Occupancy of rotational population in molecular spectra based on nonextensive statistics

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(Received 23 September 2010; revised manuscript received 26 November 2010; published 27 January 2011)

The procedure to obtain gas temperature in plasmas is to fit the experimental rotational spectrum to a theoretical one based on the Boltzmann distribution. For many systems a single distribution fails to account for the occupation of the levels. Researchers have improved the fitting by coupling two distributions and obtaining two distinct temperatures. They assigned the lowest temperature to the gas. Here, we show that these systems should be described by Tsallis nonextensive statistics and its unique associated temperature. Experimental and simulated spectra are tested and excellent agreement is obtained.

DOI: 10.1103/PhysRevE.83.017401 PACS number(s): 52.70.Kz, 33.20.Sn, 82.80.Ha

Chemical and physical processes that occur in electrical discharges are strongly influenced by temperature. Thus, it is important to have an efficient and noninvasive method to determine the plasma's temperature. For this reason optical emission spectroscopy is the usual method of choice. Physically, the application of the method rests on the hypothesis that the rotational levels are in thermal equilibrium with the gas. Thus, it is mandatory that the occupation of the rovibrational levels can be accurately described by the Boltzmann distribution [1–4]. The first negative system (FNS) of nitrogen is often used to determine the temperature of a discharge. The procedure relies on the assumption that the temperature of the gas is in equilibrium with the distribution of the rotational levels. Accordingly, the fitting of a simulated spectrum to the experimental one is the standard procedure that yields the desired rotational temperature. Linss [5,6] showed that for this system the standard method with a single temperature fails to describe the experimental spectrum. According to Linss, the explanation for such failure lies on the excitation channels available to the $N_2^+(B)$ state. Linss believes that N_2 molecules from different rotational level distributions contribute to the occupation of the $N_2^+(B)$ state. These contributions would come from the following reactions:

$$N_2(X) + e \rightarrow N_2^+(B) + e + e, \tag{1}$$

$$N_2^+(X, v = 0) + N_2(X, v \geqslant 12) \rightarrow N_2^+(B, v = 0) + N_2(X, v - 12). \tag{2}$$

Thus, he has postulated that two different populations for the molecule of $N_2^+(B)$ combine to generate the experimental spectrum. He also claimed that each individual population behaved according to its own Boltzmann distribution. Therefore, each population also had its own temperature. This means that the system cannot be considered in thermal equilibrium. As described in Eq. (1), it is the distribution of the rotational levels for neutral molecules that determines the temperature of the gas. This is the lowest of the two temperatures associated with the system; from now on it will be called T_1. The other excitation channel corresponds to collisions with molecules that are vibrationally excited [Eq. (1)], and it is related to the higher temperature (T_2).

The second positive system of nitrogen has also been used to estimate the temperature of the gas. Indeed, such an application in Ar/N_2 microplasma at atmospheric pressure was reported [7]. Once again two rotational distributions were postulated. The first population was generated by an electronic impact mechanism while the second one was generated by energy transfer from metastable states. To obtain the gas temperature, a procedure almost identical [7] to the one proposed by Linss was used, that is, estimated the temperature of Ar/N_2 plasma by using two Boltzmann distributions and two distinct temperatures. Qiang states that the lower temperature corresponds to the desired gas temperature and that the higher one may be regarded as a fitting parameter.

Here, we reexamine the occupation of rotational levels. Our interpretation does not depend on which mechanisms lead to the population of the rotational levels, but it requires that the Boltzmann picture be abandoned. Thermodynamics, according to Tsallis [8,9], is based on two concepts: energy and entropy. The first concept is related to the energy levels available to the system. Energy clearly depends on the physical system, and it is described by the Hamiltonian function. Entropy is much more subtle because it is related to the probability of the occupation of energy levels. Ubiquitously, it is assumed that the microscopic entropy does not depend on the physical system. In other words, it is usual to accept that there is a universal expression for the entropy. This is part of Boltzmann's legacy. This reasoning was applied by Linss [6] and Qiang [7] to account for the population of the rotational levels of the aforementioned systems. Thus, to achieve good agreement with the experiment, they needed to postulate that the system was simultaneously in contact with two thermal reservoirs. That led to an artificial situation: the existence of two temperatures and the necessity to disregard the highest one. In this Brief Report, we propose a different interpretation: the Boltzmann distribution does not apply to these cases. Instead another kind of statistics must be used. In 1988, Tsallis introduced a generalization of the Boltzmann statistics [8,9]. This generalization considers the nonextensivity of the entropy for a variety of systems. Boltzmann's entropy relation becomes a particular case of the generalized entropy and, consequently, the expression for the population of the rotational levels changes. Tsallis's statistics has been applied to a number of fields [10], for instance, in biology [11], astrophysics [12], turbulence [13], human sciences [14], nuclear physics [15], plasma physics [16], and studies of chemical reactions [17].

