

Generalized Boltzmann-Gibbs Distribution and the Electronic Partition Function Paradox

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Abstract

This paper generalizes the entropy maximization problem leading to the Boltzmann-Gibbs distribution through the nonadditive entropy $S_{q,s}(p) = k_s \sum_{i \geq 1}^W p_i \ln_q 1/p_i$, $q \in (0, 1)$, which is a rescaled version of S_q [1] by a factor $k_s = k^q (e_{\max}/(W^\sigma - 1))^{1-q}$, $\sigma > 0$, varying according to the underlying energy spectrum and satisfying $k_s \rightarrow k$ (Boltzmann constant) as $q \rightarrow 1$. The maximization problem based on $S_{q,s}$ is used to derive analytical generalizations of the Boltzmann-Gibbs distribution for the case of an energy spectrum that uniformly approaches a continuous, unbounded limit with a common degeneracy, the harmonic oscillator, and the one-dimensional box. Furthermore, I demonstrate that this generalized problem yields a two-tier model with finite structural parameters β for the hydrogen atom in free space and, therefore, can be used to circumvent the Electronic Partition Function Paradox and obtain a family of well-defined thermodynamic behaviors indexed by $q \in (0, 1)$. In particular, for $q = 0.5$, the specific heat of the free hydrogen atom becomes the Boltzmann constant. Finally, it is shown that all the limiting processes involved in these four cases lead naturally to the same definition of the scale factor k_s that characterizes $S_{q,s}$ (“s” stands, in this context, for “spectrum”) in order to grant finite, smooth, macroscopically observable temperature values that are related to the entropic functional by $\partial S_{q,s}/\partial U = 1/|T|_\pm^q$, which recovers $\partial S_{BG}/\partial U = 1/T$ [2] as $q \rightarrow 1$.

1. Introduction

Boltzmann-Gibbs distribution [3–5] can be obtained from the following maximization problem

$$\max \quad S_{BG}(p) \quad (1)$$

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$$\begin{aligned} \text{s.t. } p_i &\geq 0, 1 \leq i \leq W \\ \sum_{i=1}^W p_i &= 1 \\ \sum_{i=1}^W p_i E_i &= 0, \end{aligned}$$

with $S_{BG}(p) = k \sum_{i=1}^W p_i \ln 1/p_i$, $W \geq 2$ the number of microstates, $0 = e_1 \leq \dots \leq e_W = e_{\max}$ the energy levels of each microstate (all such values form the *energy spectrum*), $0 < U < e_{\max}$ the internal energy, $E_i = e_i - U$, $1 \leq i \leq W$, k the Boltzmann constant and $g(e) = \#\{1 \leq i \leq W \mid e_i = e\}$ the degeneracy function. The solution $p_* \in \mathbb{R}_{++}^W$ of (1) is given by

$$p_{*i} = \frac{\exp(-\beta E_i)}{\sum_{j=1}^W \exp(-\beta E_j)}, \quad (2)$$

for $1 \leq i \leq W$, with the structural parameter $\beta \in \mathbb{R}$ satisfying

$$\sum_{i=1}^W \exp(-\beta E_i) E_i = 0. \quad (3)$$

Following [6], I call β *structural* since, by (3), it depends solely on the energy spectrum and the internal energy of the system. Instead of passing through (3) to calculate the distribution (2), one could measure the temperature of the system $T \in \mathbb{R}/\{0\}$ and, since [2]

$$\frac{\partial S_{BG}(p_*)}{\partial U} = \frac{1}{T}, \quad (4)$$

the Envelope Theorem implies $\beta = 1/kT$ and $p_{*i} \propto \exp(-E_i/kT)$ (i.e., the Boltzmann factor), $1 \leq i \leq W$, so that

$$p_{*i} = \frac{\exp(-E_i/kT)}{\sum_{j=1}^W \exp(-E_j/kT)}, \quad (5)$$

for $1 \leq i \leq W$, which is the classical form of the Boltzmann-Gibbs distribution. One important feature to note is that the constant k defines the temperature scale and is, therefore, the link between (1) and macroscopically observed quantities, but it does not alter the optimal distribution that solves (1) (i.e., it does not alter the structural parameter β).

In this paper, I study a generalized version of (1)¹ given by

$$\begin{aligned} \max \quad & S_{q,s}(p) \\ \text{s.t. } p_i &\geq 0, 1 \leq i \leq W \\ \sum_{i=1}^W p_i &= 1 \\ \sum_{i=1}^W p_i E_i &= 0, \end{aligned} \quad (6)$$

¹See also Dognini and Tsallis [6] for the study of another class of generalized versions of (1) with the entropic functional $S_q(p) = k \sum_{i=1}^W p_i \ln_q 1/p_i$ and energy constraints of the form $\sum_{i=1}^W p_i^{q'} E_i = 0$, $q' > 0$.

with $0 < q < 1$. The entropic functional $S_{q,s}$ is given by²

$$S_{q,s}(p) = k_s \sum_{i=1}^W p_i \ln_q 1/p_i = k_s \left(\frac{\sum_{i=1}^W p_i^q - 1}{1 - q} \right), \quad (7)$$

for $p \in \mathbb{R}_+^W$, with

$$k_s = k^q \left(\frac{e_{\max}}{W^\sigma - 1} \right)^{1-q}, \quad (8)$$

for $W \geq 2$, $e_{\max} > 0$, $\sigma > 0$. In particular, $k_s \rightarrow k$ as $q \rightarrow 1$. One may notice that, for all $0 < U < e_{\max}$, there is a unique and strictly positive solution $p_*(U) \gg 0$ for (6) (c.f., Proposition 1 from Dognini and Tsallis [6]) and this solution does not depend on the specific form of the scale factor k_s , which only becomes relevant once we need to define a temperature for the system. To advance this definition, after analyzing the dimensions of (8), I *postulate* that

$$\frac{\partial S_{q,s}(p_*(U))}{\partial U} = \frac{1}{|T|_\pm^q} \quad (9)$$

with $|z|_\pm^q = \text{sign}(z)|z|^q$, $z \in \mathbb{R}$, in order to obtain a dimensionally coherent generalization of (4) that allows for both positive and negative temperature values.

Clearly, by taking $q \rightarrow 1$ in (6) we obtain (1), and in (9) we obtain (4). The entropic functional $S_{q,s}$ in (7) is a rescaled version of the traditional nonadditive³ entropic functional $S_q(p) = k \sum_{i=1}^W p_i \ln_q 1/p_i$ [1] (which is the unique one to be simultaneously trace-form and composable [8, 9]) due to the fact that the scale factor $k_s > 0$ is allowed to vary with the energy spectrum of the physical system (“s” stands, in this context, for “spectrum”).

Traditionally, one considers all these scale factors as the Boltzmann constant (i.e., $k_s = k$), regardless of the energy spectrum being analyzed. However, these different scale factors are, as the next sections demonstrate, necessary to grant finite, smooth, macroscopically observable temperature values for physical systems whose description involves some infinitude that requires a limiting process to be modeled (i.e., solving (6) for a finite energy spectrum and then taking a convenient limit to model the system of interest, such as a harmonic oscillator or the hydrogen atom, and its thermodynamic behavior).

In Sections 3, 4, and 5, I show that (8) allows one to obtain a generalized Boltzmann-Gibbs distribution for the case where the energy spectrum uniformly approaches a continuous, unbounded limit with a common degeneracy, the harmonic oscillator and the one-dimensional box. Furthermore, in Section 6, this same scale factor allows us to obtain a family of well-behaved thermodynamic predictions for the hydrogen atom in free space, circumventing the Electronic

²As a remainder, the q -logarithm $\ln_q : [0, +\infty) \rightarrow \mathbb{R}$, $q \neq 1$, is given by $\ln_q z = (z^{1-q} - 1)/(1 - q)$, $z \geq 0$, and the q -exponential $\exp_q : \mathbb{R} \rightarrow \mathbb{R}$ is given by $\exp_q z = [1 + (1 - q)z]_+^{\frac{1}{1-q}}$, $z \in \mathbb{R}$.

³See Dognini and Tsallis [7] for a discussion on nonadditive functionals and their relation to *entropic extensivity*.

Partition Function Paradox [10] that emerges from the divergence of the partition function.

The literature furnishes different methods for dealing with this divergence. For instance, one may limit the energy spectrum (e.g., Fermi criteria [11]), adopt a two-tier model [12], use zeta function regularization [13] or generalize (1) through nonadditive entropic functionals [14]. Section 6 reveals that by adopting the nonadditive functional $S_{q,s}$ and the generalized optimization problem (6), one obtains a two-tier analytical model for the hydrogen atom in free space with a family of well-behaved thermodynamic predictions indexed by $q \in (0, 1)$. In particular, for $q = 0.5$, the specific heat becomes the Boltzmann constant.

