PHYSICAL REVIEW E VOLUME 51, NUMBER 6 JUNE 1995

Departure from Boltzmann-Gibbs statistics makes the hydrogen-atom specific heat a computable quantity

Liacir S. Lucena,[1] Luciano R. da Silva,[1] and Constantino Tsallis[1,2]
[1]*Departamento de Física, Universidade Federal do Rio Grande do Norte, 59072-970 Natal, Rio Grande do Norte, Brazil*
[2]*Centro Brasileiro de Pesquisas Físicas, Rua Xavier Sigaud 150, 22290-180 Rio de Janeiro, Rio de Janeiro, Brazil and Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-1116*
(Received 15 December 1994)

The specific heat of the (nonionized) hydrogen atom in free space cannot be calculated within Boltzmann-Gibbs statistical mechanics essentially because its partition function *diverges*. We show that a recently introduced generalized formalism can overcome this difficulty for $q<1$ (the index q characterizes the statistics; Boltzmann-Gibbs corresponds to $q=1$).

PACS number(s): 05.30.Ch, 31.10.+z, 02.50.−r

Any quantum mechanics introductory textbook should contain the exact solution of five systems, namely, the (nonrelativistic) free particle, the harmonic oscillator, the spin $\frac{1}{2}$ (in the presence of an external magnetic field), the rigid rotator, and the (nonionized) hydrogen atom in free space. The first four are also present in any textbook on statistical mechanics (for the oblate-prolate rigid rotator see [1]), but very rarely is the hydrogen atom present (a relevant exception to this fact is the early discussion by Fowler [2]). The reason might be that, within Boltzmann-Gibbs (BG) thermostatistics, the partition function *diverges,* and we are therefore left practically without a prescription for attributing, as a function of the temperature, *finite* values to an equilibrium quantity such as specific heat. A way out of this is sometimes to *change the system,* or, more precisely, to consider the hydrogen atom as *not in free space but rather within a box* (or any other equivalent procedure which essentially consists of "throwing" out of the sums the bothering infinite levels that, in free space, accumulate at the ionization threshold). This type of solution can make sense if the system is thought to be *within a limited volume,* but becomes hard to accept for hydrogen atoms *in free space* (say, in interstellar space). For this particular physical situation, the only logical path that is left within BG statistical mechanics is that the hydrogen atom is in its fundamental state if the temperature T is strictly zero and is ionized for *any* positive temperature *(no matter how small T might be).*

In other words, that there is no possible thermal equilibrium for a hydrogen atom in free space. This type of approach might not properly accommodate the experimental evidence of photon emission and absorption spectra by atoms and molecules in interstellar space. The direct experimental approach of hydrogen atom thermostatistics is now, unfortunately, inaccessible since the associated energy scale is one Rydberg, which approximately corresponds to a temperature of 10^5 K. We must therefore try to discuss the problem on theoretical grounds.

In fact, the difficulties encountered for the hydrogen atom are essentially the same which make the $d=3$ self-gravitating system untractable within standard statistical mechanics and thermodynamics [3]. More generally speaking, if we consider d-dimensional systems with attractive two-body interactions characterized by a *potential energy* $\propto 1/r^{\alpha}$ ($\alpha>0$; $r\equiv$distance), its BG canonical mean value (for the potential) *diverges* at the long distance limit whenever $\alpha\le d$ (quantum effects normally produce a cutoff which avoids mathematical troubles at short distances). Of course, the hydrogen and standard gravitation correspond to $(\alpha,d)=(1,3)$ and, consequently, they constitute a typical case of untractability. A generalized statistical mechanics and thermodynamics theory is now available [4,5] and addresses precisely this type of difficulty. It consists of the proposal [4] of the following generalized entropy:

$$S_q=k\frac{1-\sum p_i^q}{q-1}\quad (q\in\mathbb{R})\ , \tag{1}$$

where k is a positive constant and $\{p_i\}$ are the probabilities of the microscopic configurations. In the $q\to 1$ limit, S_q becomes the well known Boltzmann-Gibbs-Shannon expression, $-k_B\sum p_i \ln p_i$. S_q is non-negative, extremal for equiprobability (microcanonical ensemble), and is concave (convex) if $q>0$ ($q<0$), a fact which constitutes an important ingredient for the thermodynamic stability for the system. S_q satisfies the H theorem [6], i.e., $dS_q/dt\ge 0$ (≤ 0) if $q>0$ ($q<0$); it is pseudo-additive for two independent systems Σ and Σ', i.e., if $\hat\rho_{\Sigma\cup\Sigma'}=\hat\rho_{\Sigma}\otimes\hat\rho_{\Sigma'}$ where $\hat\rho$ denotes the density operator, whose eigenvalues are $\{p_i\}$; $\hat\rho_{\Sigma\cup\Sigma'}$ acts on the tensor product of the Hilbert spaces, respectively, which are associated with Σ and Σ'. In other words it satisfies

$$\frac{S_q^{\Sigma\cup\Sigma'}}{k}=\frac{S_q^{\Sigma}}{k}+\frac{S_q^{\Sigma'}}{k}+(1-q)\frac{S_q^{\Sigma}S_q^{\Sigma'}}{k}\ . \tag{2}$$

Consequently, unless $q=1$, S_q is generically nonadditive (nonextensive).

