$$C_q = \frac{\partial U_q}{\partial T} = -\beta^2 \frac{\partial U_q}{\partial \beta^2}$$

where the internal energy $U_q$ can be written as [11]

$$U_q = \sum_j f_j^{(1-q)} \epsilon_j.$$ \hspace{1cm} (12)

In this equation, the $f_j = 1 - (1 - q) \beta \Delta_j$ are the so-called configurational characteristics [11] where $\Delta_j = \epsilon_j - U_q$. Taking the pertinent derivatives, one arrives to

$$C_q = \frac{\Delta^2 f_q^{-1}}{1 - q \beta^2 \langle \Delta_j f_q^{-1} \rangle}.$$ \hspace{1cm} (13)

which in the $q \to 1$ limit goes into the BGS specific heat. No corrections for the fact that we deal with a mixture are necessary, since the internal energy is additive in the OLM approach [11]

$$U_q^{OLM}(A + B) = U_q^{OLM}(A) + U_q^{OLM}(B).$$ \hspace{1cm} (14)
The specific heat of parahydrogen (orthohydrogen) can now be written in the fashion
\[ C_q = C + (q - 1)\Delta C, \]  
with
\[ \Delta C^{(CT)} = 2\beta \left( FC + U\beta \frac{dC}{d\beta} \right) \]
\[ - \left[ C^2 + \beta \frac{dC}{d\beta} - \frac{d}{\beta} \left( \beta \frac{dC}{d\beta} \right) \right], \]  
for the Curado-Tsallis version of the formalism, and, with \( \Delta_j = (\epsilon_j - U) \),
\[ \Delta C^{\text{OLM}} = C - 2\beta^3 \left\langle \Delta_j^3 \right\rangle + \beta^4 \left( \frac{1}{2} \left\langle \Delta_j^4 \right\rangle - \frac{3}{2} \left( \left\langle \Delta_j^2 \right\rangle \right)^2 \right), \]  
for its OLM counterpart. Notice that all quantities entering \( \Delta C \) are evaluated within the framework of the standard, BGS statistics. For the case of \( \text{H}_2 \) one has now
\[ \Delta C^{(CT)}(\text{H}_2) = \frac{1}{4} \Delta C_p^{(CT)} + \frac{3}{4} \Delta C_p^{(CT)} - \frac{3}{16} (C_p S_o + C_o S_p), \]
\[ \Delta C^{\text{OLM}}(\text{H}_2) = \frac{1}{4} \Delta C_p^{\text{OLM}} + \frac{3}{4} \Delta C_p^{\text{OLM}}, \]
where \( C_o, C_p \) (\( S_o, S_p \)) are the BGS specific heats (entropies) of ortho- and parahydrogen, respectively.

The structure of \( \Delta C \) in Eq. (10) exhibits a quite clear fashion i) a characteristic non-extensive behavior and ii) a dependence on the reference point for the energy. In Eq. (7), on the other hand, the non-extensivity is not apparent! It is hidden in the higher order momenta of the energy. Also, the troublesome dependence on the origin of the energy scale just vanishes.

Table II displays the accurate data used in this work. The theoretical BGS thermodynamic functions were computed from spectroscopic data using the usual expressions. The constants for the rotational levels were taken from Ref. [27], since they are accurate enough to get a good representation of experimental data. The O-C differences between BGS theory and experiment (Fig. 1) were used to fit the Tsallis parameter \( (q - 1) \) with a simple least squares procedure. The ensuing results are shown in the first line of table II.

These results, however, may be contaminated by systematic errors. The largest deviations from the BGS specific heat come from the data in reference [24]. Assuming that in this data there is a small deviation from the \( 3/4 - 1/4 \) mixture, the O-C differences would adopt the appearance
\[ \Delta C_{\text{obs}} = (q - 1)\Delta C + \epsilon(C_p - C_o), \]  
where \( \epsilon \) is an auxiliary parameter. In such a case one obtains the results of lines 2 and 3 of table II, which are consistent with zero at the 95% CL.