2. The constrained maximization of $S_{q,s}$

I follow the general method developed by Dognini and Tsallis [6]. For $0 < q < 1$, let $\psi : \mathbb{R}_{++}^W \rightarrow \mathbb{R}_{++}^W$ be given by

$$\psi(p) = \frac{\nabla S_{q,s}(p)}{\nabla S_{q,s}(p)p^T} = \left(\frac{p_1^{q-1}}{\sum_{i=1}^W p_i^q}, \dots, \frac{p_W^{q-1}}{\sum_{i=1}^W p_i^q} \right),$$

and notice that, since $q \neq 1$, $\psi(\cdot)$ is a diffeomorphism and

$$\psi^{-1}(x) = \left(\frac{x_1^{\frac{1}{q-1}}}{\sum_{i=1}^W x_i^{\frac{q}{q-1}}}, \dots, \frac{x_W^{\frac{1}{q-1}}}{\sum_{i=1}^W x_i^{\frac{q}{q-1}}} \right).$$

Let $p_* \in \mathbb{R}_{++}^W$ be the unique, strictly positive solution of (6) and $x_* = \psi(p_*)$. First-order conditions are

$$\frac{k_s q}{1-q} (p_{*1}^{q-1}, \dots, p_{*W}^{q-1}) = \lambda_1 (1, \dots, 1) + \lambda_2 (E_1, \dots, E_W), \quad (10)$$

for $\lambda_1, \lambda_2 \in \mathbb{R}$ the Lagrange multipliers. Then, through the constraints of (6), we obtain

$$\lambda_1 = \frac{k_s q \sum_{i=1}^W p_{*i}^q}{1-q},$$

so that we can write (10) as

$$x_* = (1, \dots, 1) + (1-q) \frac{\lambda_2}{k_s q \sum_{i=1}^W p_{*i}^q} E = (1, \dots, 1) + (1-q) \beta E,$$

with $E = (E_1, \dots, E_W)$. Since $p_* = \psi^{-1}(x_*)$ and $\sum_{i=1}^W p_{*i} = 1$, we have that $\beta \in \mathbb{R}$ satisfies

$$\sum_{i=1}^W (1 + (1-q)\beta E_i)^{\frac{1}{q-1}} = \sum_{i=1}^W (1 + (1-q)\beta E_i)^{\frac{q}{q-1}}, \quad (11)$$

which can also be written as

$$\sum_{i=1}^W \exp_{2-q}(-\beta E_i) E_i = 0. \quad (12)$$

It is worth highlighting that (12) generalizes (3), since it fully characterizes the structural parameter β that defines the solution of (6). Furthermore,

$$p_{*i} = \frac{(1 + (1 - q)\beta E_i)^{\frac{1}{q-1}}}{\sum_{j=1}^W (1 + (1 - q)\beta E_j)^{\frac{1}{q-1}}} = \frac{\exp_{2-q}(-\beta E_i)}{\sum_{j=1}^W \exp_{2-q}(-\beta E_j)}, \quad (13)$$

for $1 \leq i \leq W$, which recovers (2) as $q \rightarrow 1$. Assuming that the value function of (6) (i.e., $S_{q,s}(p_*(\cdot))$) is differentiable and $\beta \neq 0$, the Envelope Theorem and (9) imply

$$\frac{1}{|T|_{\pm}^q} = \frac{\partial S_{q,s}(p_*(U))}{\partial U} = \lambda_2 = \beta k_s q \sum_{i=1}^W p_{*i}^q = \beta k_s q \left(\sum_{i=1}^W \exp_{2-q}(-\beta E_i) \right)^{1-q},$$

so that

$$\beta = \frac{1}{|T|_{\pm}^q k_s q \left(\sum_{i=1}^W \exp_{2-q}(-\beta E_i) \right)^{1-q}}. \quad (14)$$

In particular, $\text{sign}(\beta) = \text{sign}(T)$, if $\beta \neq 0$. Finally, we obtain

$$p_{*i} = \frac{\exp_{2-q}(-E_i/k_s |T|_{\pm}^q q \left(\sum_{l=1}^W \exp_{2-q}(-\beta E_l) \right)^{1-q})}{\sum_{j=1}^W \exp_{2-q}(-E_j/k_s |T|_{\pm}^q q \left(\sum_{l=1}^W \exp_{2-q}(-\beta E_l) \right)^{1-q})}, \quad (15)$$

for $1 \leq i \leq W$, which recovers (5) as $q \rightarrow 1$. To end this section, an analytical example is presented (c.f., Proposition 3 and Example 1 in [6]).

Example 1. Let the states be $0 = e_1 < e_2 = 0.5 < e_3 = 1$ and $0 < U < 1$, so that (6) can be written as

$$\max_{0 \leq p_1 \leq 1} \frac{k_s}{(1 - q)} \left(p_1^q + \left(\frac{(1 - U) - p_1}{1 - e_2} \right)^q + \left(\frac{U - e_2 + p_1 e_2}{1 - e_2} \right)^q - 1 \right).$$

We let $k = 1$, so that $k_s = 1/2^{1-q}$. The family of optimal value functionals $\{S_q(p_*(\cdot))\}_{0 < q < 1}$ is depicted in Figure 1.

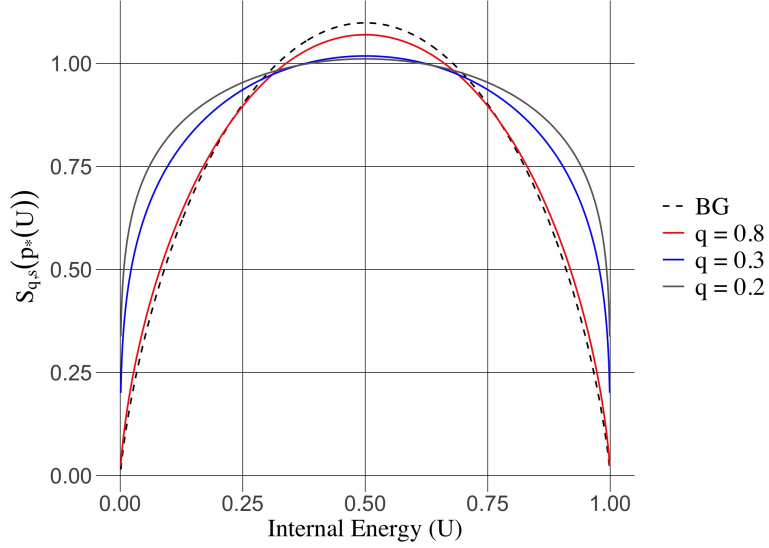


Figure 1: Graphic depiction of $S_{q,s}(p_*(U))$, $U \in [0, 1]$, $k = 1$, for $q = 0.2, 0.3, 0.8$, and the limiting Boltzmann-Gibbs (BG) case (i.e., $q \rightarrow 1$).

3. The case of an energy spectrum that uniformly approaches a continuous, unbounded limit with a common degeneracy

To illustrate the applicability of (6), I analyze the thermodynamic properties of a physical system with an energy spectrum that uniformly approaches a continuous, unbounded limit with a common degeneracy.

3.1 The Boltzmann-Gibbs distribution when the energy spectrum uniformly approaches a continuous, unbounded limit with a common degeneracy

Notice that the optimization problem (1) can also be written as

$$\begin{aligned}
 \max \quad & k \sum_{0 \leq e \leq e_{\max}} g(e) p_e \ln 1/p_e \\
 \text{s.t.} \quad & p_e \geq 0, 0 \leq e \leq e_{\max} \\
 & \sum_{0 \leq e \leq e_{\max}} g(e) p_e = 1 \\
 & \sum_{0 \leq e \leq e_{\max}} g(e) p_e e = U,
 \end{aligned} \tag{16}$$

with $p_e \geq 0$ representing the probability of a single microstate with energy e and the sums being evaluated for all values in the energy spectrum and $\sum_{0 \leq e \leq e_{\max}} g(e) = W$. Following (2), the

solution to (16) is given by

$$p_e(U) = \frac{\exp(-\beta(e - U))}{\sum_{0 \leq e \leq e_{\max}} g(e) \exp(-\beta(e - U))}$$

with $p_e(U)$ representing the optimal probability of a single microstate with energy e when the internal energy is $0 < U < e_{\max}$, and $\beta \in \mathbb{R}$ satisfying

$$\sum_{0 \leq e \leq e_{\max}} g(e) \exp(-\beta(e - U))(e - U) = 0. \quad (17)$$