If the system is in thermal equilibrium at temperature $T\equiv 1/\beta k$, we must optimize S_q under the constraints $\mathrm{Tr}\hat\rho=1$ and $\mathrm{Tr}\hat\rho^{\,q}\hat{\mathcal{H}}\equiv\langle\hat{\mathcal{H}}\rangle_q=U_q$ [4,5] where $\hat{\mathcal{H}}$ is the Hamiltonian and U_q is a *finite* quantity (generalized internal energy). We obtain

$$\hat{\rho}=\frac{[1-\beta(1-q)\hat{\mathcal{H}}]^{1/(1-q)}}{Z_q} \quad (3)$$

with the generalized partition function given by

$$Z_q=\mathrm{Tr}[1-\beta(1-q)\hat{\mathcal{H}}]^{1/(1-q)} . \quad (4)$$

In the $q\to 1$ limit, these expressions recover the BG distribution $\hat{\rho}=\exp(-\beta\hat{\mathcal{H}})/Z_1$. It can be shown [5] for all values of q that

$$\frac{1}{T}=\frac{\partial S_q}{\partial U_q} , \quad (5)$$

$$U_q=-\frac{\partial}{\partial\beta}\frac{Z_q^{1-q}-1}{1-q} , \quad (6)$$

and

$$F_q\equiv U_q-TS_q=-\frac{1}{\beta}\frac{Z_q^{1-q}-1}{1-q} . \quad (7)$$

In addition to the above properties, the present generalized statistics result in the following: (i) the statistics leave *form invariant,* for all values of q, the Legendre-transform structure of thermodynamics [5], the Ehrenfest theorem and the von Neumann equation [7], as well as the Onsager reciprocity theorem [8]; (ii) the statistics satisfy Jaynes information theory duality relations [7], necessary for the associated entropy to be considered as a measure of the (lack of) information; (iii) and they can generalize the Langevin and Fokker-Planck equations [9], the quantum statistics [10], and the fluctuation-dissipation theorem [11], among others. This generalized formalism has already been applied in a certain amount of problems: self-gravitating astrophysical problems [12,13], Lévy flights [14,15], correlated anomalous diffusion [16], optimization techniques [17], and a possible connection with quantum groups [18], among others. As mentioned above, we are primarily concerned here with the gravitational case. What has been essentially proved [12] is that many-body $d=3$ gravitation is consistent with *simultaneously finite* mass, energy, and entropy if $q<\frac{7}{9}$ (this threshold has been obtained from [12] by performing the $q\leftrightarrow 1/q$ transformation which is necessary in order to correct the fact that the authors have used the early version [4] of the generalization rather than the correct one [5]). Another argument which, in our opinion, points to $q<1$ for such systems is given by Landsberg in [3]; indeed, there it is demanded for the entropy to be *superadditive,* which only occurs here [see Eq. (2)] for $q<1$. Finally, a third argument which again suggests that $q<1$, is that, for two specific many-body astrophysical models, the exact time-dependent solutions of the associated Vlasov equations have been recovered for $q=-1$ [13]. Since, for these types of problems, the exact (α,d) dependence of q is still unknown (in contrast with Lévy flights and correlated anomalous diffusion, where it is known [14–16]) we shall address, for the positive-temperature dependence of the specific heat of the hydrogen atom, typical values of q in the range 0,7/9.

The hydrogen-atom spectrum is given by

$$\epsilon_n=R\left[1-\frac{1}{n^2}\right],\quad n=1,2,3,\ldots, \quad (8)$$

with the degeneracy

$$g_n=2n^2 , \quad (9)$$

where R is the Rydberg constant, and we have chosen the fundamental state to have zero energy. The well known BG prescription for the specific heat is given by

$$\frac{C}{k_B}=\left[\frac{R}{k_BT}\right]^2\left\{\sum_{n=1}^{\infty}\left[g_np_n\frac{\epsilon_n^2}{R^2}\right]-\left[\sum_{n=1}^{\infty}g_np_n\frac{\epsilon_n}{R}\right]^2\right\} , \quad (10)$$

where

$$p_n=\frac{e^{-(\epsilon_n/k_BT)}}{Z_1} \quad (11)$$

and

$$Z_1=\sum_{m=1}^{\infty}g_me^{-\epsilon_m/k_BT} . \quad (12)$$

A quick inspection reveals the already mentioned mathematical untractability of this calculation. For $q<1$, Eq. (10) is extended into [11,19]

