Abstract: The temperature of a discharge determines the rate of the chemical reactions that take place in plasma. The intensity distribution of the lines in the ro-vibrational spectrum is also dependent of the plasma temperature. In order to determine the gas temperature in the plasma, the usual procedure is to fit the rotational spectrum to a theoretical one based on a single Boltzmann distribution. There are systems, however, that the occupation of the rotational levels cannot be explained in terms of a single Boltzmann distribution. Researchers have, rather arbitrarily, coupled two distinct Boltzmann distributions to improve their results. Obviously, these two Boltzmann distributions lead to two distinct temperatures. They assume that the lowest temperature is the one that should be assigned to the gas temperature. In this work we propose a different interpretation. We show that the system is well described by Tsallis’ non-extensive statistics and its unique associated temperature. Both experimental and simulated spectra are tested and excellent agreement is obtained. The role played by the q factor present in Tsallis’ statistics is discussed.

Keywords: nonextensive statistics, rotational temperature, spectroscopy.

1. Introduction

Chemical and physical processes that occur in plasma are strongly related to the gas temperature. Thus, it is important to have an efficient and noninvasive method to determine this parameter. 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. In other words, the same temperature that explains the occupation of the rotational levels is used as an estimate for the gas temperature. Thus, it is mandatory that the occupation of the rovibrational levels can be accurately described by the Boltzmann distribution [1-5]. The standard procedure to determine gas temperature is to fit the rotational experimental spectrum to a theoretical (synthetic) one based on a single Boltzmann distribution. However, there are systems which one Boltzmann distribution fails to address this task. The main reason is that the occupation of energy levels cannot be described by a single Boltzmann distribution. One way of resolving this problem is assuming that the rotational energy levels should be described by two Boltzmann distributions and their related temperatures. This hypothesis was used to determine the temperature to the First Negative System (FNS) and Second Positive System (SPS) of molecular nitrogen plasmas [6,7]. These authors justify their method claiming that rotational energy populations are described by two channels of excitation, so two distributions are necessary to describe them. Although this procedure yields good results it seems to be statistical incorrectly, because it associates an equilibrium distribution function with two different temperatures. We propose a new interpretation for the distribution of the rotational levels. We believe that the Boltzmann distribution does not apply to these cases. Instead another kind of statistics must be used: Tsallis nonextensive statistics [8]. One interesting feature of our interpretation is that it does not depend on which mechanisms lead to the population of the rotational levels. On the other hand, it requires that the Boltzmann picture be abandoned. Thus, the Tsallis statistics and its unique associated temperature could be used to describe rotational levels and to determine gas temperature so far. We have tested our hypothesis in two different systems of nitrogen: the FNS spectra measured in one experimental set-up and the SPS spectra obtained in another one. In both cases the Tsallis temperature is in a good agreement with that obtained with two Boltzmann methods. We believe that our results are evidences that the spectroscopy of plasmas should not be described through Boltzmann equilibrium statistics.
2. Nonextensive Statistics

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 [9].

The entropic form of Tsallis statistics to a W number of microscopic states is:

\[ S_q \equiv k \frac{1 - \sum_{i=1}^{W} p_i^q}{q-1} \]  

The entropic parameter q is related to the process of occupation of microscopic states.

One of the most features of Tsallis statistics is that: If two systems A e B are independent in the sense of theory of probabilities then:

\[ \frac{S_q(A+B)}{k} = \frac{S_q(A)}{k} + \frac{S_q(B)}{k} + (1 - q) \frac{S_q(A) S_q(B)}{k} \]  

This characteristic is an evidence of the reason this statistics is called “nonextensive”.

For this generalized statistics the equilibrium distribution function associated with canonical ensemble is [8]:

\[ p_i \propto (1 - (1 - q)\beta E_i)^{(1-q)} \]  

Where \( \beta = \frac{1}{kT} \) and \( E_i \) is the energy of i-state.

Our hypothesis is to change the two Boltzmann distribution functions by the expression in equation 3. Thus the unique temperature could be used to estimate gas temperature. 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 and it could be used to determine rotational temperature.

3. Simulating spectra

In order to determine gas temperature a synthetic spectrum must be created with temperature as a parameter. When the synthetic spectrum fits the experimental one, the temperature is determined.

To simulate a spectrum one must know the parameters that define intensities and the widths of the spectral lines. 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 [5]:

\[ N_j \propto (2J + 1) e^{-\frac{E_j}{kT}} \]  

The number \( N_j \) determines the intensities of rotational lines. The line broadening is generally Gaussian. A composition between the term for intensities and for rotational widths is used to simulate a spectrum under Boltzmann statistics:

\[ I_{arb}(\lambda, T_{rot}) = \sum_j H(j) \exp \left( \frac{-E_j}{kT_{rot}} \right) \text{ (gaussian func.)} \]  

When one temperature fails to complete takes account the experimental intensities lines, it is assumed two temperatures, so the spectrum could be simulated as follow:

\[ I_{arb}(\lambda, T_{rot1}, T_{rot2}, R) = I_{arb1}(T_{rot1}) + R I_{arb2}(T_{rot2}) \]  

The term R represents the contribution of the “hot” temperature to the intensities lines. We have used Levenberg-Marquardt algorithm to determine the temperatures and the R parameter. A detailed discussion of this procedure to the FNS and to the SPS of nitrogen can be found in references 6 and 7.