Let

$$e_n(e_{\max}, N) = \frac{(n - 1)e_{\max}}{N - 1}, \quad (18)$$

for $1 \leq n \leq N$, $N \geq 2$, $e_{\max} > 0$. The energy spectrum is given by $0 = e_1(e_{\max}, N) < \dots < e_W(e_{\max}, N) = e_{\max}$ and the degeneracy function is $g(e_n) = m \geq 1$, $1 \leq n \leq N$ (clearly, for $m = 1$, the system is non-degenerate), so that

$$\sum_{0 \leq e \leq e_{\max}} g(e) = mN = W. \quad (19)$$

Let $\beta(U, e_{\max}, N) \in \mathbb{R}$ satisfy (17) when the internal energy is $0 < U < e_{\max}$. Then, we can write (17) as

$$\frac{e_{\max}}{N - 1} \sum_{n=1}^N \exp(-\beta(U, e_{\max}, N)(e_n(e_{\max}, N) - U))(e_n(e_{\max}, N) - U) = 0 \quad (20)$$

Assuming $\lim_{N \rightarrow \infty} \beta(U, e_{\max}, N) = \beta(U, e_{\max})$ and the appropriate convergence, (20) can be seen as approximating a Riemann sum that yields the following integral equation for $\beta(U, e_{\max})$

$$\int_0^{e_{\max}} \exp(-\beta(U, e_{\max})(e - U))(e - U) de = 0. \quad (21)$$

Further assuming $\lim_{e_{\max} \rightarrow \infty} \beta(U, e_{\max}) = \beta(U)$, (21) furnishes

$$\int_0^{\infty} \exp(-\beta(U)(e - U))(e - U) de = \frac{1}{\beta(U)^2} \exp(x)(x - 1) \Big|_{\beta(U)U}^{-\infty} = 0,$$

and, therefore,

$$\beta(U) = \frac{1}{U}. \quad (22)$$

In particular, (22) can be seen as a statement that, for $N \gg e_{\max} \gg 1$ (the order of the previous limits yields this relation on the orders of magnitude of N and $e_{\max}$), we have

$$\beta(U, e_{\max}, N) \approx 1/U.$$

Next, define the following function $\rho(\cdot, U, e_{\max}, N) : [0, e_{\max}] \rightarrow \mathbb{R}_+$,

$$\rho(e, U, e_{\max}, N) = \begin{cases} mp_{e_2(e_{\max}, N)}(U)(N-1)/e_{\max}, & \text{if } 0 = e_1(e_{\max}, N) \leq e \leq e_2(e_{\max}, N) \\ \dots & \\ mp_{e_N(e_{\max}, N)}(U)(N-1)/e_{\max}, & \text{if } e_{N-1}(e_{\max}, N) < e \leq e_N(e_{\max}, N), \end{cases}$$

and notice that $\rho(\cdot, U, e_{\max}, N)$ is a *density estimate* over the energy spectrum. Then, for $2 \leq n(e) \leq N$ satisfying $e_{n(e)-1}(e_{\max}, N) \leq e < e_{n(e)}(e_{\max}, N)$,

$$\begin{aligned} \int_{e_{n(e)-1}(e_{\max}, N)}^{e_{n(e)}(e_{\max}, N)} \rho(s, U, e_{\max}, N) ds &= \rho(e, U, e_{\max}, N) \frac{e_{\max}}{N-1} \\ &= mp_{e_{n(e)}(e_{\max}, N)} \\ &= \frac{m \exp(-\beta(U, e_{\max}, N)(e_{n(e)}(e_{\max}, N) - U)/k)}{\sum_{j=1}^N m \exp(-\beta(U, e_{\max}, N)(e_j(e_{\max}, N) - U)/k)} \end{aligned}$$

and, therefore,

$$\rho(e, U, e_{\max}, N) = \frac{\exp(-\beta(U, e_{\max}, N)(e_{i(e)}(e_{\max}, N) - U))}{\frac{e_{\max}}{N-1} \sum_{j=1}^N \exp(-\beta(U, e_{\max}, N)(e_j(e_{\max}, N) - U))}.$$

Since $\lim_{e_{\max} \rightarrow \infty} (\lim_{N \rightarrow \infty} \beta(U, e_{\max}, N)) = \beta(U) = 1/U$ and $\lim_{N \rightarrow \infty} e_{n(e)}(U, e_{\max}, N) = e$, the continuous Boltzmann-Gibbs distribution over the energy spectrum is given by

$$\rho(e, U) = \lim_{e_{\max} \rightarrow \infty} (\lim_{N \rightarrow \infty} \rho(e, U, e_{\max}, N)) = \frac{\exp(1 - e/U)}{\int_0^{+\infty} \exp(1 - s/U) ds} = \frac{\exp(-e/U)}{U}. \quad (23)$$

Furthermore, since

$$T(U, e_{\max}, N) = \frac{1}{k\beta(U, e_{\max}, N)},$$

we can define the limiting temperature of our system as

$$T = \lim_{e_{\max} \rightarrow +\infty} \left(\lim_{N \rightarrow +\infty} \frac{1}{k\beta(U, e_{\max}, N)} \right) = \frac{1}{k\beta(U)} = \frac{U}{k}, \quad (24)$$

thus obtaining a constant specific heat $dU/dT = k$ and, finally,

$$\rho(e, T) = \frac{\exp(-e/kT)}{kT}. \quad (25)$$

3.2 The generalized Boltzmann-Gibbs distribution when the energy spectrum uniformly approaches a continuous, unbounded limit with a common degeneracy

This subsection reveals that (6) provides a well-behaved generalization of our previous results for $1/2 \leq q < 1$ and $\sigma = 1$ in (8). Notice that (11) can be written as

$$\begin{aligned} \frac{e_{\max}}{N-1} \sum_{n=1}^N (1 + (1-q)\beta(U, e_{\max}, N)(e_n(e_{\max}, N) - U))^{\frac{1}{q-1}} = \dots \\ \dots \frac{e_{\max}}{N-1} \sum_{n=1}^N (1 + (1-q)\beta(U, e_{\max}, N)(e_n(e_{\max}, N) - U))^{\frac{q}{q-1}}. \end{aligned} \quad (26)$$

Assuming $\lim_{W \rightarrow \infty} \beta(U, e_{\max}, N) = \beta(U, e_{\max})$ and the appropriate convergence, (26) can be seen as approximating a Riemann sum that yields the following integral equation for $\beta(U, e_{\max})$,

$$\int_0^{e_{\max}} (1 + (1-q)\beta(U, e_{\max})(e - U))^{\frac{1}{q-1}} de = \int_0^{e_{\max}} (1 + (1-q)\beta(U, e_{\max})(e - U))^{\frac{q}{q-1}} de. \quad (27)$$

Further assuming $\lim_{e_{\max} \rightarrow \infty} \beta(U, e_{\max}) = \beta(U) > 0$, (27) furnishes

$$\int_0^{+\infty} (1 + (1-q)\beta(U)(e - U))^{\frac{1}{q-1}} de = \int_0^{+\infty} (1 + (1-q)\beta(U)(e - U))^{\frac{q}{q-1}} de. \quad (28)$$

Since $\beta(U) > 0$,

$$\int_0^{+\infty} (1 + (1-q)\beta(U)(e - U))^{\frac{1}{q-1}} de = \frac{(1 - (1-q)\beta(U)U)^{\frac{q}{q-1}}}{\beta(U)q},$$

Also, $\beta(U) > 0$ and $1/2 \leq q < 1$ imply

$$\int_0^{+\infty} (1 + (1-q)\beta(U)(e - U))^{\frac{q}{q-1}} de = \frac{(1 - (1-q)\beta(U)U)^{\frac{2q-1}{q-1}}}{\beta(U)(2q-1)}.$$

Therefore,

$$\frac{(1 - (1-q)\beta(U)U)^{\frac{q}{q-1}}}{\beta(U)q} = \frac{(1 - (1-q)\beta(U)U)^{\frac{2q-1}{q-1}}}{\beta(U)(2q-1)} \implies \beta(U) = \frac{1}{qU} > 0, \quad (29)$$

which generalizes (22). By the same reasoning that leads to (23), (13) and (29) imply

$$\rho(e, U) = \frac{\exp_{2-q}(-\beta(U)(e - U))}{\int_0^{+\infty} \exp_{2-q}(-\beta(U)(s - U)) ds} = \frac{1}{U} \left(\frac{2q-1}{q} \right)^{\frac{q}{1-q}} \exp_{2-q} \left(\frac{1}{q} - \frac{e}{qU} \right), \quad (30)$$

which generalizes (23). Since $\beta(U) > 0$, for $N, e_{\max} \gg 1$ we have $\beta(U, e_{\max}, N) > 0$, so that (14) implies that the corresponding temperature is positive and given by

$$T(U, e_{\max}, N)^q = \frac{1}{q\beta(U, e_{\max}, N)} \frac{1}{k_s (\sum_{i=1}^N m \exp_{2-q}(-\beta(U, e_{\max}, N)(e_i(e_{\max}, N) - U)))^{1-q}}. \quad (31)$$