This suggest the existence of systematic errors in the data.

As a final result, we can state that the Tsallis parameter is consistent with zero at the 95% confidence limit:
\[ |q - 1|_{CT} < 5 \times 10^{-4} \]  
\[ |q - 1|_{OLM} < 1.2 \times 10^{-3} \]  
The above equations constitute the main result of this communication.

Our results show that the BGS statistics is, among the set of theories parameterized by \( q - 1 \), the one that describes the available data with an accuracy better than \( 10^{-3} \). Within this level of accuracy, there is no evidence on a non-extensive behavior in this simple system.

With better experiments, the accuracy of our results [21] and [22] could be improved, in principle, by several orders of magnitude. Indeed, spectroscopic data have a potential accuracy of \( 10^{-6} \), while an accuracy of \( 10^{-4} \) should be easily attained with the use of modern experimental techniques. In such a way a stricter test for the validity of the BGS statistics (or, alternatively, for the existence of non-extensivity) would become available for this system.

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TABLE I. Experimental data on the \( \text{H}_2 \) specific heat. The columns display, respectively, the temperature in K, the molar specific heat in units of \( R \) with our adopted standard deviation, and the corresponding bibliographic reference.

| \( T \) (K) | \( C \) | \( \text{Ref} \) | \( T \) (K) | \( C \) | \( \text{Ref} \) | \( T \) (K) | \( C \) | \( \text{Ref} \) |
|------------|-------|----------|------------|-------|----------|------------|-------|----------|
| 35.00      | 1.505±0.005 | 24 | 94.12      | 1.688±0.012 | 24 | 165.58 | 2.147±0.005 | 24 |
| 40.00      | 1.505±0.010 | 24 | 100.00     | 1.727±0.046 | 24 | 182.41 | 2.213±0.005 | 24 |
| 45.00      | 1.515±0.008 | 24 | 100.42     | 1.746±0.012 | 24 | 203.63 | 2.298±0.005 | 24 |
| 50.00      | 1.520±0.018 | 24 | 106.64     | 1.777±0.012 | 24 | 238.23 | 2.390±0.005 | 24 |
| 60.00      | 1.510±0.018 | 24 | 110.00     | 1.828±0.030 | 24 | 269.02 | 2.444±0.005 | 24 |
| 65.00      | 1.535±0.004 | 24 | 112.52     | 1.819±0.012 | 24 | 273.10 | 2.444±0.035 | 24 |
| 70.00      | 1.565±0.007 | 24 | 118.63     | 1.847±0.004 | 24 | 294.27 | 2.466±0.005 | 24 |
| 80.00      | 1.586±0.004 | 24 | 135.71     | 1.967±0.004 | 24 | 308.96 | 2.486±0.006 | 24 |
| 81.12      | 1.601±0.004 | 26 | 136.62     | 1.957±0.013 | 27 | 333.31 | 2.505±0.006 | 26 |
| 82.00      | 1.611±0.007 | 24 | 142.89     | 1.975±0.014 | 24 | 369.40 | 2.504±0.006 | 24 |
| 85.00      | 1.621±0.012 | 24 | 145.64     | 2.041±0.005 | 26 | 372.52 | 2.516±0.006 | 24 |
| 90.00      | 1.646±0.010 | 24 | 148.98     | 2.041±0.014 | 24 |

TABLE II. Results of the analysis performed in this work. The columns of the table display the adjusted parameters’ names and their values (in units of \( 10^{-3} \)) for the two versions, CT and OLM, of the theory. The first line lists a raw fit to the residuals, while the second and third lines display a fit that assumes a small departure from the \( 1/4−3/4 \) proportions of the mixture.

\[
\begin{array}{c|cc}
\text{Parameter} & \text{CT Version} & \text{OLM Version} \\
\hline
q−1 & -0.21±0.05 & 0.89±0.23 \\
q−1 & -0.11±0.07 & 0.52±0.57 \\
\epsilon & 1.0±3.7 & 2.9±4.1 \\
\end{array}
\]

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