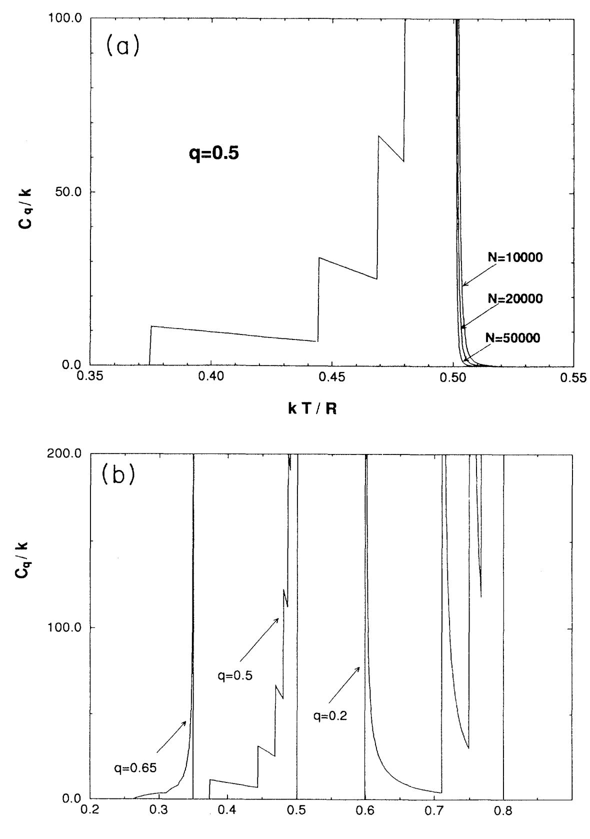

FIG. 1. Temperature dependence of the specific heat: (a) $q=0.5$ (when the number N of terms in the sum diverge, C_q vanishes for all $kT/R>0.5$); (b) for typical values of q below $\frac{7}{9}$ (exact results). Whenever kT crosses the hydrogen-atom levels, the specific heat presents divergences if $0<q<1/2$, cusps if $q=1/2$, and discontinues in its derivative if $1/2<q<1$.

$$\frac{C}{k}=\frac{q}{t^2}\left\{\sum_{n=1}^{\infty} g_n\left[p_n^q\frac{(\epsilon_n/R)^2}{1-\frac{1-q}{t}\left[\frac{\epsilon_n}{R}\right]}\right]-\left[\sum_{n=1}^{\infty} g_n p_n^q(\epsilon_n/R)\right]\left[\sum_{n=1}^{\infty} g_n p_n\frac{(\epsilon_n/R)}{1-\frac{1-q}{t}\left[\frac{\epsilon_n}{R}\right]}\right]\right\}, \tag{13}$$

where

$$t\equiv\frac{kT}{R} \tag{14}$$

and

$$p_n=\begin{cases}\dfrac{\left[1-\frac{1-q}{t}\left[\frac{\epsilon_n}{R}\right]\right]^{1/(1-q)}}{Z_q}, & \text{if } \frac{1-q}{t}\left[\frac{\epsilon_n}{R}\right]<1\\ 0, & \text{otherwise}\end{cases} \tag{15}$$

with

$$Z_q\equiv\sum_{n=1}^{\infty}{}'\left[1-\frac{1-q}{t}\frac{\epsilon_n}{R}\right]^{1/(1-q)}. \tag{16}$$

The sum $\sum'$ is interrupted whenever the argument becomes negative. In practice, all these sums are replaced by $\lim_{N\to\infty}\sum_{n=1}^{N}$. The results are indicated in Fig. 1. As illustrated for $q=0.5$ in Fig. 1(a), anomalies occur at all dimensionless temperatures $t_n=(1-q)[1-(1/n^2)]$ ($n=2,3,4,\ldots,$); the limit $N\to\infty$ has C_q equal to zero for all dimensionless temperatures $t>(1-q)$. In Fig. 1(b) we present the exact specific heat associated with three typical values of q below $\frac{7}{9}$. In the $q\to 1$ limit, the entire function collapses into the physically inacessible $T=0$ axis.