Then, notice that

$$\begin{aligned} T(U)^q &= \lim_{e_{\max} \rightarrow +\infty} \left(\lim_{N \rightarrow +\infty} T(U, e_{\max}, N)^q \right) \\ &= \frac{U}{(\int_0^{+\infty} \exp_{2-q}(-\beta(U)(s - U))ds)^{1-q}} \lim_{e_{\max} \rightarrow +\infty} \left(\lim_{N \rightarrow +\infty} \frac{e_{\max}^{1-q}}{(N-1)^{1-q} m^{1-q} k_s} \right) \\ &= \frac{U}{k^q (\int_0^{+\infty} \exp_{2-q}(-\beta(U)(s - U))ds)^{1-q}}, \end{aligned}$$

where the last equality is due to (8), with $\sigma = 1$, and (19), since

$$\lim_{e_{\max} \rightarrow +\infty} \left(\lim_{N \rightarrow +\infty} \frac{e_{\max}^{1-q}}{(N-1)^{1-q} m^{1-q} k_s} \right) = \lim_{N \rightarrow +\infty} \frac{1}{k^q} \left(\frac{1 - 1/Nm}{1 - 1/N} \right)^{1-q} = \frac{1}{k^q}.$$

Therefore,

$$T(U)^q = \frac{U}{k^q (\int_0^{+\infty} \exp_{2-q}(-\beta(U)(s - U))ds)^{1-q}} = \frac{1}{k^q} \left(\frac{2q-1}{q} \right)^q U^q \implies T = \frac{2q-1}{kq} U,$$

so that

$$U = \frac{qkT}{2q-1}, \quad (32)$$

which generalizes (24). In particular, the specific heat is constant and given by

$$\frac{dU}{dT} = \frac{qk}{2q-1}, \quad (33)$$

what is illustrated in Figure 3.

Finally, (32) implies

$$\rho(e, T) = \left(\frac{2q-1}{q} \right)^{\frac{1}{1-q}} \frac{\exp_{2-q}(q^{-1} - (2q-1)e/q^2 kT)}{kT}. \quad (34)$$

which generalizes the Boltzmann-Gibbs distribution (25) through the entropic functional $S_{q,s}$, $1/2 \leq q < 1$. Furthermore, Figure 3 depicts (34) and reveals that the reduction of q furnishes distributions with fat tails for the same temperature value.

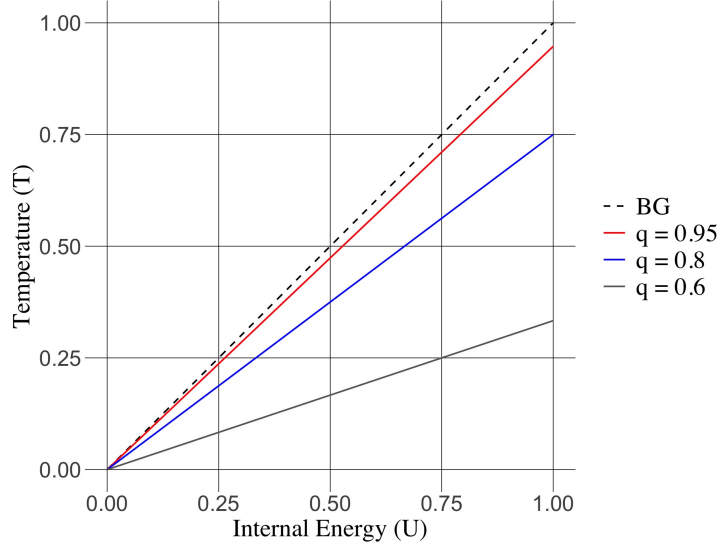


Figure 2: Graphic depiction of the temperature and the internal energy for a system with an energy spectrum that uniformly approaches a continuous, unbounded limit with a common degeneracy, using Boltzmann-Gibbs entropy and $S_{q,s}$ with $q = 0.6, 0.8, 0.95$, for $k = 1$.

4. The harmonic oscillator

To further illustrate the applicability of (6), this section analyzes the thermodynamic properties of the harmonic oscillator, starting with the classical distribution obtained from (1). Before doing so, however, I need some extra notation that will also be used in Sections 5 and 6.

Let the energy spectrum *without degeneracy* be $0 = e_1 < \dots < e_n < \dots < e_N = e_{\max}$ (notice that the inequalities are strict and the index “ n ” is adopted when the spectrum is written this way) and the degeneracy function be $g(e_n) = \#\{1 \leq i \leq W \mid e_i = e_n\}$, $1 \leq n \leq N$. Also, let $e_t < U \leq e_{t+1}$, $t + 1 \leq N$.

Notice that (3) and (12) can be gathered as

$$\sum_{n=1}^t g(e_n) \exp_{2-q}(\beta_N |E_n|) |E_n| = \sum_{n=t+1}^N g(e_n) \exp_{2-q}(-\beta_N |E_n|) |E_n| \quad (35)$$

for $q \in (0, 1]$, $\beta_N \in \mathbb{R}$. Define the auxiliary functions $f_{t,q} : (-\infty, 1/(1-q)U) \rightarrow (0, +\infty)$ and $g_{t,N,q} : (-1/(1-q)E_{t+1}, +\infty) \rightarrow (0, +\infty)$ as

$$\begin{aligned} f_{t,q}(x) &= \sum_{n=1}^t g(e_n) \exp_{2-q}(x |E_n|) |E_n| \\ g_{t,N,q}(x) &= \sum_{n=t+1}^N g(e_n) \exp_{2-q}(-x |E_n|) |E_n|. \end{aligned}$$

Notice that (35) can be written as $f_{t,q}(\beta_N) = g_{t,N,q}(\beta_N)$, $f_{t,q}(\cdot)$ is strictly increasing and $g_{t,N,q}(\cdot)$

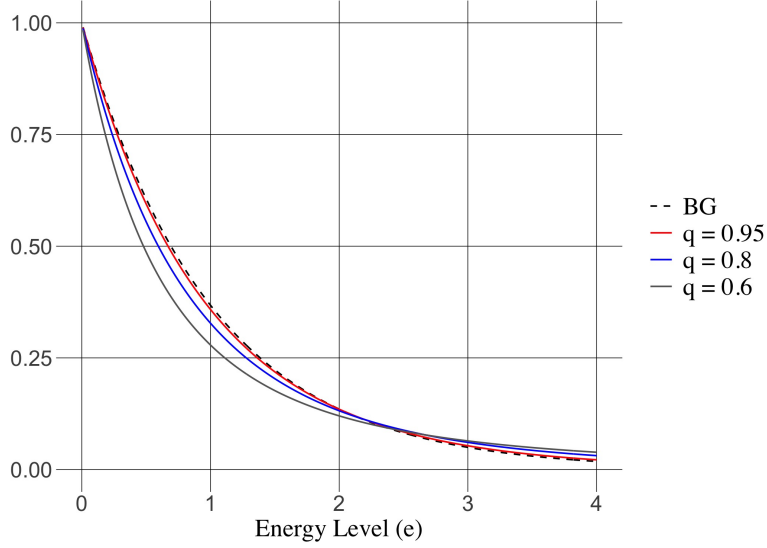


Figure 3: Graphic depiction of $\rho(e, T)$ in (25) and (34) with $q = 0.6, 0.8, 0.95$, for $k = T = 1$.

is strictly decreasing, with

$$\lim_{x \rightarrow -\infty} f_{t,q}(x) = \lim_{x \rightarrow +\infty} g_{t,N,q}(x) = 0,$$

and

$$\lim_{x \rightarrow 1/(1-q)U} f_{t,q}(x) = \lim_{x \rightarrow -1/(1-q)E_{t+1}} g_{t,N,q}(x) = +\infty.$$

Then, indeed, the Intermediate Value Theorem and the strict monotonicity of $f_{t,q}(\cdot)$ and $g_{t,N,q}(\cdot)$ imply the existence of a single β_N that satisfies $f_{t,q}(\beta_N) = g_{t,N,q}(\beta_N)$. Also,

$$g_{t,N,q}(0) - f_{t,q}(0) = \sum_{n=1}^N g(e_n)E_n.$$

Therefore, if there is $N_1 \geq t + 1$ such that

$$\sum_{n=1}^N g(e_n)E_n > 0, \tag{36}$$

for $N \geq N_1$, we can also conclude that $\beta_N > 0$ for $N \geq N_1$. Next, notice that $g_{t,N+1,q}(x) > g_{t,N,q}(x)$, $x \geq 0$. Suppose (36) is valid and $0 < \beta_{N+1} \leq \beta_N$, $N \geq N_1$. Then, $f_{t,q}(\beta_{N+1}) \leq f_{t,q}(\beta_N)$ and

$$f_{t,q}(\beta_N) = g_{t,N,q}(\beta_N) < g_{t,N+1,q}(\beta_N) \leq g_{t,N+1,q}(\beta_{N+1}) = f_{t,q}(\beta_{N+1}),$$

absurd. We conclude that if (36) is valid, then $\{\beta_N\}_{N \geq N_1}$ is a strictly increasing sequence. If