Although this method yields good results, it is deemed in statistical point of view and the “hot” temperature stays as a fitting parameter.

In our method we change the Boltzmann term, so one does not need two temperatures to fitting the experimental spectrum. The spectrum can be simulated as:

\[ I_{arb}(\lambda, T_x) = \sum_j H(j)[1 - (1 - q)\beta E_j]^{\frac{1}{1-q}} \text{ (gaussian func.)} \]  

Our results shows that an unique temperature in Tsallis statistics works very well and this temperature is very close to that one obtained by the two Boltzmann method.

In order to determine the fitting we defined the function:

\[ \chi^2 = \sum_{i=1}^{n} \frac{(I_{exp}(\lambda_i) - I_{arb}(\lambda_i))^2}{n} \]  

When the function in equation 7 is near zero, we have a fitting between simulated spectrum and experimental one.

4. Experimental Set-Up

In order to obtain the FNS and the SPS of nitrogen we have used two different experimental set-ups. To the FNS the experimental set-up can be seen in figure 1.

The glow discharge tube has 1.6 cm internal diameter and is 20 cm long. The cathode and anode were made of tungsten and are 16 cm apart. The pressure is measured in the central region of the tube with the aid of a capacitive transducer Baratron, the pressure was varied from 0.3 to 5.0 Torr. The light emitted by the discharge is focused by means of a lens, 15 cm focal length, into the entrance slit of 1m monochromator Jovin-Yvon THR 1000. The monochromator has a grating of 1800 lines mm⁻¹, blazed in the region 450–850 nm. The optical system was calibrated with the aid of a tungsten lamp. The discharge current was measured by an external amperemeter and was varied from 5.0 up to 50 mA.
To the SPS the experimental set-up can be seen in figure 2. The plasma is generated by a Sufatron launcher operating at atmospheric pressure, frequency of 2.45 GHz, argon flux of 2.5 slm. With applied power of 56 W a xxx mm plasma flame is created. Using a iHR550 Jobin Yvon monochromator, with grating of 1800 lines/mm and a CCD of 1024 x 256, spectra as a function of length is recorded.

5. Results and Discussion

We have tested our hypothesis in two systems of nitrogen: FNS and SPS. To the FNS we have measured spectra under various experimental conditions and we determined the temperature through Tsallis distribution and by two Boltzmann distribution. In both cases the temperature are analogous. The error in our simulations to the temperatures is near 60K. In figure 3 we show the distribution of temperatures to the pressure of 0.5 Torr and discharge current varying from 5mA to 50,0mA.

In figure 3 one can notice that there is a good agreement between two Boltzmann method and Tsallis one. But in nonextensive statistics only one temperature is needed. We still have investigated whether there is a relation between R factor of two Boltzmann method and “q” entropic parameter. This investigation can be seen in figure 4.

Figure 4 shows that there is a linear dependence between q and R to the FSN. A discussion of these results to the FNS can be founded in reference 1.

To the SPS system we have determined the temperature to the set-up showed in figure 2. We have measured the spectrum in various positions from the exit of the discharge. These measurements allowed us to determine the spatial distribution of temperatures of SPS. The power of our discharge was maintained in 56W and the flux of 2.5 slm. To each position we have measured a spectrum and determined the temperature through two Boltzmann
distributions and Tsallis one. This fit means to optimize the function in equation 7. One example of this procedure is shown in figure 5. This figure shows an experimental spectrum for position of 8mm and the corresponding simulated on through two Boltzmann method. In these simulations to the SPS the error in temperature is near 100K.

In figure 6 we show the same experimental spectrum but the simulated one was through Tsallis method.

In figure 7 we show the distribution of temperatures for positions from 0.0mm to 10mm from the exit of the discharge.

6. Conclusions.

We have shown that Tsallis nonextensive statistics can be used to determine rotational temperatures in plasma. We have measured experimental spectra for two system of nitrogen, the FNS and SPS in different experimental apparatus. For these spectra we have determined the temperatures through two Boltzmann distributions, usual but inconsistent one, and through Tsallis distribution. In both system we have find similar results to the rotational temperatures. We proposed this method based on nonextensive statistics because the standard procedure makes use of two Boltzmann equilibrium distributions to describe the same system. Even this method yields good results it seemed to be unphysical in statistical point of view. By the other hand, Nonextensive method is consistent because it only needs one equilibrium distribution to the system. We believe that nonextensive method could be extended to other systems of nitrogen and to other molecular plasmas.

References.

[10] For a complete and updated list of references, see the website [http://cat.cbpf.br/biblio.htm].