It is our goal to show that the Tsallis statistics yields a consistent interpretation of the population of the rotational levels, mainly, for the nitrogen systems. Notice that we are not discussing the validity of the physical processes that were brought forward by Linss and Qiang. Instead, we believe that the use of a nonextensive statistics is justified by the very existence of these processes. In this Brief Report, we show that the results we get from Tsallis's statistics are at least as good as those obtained from two Boltzmann distributions. We will also show that the temperature of the Tsallis distribution is (for all cases we have tested) quite close to the lowest temperature of the two-distribution analysis.

One must know the parameters that define intensities and widths of the spectral lines to generate a simulated spectrum. Intensity depends on transition probability, wavelengths, and the number of molecules in the initial state. As thermal equilibrium is the standard hypothesis used to calculate the number of molecules, the occupation follows the Boltzmann distribution. The rotational level J is $2J + 1$ degenerate. In our simulations of the FNS, we have assumed that line broadening comes from the Doppler effect [6]. Consequently, the expression for the intensities of the simulated spectrum is [4,6]

$$I_{\text{arb}}(\lambda,T,\delta\lambda,\Delta\lambda) = \sum_{i=P,R,\text{branch}} \sum_{J} (2J+1) \exp\left(\frac{-BJ(J+1)}{k_B T}\right) \exp\left(\frac{-4\ln 2[\lambda+\Delta\lambda-\lambda_0(J)]}{(\delta\lambda)^2}\right). \quad (3)$$

The validity of the standard procedure was first questioned in 1941 [18]. As far as we know, Lavrov [19] was the first to state that a non-Boltzmann distribution should be used to accurately describe the intensities of rovibrational spectra. One alternative approach to circumvent such problems was to postulate that the population of the levels was described by two complementary Boltzmann distributions [5–7]. Henceforth, the intensity of the spectral lines was given by [7]

$$I(\lambda) = I_{\text{arb}1}(\lambda,T_1,\delta\lambda,\Delta\lambda) + R I_{\text{arb}2}(\lambda,T_2,\delta\lambda,\Delta\lambda). \quad (4)$$

Parameter R measures the ratio of the contribution for the line intensity from T_2 as compared to T_1. Linss [5,6] showed that for his experimental conditions, the intensities of the FNS had a larger contribution from the low-temperature T_1 and a smaller one from the high-temperature T_2. The open channels that populate the rotational levels have been shown in Eq. (2). Although we trust that his explanation of the excitation channels is correct, we disagree with the application of the Boltzmann functional form. Our argument is based on the fact that such an expression is only valid for systems in thermal equilibrium. Clearly, if two temperatures, T_1 and T_2, are necessary to describe the population of the rotational levels, the system is not in equilibrium. We believe that the ergodic hypothesis is not satisfied and the statistics of the occupation of these rotational levels should be reevaluated. We consider that instead of using two Boltzmann distributions, the population of the rotational levels should be described by a single Tsallis distribution [20,21]. The Tsallis statistics can hardly be achieved in most cases from first principles, as shown by DeVoe [22]. Thus, we have followed DeVoe's footsteps in this work. Consequently, the spectral line intensity is

$$I_{\text{arb}}(\lambda,T_s,\delta\lambda,\Delta\lambda) = \sum_{i=P,R,\text{branch}} \sum_{J} (2J+1) \left(1-(1-q)\frac{E}{k_B T_s}\right)^{\frac{1}{1-q}} \exp\left(\frac{-4\ln 2[\lambda+\Delta\lambda-\lambda_0(J)]}{(\delta\lambda)^2}\right). \quad (5)$$

Therefore, Eq. (5) replaces Eq. (4). Now, a single temperature describes the statistics of the whole system. The nonextensivity parameter, q, is related to the occupation processes of the rotational levels [23].