$q \in (0, 1)$, then $\beta_N < 1/(1 - q)U$ and, therefore, there is $\beta > 0$ satisfying

$$\lim_{N \rightarrow \infty} \beta_N = \beta \leq \frac{1}{(1 - q)U}.$$

Define, then,

$$\delta_N = \frac{1}{(1 - q)U} - \beta_N$$

for $N \geq N_1$. Then, $\{\delta_N\}_{N \geq N_1}$ is a strictly decreasing sequence with

$$\lim_{N \rightarrow \infty} \delta_N = \delta = \frac{1}{(1 - q)U} - \beta \geq 0.$$

Also,

$$(1 - q)U\delta_N = 1 - (1 - q)U\beta_N, \quad (37)$$

so that

$$\exp_{2-q}(-\beta E_n) = ((1 - q)U\delta_N + (1 - q)e_n\beta_N)^{\frac{1}{q-1}},$$

for $n \geq 1$. Therefore, (13) implies

$$p_{*n}^N = \left(\frac{U\delta_N}{U\delta_N + e_n\beta_N} \right)^{\frac{1}{1-q}} p_{*1}^N, \quad (38)$$

for $2 \leq n \leq N$, with p_{*n}^N representing the probability of a single microstate of energy e_n when the energy spectrum extends to e_N . It is also convenient to define

$$r_n^N = \frac{p_{*n}^N}{p_{*1}^N} = \left(\frac{U\delta_N}{U\delta_N + e_n\beta_N} \right)^{\frac{1}{1-q}}$$

for $1 \leq n \leq N$. Therefore, $r_n^N > r_{n+1}^N > 0$, $1 \leq n \leq N - 1$, and $0 < r_n^{N+1} < r_n^N$, $2 \leq n \leq N$, with their limit given by

$$\lim_{N \rightarrow \infty} r_n^N = r_n = \left(\frac{U\delta}{U\delta + e_n\beta} \right)^{\frac{1}{1-q}} \quad (39)$$

for $n \geq 2$

Finally, for $q = 1$, suppose

$$\lim_{N \rightarrow \infty} g_{t,N,1}(x) = \lim_{N \rightarrow \infty} \sum_{n=t+1}^N g(e_n) \exp(-x|E_n|)|E_n| < +\infty. \quad (40)$$

for $x > 0$. Then, if $\lim_{N \rightarrow +\infty} \beta_N = +\infty$, we have

$$+\infty > \lim_{N \rightarrow +\infty} g_{t,N,1}(\beta_{N_1}) > \lim_{N \rightarrow +\infty} g_{t,N,1}(\beta_N) = \lim_{N \rightarrow +\infty} f_{t,1}(\beta_N) = +\infty,$$

absurd. Therefore, for $q = 1$, if (40) is valid, one can also conclude that there is $\lim_{N \rightarrow \infty} \beta_N = \beta > 0$.

4.1 The Boltzmann-Gibbs distribution for the harmonic oscillator

The energy spectrum of the harmonic oscillator⁴ is $e_n = (n - 1)\hbar\omega$, $\hbar\omega > 0$, $n \geq 1$ and the degeneracy function is $g(e_n) = 1$, $n \geq 1$. Let $e_t < U \leq e_{t+1}$, $t \geq 1$. For $N \geq t + 1$, consider (1) with only the first N energy values $0 = e_1 < \dots < e_N = (N - 1)\hbar\omega$. Notice that (40) is valid, since

$$\lim_{N \rightarrow \infty} \sum_{n=t+1}^N \exp(-x((n - 1)\hbar\omega - U))((n - 1)\hbar\omega - U) < +\infty,$$

and we have $\lim_{N \rightarrow \infty} \beta_N = \beta > 0$. Assuming adequate convergence of (3), we have

$$0 = \lim_{N \rightarrow \infty} \sum_{n=1}^N \exp(-\beta_N E_n) E_n = -\frac{d}{d\beta} \sum_{n=1}^{\infty} \exp(-\beta E_n) = -\frac{d}{d\beta} \left(\frac{\exp(\beta U)}{1 - \exp(-\beta \hbar\omega)} \right),$$

so that

$$U = \frac{\hbar\omega \exp(-\beta \hbar\omega)}{1 - \exp(-\beta \hbar\omega)} \implies \beta = \frac{1}{\hbar\omega} \log \left(\frac{\hbar\omega + U}{U} \right).$$

Once the structural parameter $\beta > 0$ is calculated, the probabilities are given by (2) as

$$p_{*n} = \exp(-\beta \hbar\omega(n - 1)) - \exp(-\beta \hbar\omega n),$$

for $n \geq 1$. Finally, the temperature relates to β and U as

$$T = \frac{1}{k\beta} = \left(\frac{k}{\hbar\omega} \log \left(\frac{\hbar\omega + U}{U} \right) \right)^{-1}. \quad (41)$$

4.2 The generalized Boltzmann-Gibbs distribution for the harmonic oscillator

Let $q \in (0, 1)$ and notice that

$$\sum_{n=1}^N g(e_n) E_n = \sum_{n=1}^N ((n - 1)\hbar\omega - U) = \frac{N(N + 1)\hbar\omega}{2} - (\hbar\omega + U)N$$

⁴This is actually a shifted version of the energy spectrum so that $e_1 = 0$.

which is positive for $N \gg 1$. Therefore, (36) is valid for some $N_1 \gg 1$ and we have $\{\beta_N\}_{N \geq N_1}$ strictly increasing with

$$0 < \lim_{N \rightarrow \infty} \beta_N = \beta \leq \frac{1}{(1-q)U}.$$

Next, we have

$$g_{t,N,q}(1/(1-q)U) = \sum_{n=k+1}^N \left(\frac{(n-1)\hbar\omega}{U} \right)^{\frac{1}{q-1}} ((n-1)\hbar\omega - U). \quad (42)$$

If $q \leq 1/2$, the fact that $g_{t,N,q}(\cdot)$ is decreasing implies that

$$\lim_{N \rightarrow \infty} f_{t,q}(\beta_N) = \lim_{N \rightarrow \infty} g_{t,N,q}(\beta_N) \geq \lim_{N \rightarrow \infty} g_{t,N,q}(1/(1-q)U) = +\infty,$$

where the last equality is derived from (42) and the fact that $q \leq 1/2$ implies $q/(1-q) \leq 1$. Therefore, if $q \leq 1/2$, then

$$\beta = \frac{1}{(1-q)U}. \quad (43)$$

Assuming $\lim_{N \rightarrow +\infty} p_{*1}^N = p_{*1}$, (39) implies

$$\lim_{N \rightarrow +\infty} p_{*n}^N = p_{*n} = r_n p_{*1}. \quad (44)$$

If $\delta = 0$ (i.e., $\beta = 1/(1-q)U$), then (39) implies $r_n = 0$ and $p_{*n} = 0$, $n \geq 2$. Suppose, then, $\delta > 0$ (i.e., $\beta < 1/(1-q)U$). Notice that (12) can also be written as

$$U = \sum_{n=1}^N p_{*n}^N e_n = p_{*1}^N \sum_{n=1}^N r_n^N (n-1)\hbar\omega.$$

Assuming the appropriate convergence, we have

$$\lim_{N \rightarrow \infty} p_{*1}^N \sum_{n=1}^N r_n^N (n-1)\hbar\omega = p_{*1} \sum_{n=1}^{\infty} r_n (n-1)\hbar\omega = U,$$

and

$$\lim_{N \rightarrow \infty} \sum_{n=1}^N p_{*n}^N = \lim_{N \rightarrow \infty} p_{*1}^N \sum_{n=1}^N r_n^N = p_{*1} \sum_{n=1}^{\infty} r_n = 1.$$

Therefore,

$$\frac{\sum_{n=1}^{\infty} r_n (n-1)\hbar\omega}{\sum_{n=1}^{\infty} r_n} = U.$$

As a remark, note that

$$\begin{aligned} r_n &\approx \left(\frac{\delta U}{\beta \hbar \omega} \right)^{\frac{1}{1-q}} \frac{1}{n^{\frac{1}{1-q}}} \\ r_n(n-1) &\approx \left(\frac{\delta U}{\beta \hbar \omega} \right)^{\frac{1}{1-q}} \frac{1}{n^{\frac{q}{1-q}}}, \end{aligned}$$

for $n \gg 1$, and to ensure the convergence of both series, we must have

$$1 < \frac{q}{1-q} < \frac{1}{1-q} \implies q > \frac{1}{2}. \quad (45)$$

Then, (43) allows us to state that $q \leq 1/2$ implies $\delta = 0$ (i.e., $\beta = 1/(1-q)U$), and (45) indicates, although not formally proven, that $1/2 < q < 1$ implies $\delta > 0$ (i.e., $\beta < 1/(1-q)U$).