As mentioned before, it seems to be difficult today for any calorimetric experiment on (highly diluted) nonionized hydrogen atoms for which comparison could be attempted. But, on theoretical grounds, one point has been achieved: within the framework of the recently generalized statistical mechanics, for $q<1$, the free space (nonionized) hydrogen-atom specific heat becomes a *computable quantity*. So, in some sense, we can say that analogous to what happens with the gravitational systems [12,13], the cutoff naturally appearing in the formalism whenever $q<1$ regularizes the theory. Further understanding of its physical significance would be very welcome.

We acknowledge interesting discussions with D. P. Prato as well as the computational assistance of J. M. Araújo. One of us (C.T.) is grateful for the warm hospitality received at the Universidade Federal do Rio Grande do Norte.

[1] A. O. Caride and C. Tsallis, J. Stat. Phys. **35**, 187 (1984).
[2] R. H. Fowler, *Statistical Mechanics* (Cambridge University, Cambridge, 1936), Chap. XIV.
[3] A. M. Salzberg, J. Math. Phys. **6**, 158 (1965); P. T. Landsberg, J. Stat. Phys. **35**, 159 (1984); L. G. Taff, *Celestial Mechanics* (Wiley, New York, 1985), pp. 437 and 438; W. C. Saslaw, *Gravitational Physics of Stellar and Galactic Systems* (Cambridge University, Cambridge, 1985), pp. 217 and 218; S. Tremaine, M. Hénon, and D. Lynden-Bell, Mon. Not. R. Astron. Soc. **219**, 285 (1986); J. Binney and S. Tremaine, *Galactic Dynamics* (Princeton University, Princeton, N.J., 1987), p. 268; D. Pavón, Gen. Rel. Grav. **19**, 375 (1987); H. E. Kandrup, Phys. Rev. A **40**, 7265 (1980); R. Balian, *From Microphysics to Macrophysics* (Springer-Verlag, Berlin, 1991), Vol. 1, p. 134; O. Kaburaki, Phys. Lett. A **185**, 21 (1994).
[4] C. Tsallis, J. Stat. Phys. **52**, 479 (1988).
[5] E. M. F. Curado and C. Tsallis, J. Phys. A **24**, L69 (1991); corrigenda: J. Phys. A **24**, 3187 (1991); **25**, 1019 (1992).
[6] A. M. Mariz, Phys. Lett. A **165**, 409 (1992); J. D. Ramshaw, *ibid.* **175**, 169 (1993); J. D. Ramshaw, *ibid.* **175** 171 (1993).
[7] A. R. Plastino and A. Plastino, Phys. Lett. A **177**, 177 (1993); Physica A **202**, 438 (1994).
[8] A. Chame and E. V. L. de Mello (unpublished); M. O. Caceres (unpublished).
[9] D. A. Stariolo, Phys. Lett. A **185**, 262 (1994).
[10] F. Buyukkiliç and D. Demirhan, Phys. Lett. A **181**, 24 (1993); F. Buyukkiliç, D. Demirhan, and A. Guleç, *ibid.* **197**, 209 (1995).
[11] A. Chame and E. V. L. de Mello, J. Phys. A **27**, 3663 (1994).
[12] A. R. Plastino and A. Plastino, Phys. Lett. A **174**, 384 (1993); J. J. Aly, in *Proceedings of the Meeting Held at Aussois-France,* March 1993, edited by F. Combes and E. Athanassoula (Publications de l'Observatoire de Paris, Paris, 1993), p. 19.
[13] A. R. Plastino and A. Plastino, Phys. Lett. A **193**, 251 (1994); see also P. Jund, S. G. Kim, and C. Tsallis, Phys. Rev. B (to be published), and C. Tsallis, F. C. Sá Barreto, and E. D. Loh, Phys. Rev. E (to be published).
[14] P. A. Alemany and D. H. Zanette, Phys. Rev. E **49**, R956 (1994).
[15] C. Tsallis, A. M. C. de Souza, and R. Maynard, in *Levy Flights and Related Topics in Physics,* edited by M. F. Shlesinger, G. M. Zaslavsky, and U. Frisch (Springer, Berlin, to be published).
[16] P. M. Duxbury (private communication).
[17] T. J. P. Penna, Phys. Rev. E **51**, 1 (1995).
[18] C. Tsallis, Phys. Lett. A **195**, 329 (1994).
[19] E. P. da Silva, C. Tsallis, and E. M. F. Curado, Physica A **199**, 137 (1993); **203**, 160(E) (1994); C. Tsallis, in *New Trends in Magnetic Materials and Their Applications,* edited by J. L. Morán Lopez and J. M. Sanchez (Plenum, New York, 1994), p. 451; F. D. Nobre and C. Tsallis, Physica A **213**, 337 (1995); S. Curilef and C. Tsallis, Physica A (to be published).