Although our arguments seem consistent, they must be submitted to testing. Does a single-temperature Tsallis statistics yield an occupation of the rotational levels that is equivalent to the one provided by the Boltzmann statistics with two temperatures? Figure 1 shows a comparison between these two approaches. The dotted line corresponds to a line intensity spectrum generated by two Boltzmann distributions. There $T_1 = 500$ K and $T_2 = 2500$ K, and the ratio R equals 10%. The solid line corresponds to a single Tsallis distribution with $T_s = 600$ K and a factor $q = 1.26$.

Figure 1 clearly shows an excellent agreement between both curves, that is, the spectrum created through Tsallis statistics matches perfectly the one generated by two Boltzmann distributions. As expected, one can also notice that the Tsallis temperature ($T_s = 620$ K) is much closer to $T_1 = 500$ K than to $T_2 = 2500$ K. Next, the new interpretation was submitted to another test in a practical, experimental situation. We have used the same experimental apparatus described in detail in Ref. [1]. We have measured spectra for FNS in a dc positive column with pressure conditions ranging from 0.3 up to 5.0 Torr and currents from 5.0 up to 50 mA.

First, we have followed Linss's [6] reasoning, that is, we have applied the method based on two Boltzmann

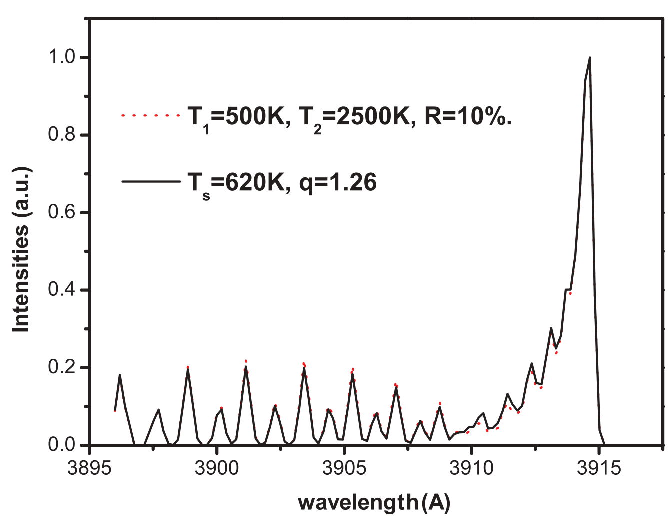

FIG. 1. (Color online) Comparison between two simulated spectra. The dotted line corresponds to a spectrum generated through the two–Boltzmann distribution method and the solid one corresponds to a single Tsallis distribution. Temperatures and the parameters R and q are shown.

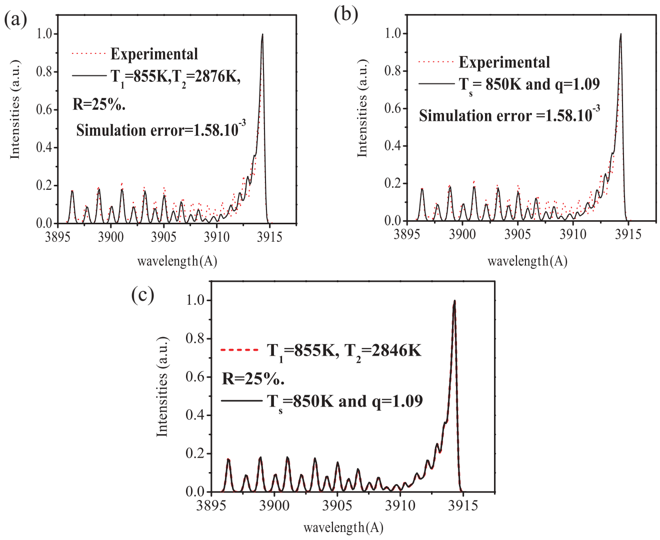

FIG. 2. (Color online) Experimental and simulated spectra for the FNS for 1.0 Torr of pressure and current of 30 mA. (a) Experimental vs the two–Boltzmann distribution method. (b) Experimental vs Tsallis single-temperature distribution. (c) Confrontation of the two simulated spectra.

distributions/two temperatures to fit these spectra. It does fit the spectrum better than a single Boltzmann distribution. Next, we have used the Tsallis distribution to generate the spectra. Once again, this new approach yielded results that are as good as those previously mentioned. This comparison is shown in Fig. 2. One may notice a small deviation between wavelengths of the experimental and simulated spectra. This shift is created by a nonlinearity in the experimental apparatus already described in Ref. [1]. The fact that the exact same procedure was applied to both two Boltzmann distributions and the one introduced by Tsallis renders this dislocation irrelevant.