Since $\beta_N > 0$, $N \gg 1$, the temperature of the truncated system is positive and given by

$$T_N^q = \frac{1}{q\beta_N k_s (\sum_{n=1}^N \exp_{2-q}(-\beta E_n))^{1-q}} = \frac{(p_{*1}^N)^{1-q}(1-q)\delta_N U}{q\beta_N k_s}.$$

Let $\sigma = 1$ in (8), so that

$$k_s = k^q \left(\frac{e_{\max}}{W-1} \right)^{1-q} = k^q \left(\frac{(N-1)\hbar\omega}{N-1} \right)^{1-q} = k^q (\hbar\omega)^{1-q}.$$

for $N \geq t+1$. The temperature of the harmonic oscillator is, therefore, given by

$$T = \lim_{N \rightarrow \infty} T_N = \frac{1}{k} \left(\frac{p_{*1}^{1-q}(1-(1-q)\beta U)}{q\beta(\hbar\omega)^{1-q}} \right)^{\frac{1}{q}}, \quad (46)$$

which generalizes (41), with

$$p_{*1} = \left(\sum_{n=1}^{\infty} r_n \right)^{-1}$$

and

$$\frac{\sum_{n=1}^{\infty} r_n(n-1)\hbar\omega}{\sum_{n=1}^{\infty} r_n} = U.$$

Figure 4 depicts the generalized thermodynamic behavior of the harmonic oscillator.

5. The one-dimensional box

To further illustrate the applicability of (6), I will analyze the thermodynamic properties of a one-dimensional box (i.e., the trapped particle).

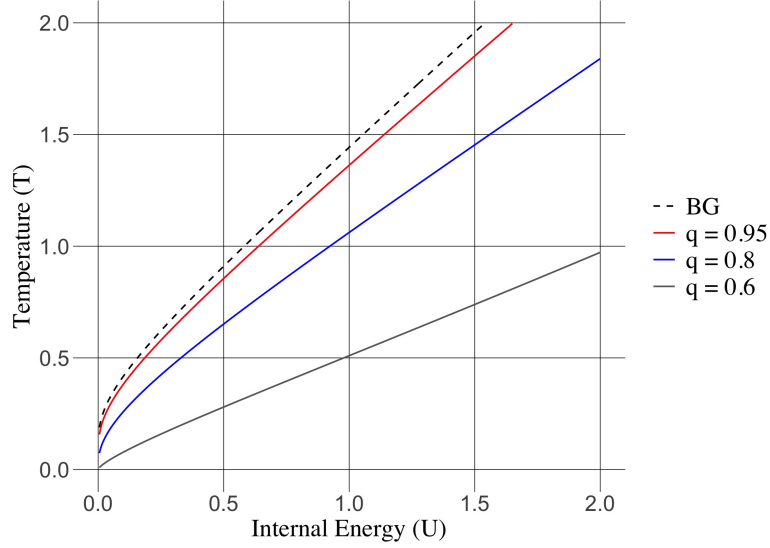


Figure 4: Graphic depiction of the temperature and the internal energy for the harmonic oscillator using Boltzmann-Gibbs entropy and $S_{q,s}$ with $q = 0.6, 0.8, 0.95$, for $k = \hbar\omega = 1$.

5.1 The Boltzmann-Gibbs distribution for the one-dimensional box

The energy spectrum of the one-dimensional box⁵ is $e_n = (n^2 - 1)\hbar^2\pi^2/2mL^2 = (n^2 - 1)\gamma$, $\gamma > 0$, $n \geq 1$, and the degeneracy function is $g(e_n) = 1$, $n \geq 1$. Let $e_t < U \leq e_{t+1}$, $t \geq 1$. For $N \geq t+1$, consider (1) with only the first N energy values $0 = e_1 < \dots < e_N = (N-1)\gamma$. Notice that (40) is valid, since

$$\lim_{N \rightarrow \infty} \sum_{n=t+1}^N \exp(-x((n^2 - 1)\gamma - U))((n^2 - 1)\gamma - U) < +\infty,$$

and we have $\lim_{N \rightarrow \infty} \beta_N = \beta > 0$. Assuming adequate convergence of (3), we have

$$\frac{\sum_{n=1}^{\infty} \exp(-\beta(n^2 - 1)\gamma)}{\sum_{n=1}^{\infty} n^2 \exp(-\beta(n^2 - 1)\gamma)} = \frac{e}{U + e}. \quad (47)$$

Once the structural parameter $\beta > 0$ is calculated through (47), the probabilities are given by

$$p_{*n} = \frac{\exp(-\beta(e_n - U))}{\sum_{i=1}^{\infty} \exp(-\beta(e_i - U))}$$

for $n \geq 1$. Finally, the temperature relates to β as $T = 1/k\beta$.

⁵This is actually a shifted version of the energy spectrum so that $e_1 = 0$.

5.2 The generalized Boltzmann-Gibbs distribution for the one-dimensional box

Let $q \in (0, 1)$ and notice that

$$\sum_{n=1}^N g(e_n) E_n = \sum_{n=1}^N ((n^2 - 1)\gamma - U) = \frac{N(N+1)(2N+1)\gamma}{2} - (\gamma + U)N$$

which is positive for $N \gg 1$. Therefore, (36) is valid for some $N_1 \gg 1$ and we have $\{\beta_N\}_{N \geq N_1}$ strictly increasing with

$$0 < \lim_{N \rightarrow \infty} \beta_N = \beta \leq \frac{1}{(1-q)U}.$$

Next, we have

$$g_{t,N,q}(1/(1-q)U) = \sum_{n=k+1}^N \left(\frac{(n^2 - 1)\gamma}{U} \right)^{\frac{1}{q-1}} ((n^2 - 1)\gamma - U). \quad (48)$$

If $q \leq 1/3$, the fact that $g_{t,N,q}(\cdot)$ is decreasing implies that

$$\lim_{N \rightarrow \infty} f_{t,q}(\beta_N) = \lim_{N \rightarrow \infty} g_{t,N,q}(\beta_N) \geq \lim_{N \rightarrow \infty} g_{t,N,q}(1/(1-q)U) = +\infty,$$

where the last equality is derived from (48) and the fact that $q \leq 1/3$ implies $2q/(1-q) \leq 1$. Therefore, if $q \leq 1/3$, then

$$\beta = \frac{1}{(1-q)U}. \quad (49)$$

Assuming $\lim_{N \rightarrow +\infty} p_{*1}^N = p_{*1}$, (39) implies

$$\lim_{N \rightarrow +\infty} p_{*n}^N = p_{*n} = r_n p_{*1}. \quad (50)$$

If $\delta = 0$ (i.e., $\beta = 1/(1-q)U$), then (39) implies $r_n = 0$ and $p_{*n} = 0$, $n \geq 2$. Suppose, then, $\delta > 0$ (i.e., $\beta < 1/(1-q)U$). Notice that (12) can also be written as

$$U = \sum_{n=1}^N p_{*n}^N e_n = p_{*1}^N \sum_{n=1}^N r_n^N (n^2 - 1)\gamma.$$

Assuming the appropriate convergence, we have

$$\lim_{N \rightarrow \infty} p_{*1}^N \sum_{n=1}^N r_n^N (n^2 - 1)\gamma = p_{*1} \sum_{n=1}^{\infty} r_n (n^2 - 1)\gamma = U,$$

and

$$\lim_{N \rightarrow \infty} \sum_{n=1}^N p_{*n}^N = \lim_{N \rightarrow \infty} p_{*1}^N \sum_{n=1}^N r_n^N = p_{*1} \sum_{n=1}^{\infty} r_n = 1.$$

Therefore,

$$\frac{\sum_{n=1}^{\infty} r_n (n^2 - 1) \gamma}{\sum_{n=1}^{\infty} r_n} = U.$$

As a remark, note that

$$\begin{aligned} r_n &\approx \left(\frac{\delta U}{\beta e} \right)^{\frac{1}{1-q}} \frac{1}{n^{\frac{2}{1-q}}} \\ r_n (n^2 - 1) &\approx \left(\frac{\delta U}{\beta e} \right)^{\frac{1}{1-q}} \frac{1}{n^{\frac{2q}{1-q}}}, \end{aligned}$$

for $n \gg 1$, and to ensure the convergence of both series, we must have

$$1 < \frac{2q}{1-q} < \frac{2}{1-q} \implies q > \frac{1}{3}. \quad (51)$$

Then, (49) allows us to state that $q \leq 1/3$ implies $\delta = 0$ (i.e., $\beta = 1/(1-q)U$), and (51) indicates, although not formally proven, that $1/3 < q < 1$ implies $\delta > 0$ (i.e., $\beta < 1/(1-q)U$).

Since $\beta_N > 0$, $N \gg 1$, the temperature of the truncated system is positive and given by

$$T_N^q = \frac{1}{q\beta_N k_s (\sum_{n=1}^N \exp_{2-q}(-\beta E_n))^{1-q}} = \frac{(p_{*1}^N)^{1-q} (1-q) \delta_N U}{q\beta_N k_s}.$$

Let $\sigma = 2$ in (8), so that

$$k_s = k^q \left(\frac{e_{\max}}{W^2 - 1} \right)^{1-q} = k^q \left(\frac{(N^2 - 1)\gamma}{N^2 - 1} \right)^{1-q} = k^q \gamma^{1-q}.$$

for $N \geq t + 1$. The temperature of the one dimensional box is, therefore, given by

$$T = \lim_{N \rightarrow \infty} T_N = \frac{1}{k} \left(\frac{p_{*1}^{1-q} (1 - (1-q)\beta U)}{q\beta \gamma^{1-q}} \right)^{\frac{1}{q}} \quad (52)$$

with

$$p_{*1} = \left(\sum_{n=1}^{\infty} r_n \right)^{-1}$$

and

$$\frac{\sum_{n=1}^{\infty} r_n (n^2 - 1) \gamma}{\sum_{n=1}^{\infty} r_n} = U.$$

Figure 5 depicts the generalized thermodynamic behavior of the harmonic oscillator.

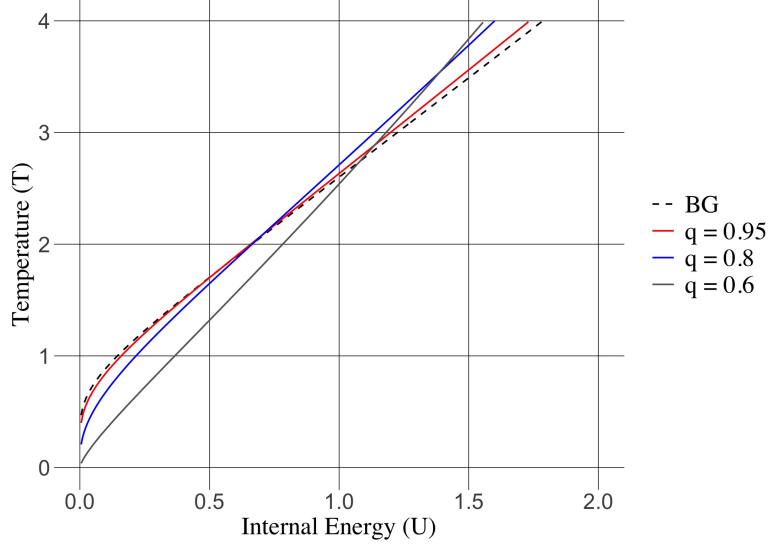


Figure 5: Graphic depiction of the temperature and the internal energy for the one-dimensional box using Boltzmann-Gibbs entropy and $S_{q,s}$ with $q = 0.6, 0.8, 0.95$, for $k = \hbar^2 \pi^2 / 2mL^2 = 1$.

6. The Electronic Partition Function Paradox

The energy spectrum of the hydrogen atom in free space is given by

$$e_n = \left(1 - \frac{1}{n^2}\right) e_{ion},$$

for $n \geq 1$, with $e_{ion} = 13.6$ eV the ionization energy, and the degeneracy function is $g(e_n) = 2n^2$, $n \geq 1$. Let $e_t < U \leq e_{t+1}$, $t \geq 1$, and $q \in (0, 1)$. For $N \geq t + 1$, consider (1) with only the first N energy values $0 = e_1 < \dots < e_N = (1 - \frac{1}{N^2})e_{ion}$. Notice that

$$\sum_{n=1}^N g(e_n) E_n = \sum_{n=1}^N 2n^2 \left(\left(1 - \frac{1}{n^2}\right) e_{ion} - U \right) = \sum_{n=1}^N 2n^2 (e_{ion} - U) - 2N e_{ion}$$

which is positive for $N \gg 1$. Therefore, (36) is valid for some $N_1 \gg 1$ and we have $\{\beta_N\}_{N \geq N_1}$ strictly increasing with

$$0 < \lim_{N \rightarrow \infty} \beta_N = \beta \leq \frac{1}{(1-q)U}.$$

Next, notice that

$$g_{t,N,q}(x) = \sum_{n=t+1}^N 2n^2 \exp_{2-q}(-x|E_n|)|E_n| \geq \sum_{n=t+1}^N 2n^2 \exp_{2-q}(-x)|E_{t+1}|$$

for $x > 0$. Therefore,

$$\lim_{N \rightarrow \infty} f_{t,q}(\beta_N) = \lim_{N \rightarrow \infty} g_{t,N,q}(\beta_N) \geq \lim_{N \rightarrow \infty} g_{t,N,q}(\beta_{N_1}) = +\infty,$$

and this implies

$$\beta = \frac{1}{(1-q)U}.$$

Next, (12) allows us to write

$$\sum_{n=1}^N 2n^2 \exp_{2-q}(-\beta_N E_n) E_n = 0 \implies \sum_{n=1}^N n^2 \exp_{2-q}(-\beta_N E_n) \frac{(e_{ion} - U)}{e_{ion}} = \sum_{n=1}^N \exp_{2-q}(-\beta_N E_n).$$

Therefore, (13) and (37) imply

$$g(e_1)p_{*1}^N = \frac{2 \exp_{2-q}(\beta_N U)}{\sum_{n=1}^N 2n^2 \exp_{2-q}(-\beta_N E_n)} = \frac{e_{ion} - U}{e_{ion}} \frac{1}{1 + (U\delta_N)^{\frac{1}{1-q}} \sum_{n=2}^N (U\delta_N + e_n \beta_N)^{\frac{1}{q-1}}}. \quad (53)$$

I proceed with the following lemma.

Lemma 1. *Let $f_{t,q}(\cdot)$, $g_{t,N,q}(\cdot)$, $N \geq t+1$, and $\{\delta_N\}_{N \geq N_1}$ be as defined above. Then,*

$$\lim_{N \rightarrow \infty} N^{3(1-q)} \delta_N = \frac{3^{1-q} e_{ion}}{2^{1-q} (1-q) (e_{ion} - U)^{1-q} U^{1+q}}.$$

Lemma 1 implies that

$$0 < \lim_{N \rightarrow \infty} (U\delta_N)^{\frac{1}{1-q}} \sum_{n=2}^N (U\delta_N + e_n \beta_N)^{\frac{1}{q-1}} < \lim_{N \rightarrow \infty} \left(\frac{U\delta_N N^{3(1-q)}}{e_2 \beta_{N_1}} \right)^{\frac{1}{1-q}} \frac{1}{N^2} = 0,$$

so that, by (53), we have

$$g(e_1)p_{*1} = \lim_{N \rightarrow \infty} g(e_1)p_{*1}^N = 1 - \frac{U}{e_{ion}}. \quad (54)$$

Since $\delta = 0$, (39) implies $r_n = 0$, $n \geq 2$, so that

$$\lim_{N \rightarrow \infty} g(e_n)p_{*n}^N = 0, \quad (55)$$

for $n \geq 2$. Notice, however, that although (55) implies that the limit of the probability of every energy level $n \geq 2$ tends towards zero, this only means that the $U/e_{ion} > 0$ remaining probability

from (54) is, when $N \rightarrow \infty$, moving towards the upper energy levels. One can represent this behavior by adding one last energy level $e_\infty = e_{ion}$ and assigning it a *total probability* $p_{*\infty} \in (0, 1)$ (in contrast to p_{*n} , $1 \leq n < \infty$, which indicates the probability of a single microstate with energy e_n) of

$$p_{*\infty} = \frac{U}{e_{ion}}.$$

Therefore, this two-tier probability distribution concentrates on the first and the “outermost” energy level e_{ion} , with the average energy given by

$$g(e_1)p_{*1}0 + p_{*\infty}e_{ion} = U.$$

Remarkably, this behavior of the limiting optimal probability distribution does not depend on the actual value of $0 < q < 1$.