It is worth mentioning that although only one case is shown in Fig. 2, the test was performed to 16 different experimental conditions with exactly the same results. In order to estimate the fitting error, the following expression was used:

$$E = \sum_{i=1}^{N} [I_{\text{obs}}(\lambda_i) - I_{\text{sim}}(\lambda_i)]^2, \tag{6}$$

where $I_{\text{obs}}(\lambda_i)$ and $I_{\text{sim}}(\lambda_i)$ $(i = 1,2,3,\ldots N)$ are the experimental and simulated intensities [by Eqs. (4) and (5)] at wavelength λ_i, respectively.

Temperatures for both methods (Boltzmann and Tsallis) and parameter R had been determined by minimizing the error function, Eq. (6). We have observed that for all simulations, the simulation error is not affected by temperature variations of ± 30 K. Thus, we have taken this value as a measure of the error in the calculated temperatures. For parameter R, following the same criterion, the estimated error is ± 0.01, and for q, it is ± 0.02. According to Refs. [5] and [6], as we have already mentioned, the lowest temperature (T_1) is the best estimate for the gas temperature. Figure 3 shows T_1 and the temperature (T_s) attributed to the gas by Tsallis distribution as a function of the current when the pressure is kept constant and equal to 1.0 Torr.

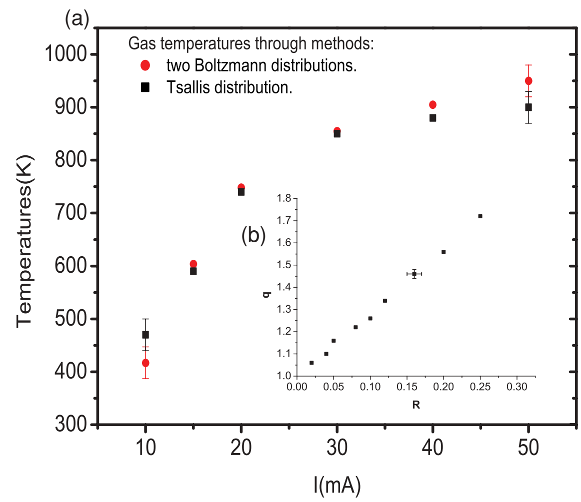

FIG. 3. (Color online) (a) Calculated gas temperature obtained through two-Boltzmann (circles) and Tsallis (squares) distributions. Pressure was kept at 1.0 Torr and current varied in the range from 10 to 50 mA. (b) Relationship between the two–Boltzmann distribution factor R and the entropic Tsallis method factor q.

Figure 3 shows a comparison between the gas temperature as obtained by using the two-temperature method (red circle) and our method (black square) based on Tsallis statistics. It is clear that the estimated temperatures as a function of the current show a very similar pattern.

In Tsallis' generalized statistics, the parameter q plays an important role. This parameter is related to the degree of nonextensivity of the system [24] and it is closely related to the dynamics of the microscopical processes [23]. For instance, $q = 1$ leads to the standard Boltzmann statistics. Its interpretation is usually very difficult, and it is sometimes seen as the "Achilles heel" of this statistics. Luckily, in the present case, we found that q is directly related to the occupation processes of the rotational levels. In other words, q is related to parameter R and this is shown in Fig. 3(b).

We have introduced and tested a procedure to determine the temperature of a discharge. The standard method assumes that the distribution of the energy levels is in equilibrium in order to apply Boltzmann's statistics. However, the literature presents many cases where the standard procedure fails. In this case, a composition of two Boltzmann distributions was used to describe the occupation of the energy levels. Numerically, this procedure needs three parameters: two temperatures T_1 and T_2 and a mixing parameter R. The existence of more than one excitation channel that was used to justify the two-distribution method can equally well justify the use of the nonextensive statistics. Here we have shown that the Boltzmann distribution is not appropriate to the experimental conditions. There is a need to apply a nonextensive statistics to describe correctly the occupancies of the levels. Our interpretation yields results that are similar to those obtained with two temperatures and it introduces only two numerical parameters: the gas temperature T_s and the entropic factor q. We also show that the q factor is related to the process of occupation of the energy levels and to the parameter R. We believe that our interpretation is evidence that the spectroscopy of a discharge should not be described through equilibrium statistics.

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