Next, the temperature of the truncated system is given by (14) as

$$T_N^q = \frac{1}{qk_s\beta_N(\sum_{n=1}^N n^2 \exp_{2-q}(-\beta_N E_n))^{1-q}} = \frac{(p_{*1}^N)^{1-q}U(1-q)}{q\beta_N} \frac{\delta_N}{k_s}. \quad (56)$$

Let $\sigma = 1$ in (8), so that

$$k_s = k^q \left(\frac{e_{\max}}{W-1} \right)^{1-q} = k^q \left(\frac{(1-N^{-2})e_{ion}}{\sum_{n=1}^N 2n^2 - 1} \right)^{1-q} = k^q \left(\frac{3(1-N^{-2})e_{ion}}{N(N+1)(2N+1)-3} \right)^{1-q},$$

for $N \geq t+1$, so that, by Lemma 1,

$$\lim_{N \rightarrow \infty} \frac{\delta_N}{k_s} = \lim_{N \rightarrow \infty} \frac{N^{3(1-q)}\delta_N}{N^{3(1-q)}k_s} = \frac{e_{ion}^q}{k^q(1-q)(e_{ion}-U)^{1-q}U^{1+q}}.$$

Therefore, (56) implies

$$T^q = \lim_{N \rightarrow \infty} T_N^q = \frac{(1-q)U^{1-q}}{qk^q e_{ion}^{1-2q}},$$

and we conclude that

$$T = \left(\frac{1-q}{q} \right)^{\frac{1}{q}} \left(\frac{U}{e_{ion}} \right)^{\frac{1-q}{q}} \frac{e_{ion}}{k}. \quad (57)$$

Figure 6 depicts (57) for different values of $q \in (0, 1)$.

In particular, the critical ionization temperature $T_{ion} > 0$ is related to $q \in (0, 1)$ according to

$$T_{ion} = \left(\frac{1-q}{q} \right)^{\frac{1}{q}} \frac{e_{ion}}{k}. \quad (58)$$

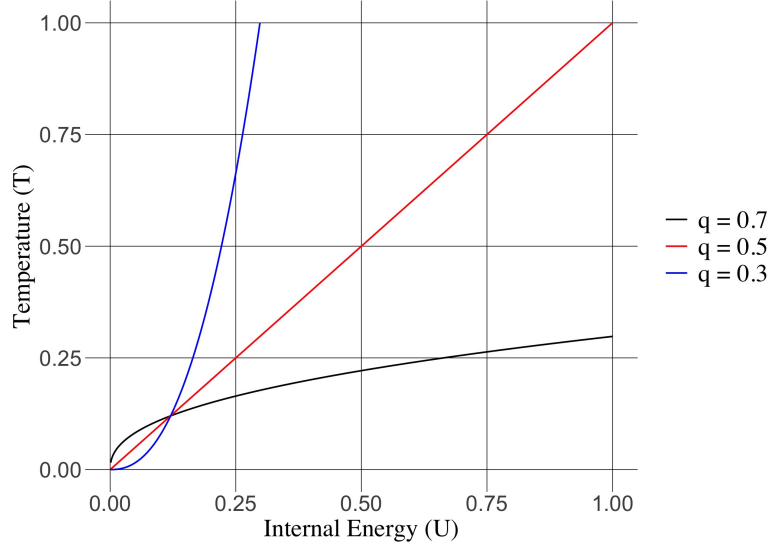


Figure 6: Graphic depiction of the temperature and the internal energy of the hydrogen atom in free space with $q = 0.3, 0.5, 0.7$, for $k = e_{ion} = 1$.

and (57) can also be written as

$$T = T_{ion} \left(\frac{U}{e_{ion}} \right)^{\frac{1-q}{q}}. \quad (59)$$

Figure 7 depicts the order of magnitude of the critical ionization temperature given by (58).

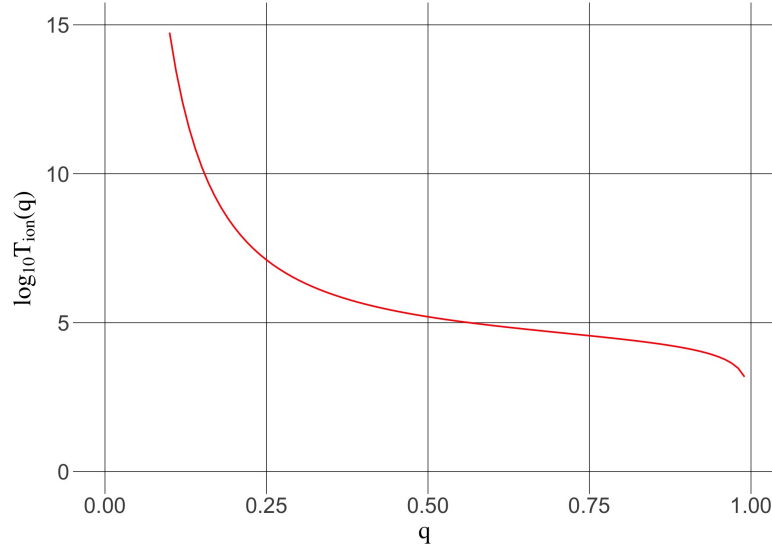


Figure 7: Graphic depiction of the logarithm (base 10) of the critical ionization temperature of the hydrogen atom in free space (i.e., $\log_{10} T_{ion}(q)$, $q \in (0, 1)$).

Although this theoretical framework admits several possible values for $q \in (0, 1)$, it is worth highlighting that, for $q = 1/2$, (57) simplifies to

$$T = \frac{U}{k}, \quad (60)$$

and the specific heat of the hydrogen atom in free space becomes, in this case, equal to the Boltzmann constant. Furthermore, (60) predicts for $q = 0.5$ a critical ionization temperature given by

$$T_{ion} = \frac{e_{ion}}{k} = \frac{13.6 \text{ eV}}{8.617\text{e-}5 \text{ eV/K}} \approx 1.6\text{e+}5 \text{ K.} \quad (61)$$

Finally, to compare the order of magnitude of (61), we proceed in the following manner. Saha's equation for hydrogen is given by

$$\frac{x^2}{1-x} = \frac{1}{\eta} \left(\frac{2\pi m_e k T}{h^2} \right)^{\frac{3}{2}} \exp\left(\frac{13.6 \text{ eV}}{k T} \right), \quad (62)$$

with $x \in (0, 1)$ the fraction of ionized hydrogen and $\eta > 0$ the density parameter. Given a density parameter η , the critical ionization temperature T_{ion} can be estimated by taking $x = 99.9\%$ in (62), so that

$$1000 \approx \frac{x^2}{1-x} = \frac{1}{\eta} \left(\frac{2\pi m_e k T_{ion}}{h^2} \right)^{\frac{3}{2}} \exp\left(\frac{13.6 \text{ eV}}{k T_{ion}} \right). \quad (63)$$

For this 99.9% ionization level and the density parameter η varying between $1\text{e+}13 \text{ m}^{-3}$ to $1\text{e+}27 \text{ m}^{-3}$, we obtain temperatures that range approximately from $6.2\text{e+}3 \text{ K}$ to $6.5\text{e+}5 \text{ K}$. Therefore, $T_{ion} = 1.6\text{e+}5 \text{ K}$ given by (61) and the range of temperature values in Figure 7 seem fairly coherent with this interval.

7. Concluding remarks

This paper provides a generalization of the Boltzmann-Gibbs distribution (5) through the non-additive entropic functional $S_{q,s}$, $0 < q < 1$, and the optimization problem (6). In particular, Sections 3-6 highlight the relevance of the scale factor k_s given by (8) to ensure a well-behaved macroscopic temperature pattern when the system structure presents certain infinities that can be modeled by an underlying limiting process.

It is worth noting that the structural parameter β calculated from (3) and, more generally, from (12), *does not depend* on the actual value assigned to k_s . It depends only on $q \in (0, 1]$, the energy spectrum, and the internal energy.

Therefore, the structural parameter is the same whether we adopt $S_{q,s}$ or S_q in (6). Furthermore, the family of entropic functionals $\{S_q\}_{q \in (0,1]}$ is particularly well-behaved for measuring disorder in a smoothly varying manner. For instance, they are concave, reach their maximum for equal probabilities, and are zero-valued when the outcome is certain.

The relevance of k_s (and, therefore, of the family $\{S_{q,s}\}_{q \in (0,1]}$) emerges when one needs to bridge the microscopic configuration of the physical system and the macroscopically observable temperature $T \in \mathbb{R}$. Since k_s is a scale factor, a possible way to view it is as making the

necessary adjustments to “translate” the limiting disorder measured by S_q to our macroscopic thermometer scale (in Kelvin, for instance).

In this sense, (8) reveals that the adequate scale factor is naturally embedded in the very essence of the physical system: its energy spectrum and the value of $q \in (0, 1)$. Along with the Boltzmann constant k and an adjustment parameter $\sigma > 0$, these quantities entirely define the adequate scale factor k_s and grant finite, smooth, macroscopically observable temperature values for the entire range of possible internal energies.

Lastly, the choice of $q \in (0, 1)$ that describes a specific thermodynamic behavior according to (32), (46), (52), and (60) (see Figures 2, 4, 5, and 6) requires further constraints in the model or empirical measurements that extend beyond the boundaries of this paper.

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Appendix

Proof of Lemma 1. To ease notation, I write $f \equiv f_{t,q}$ and $g_N \equiv g_{t,N,q}$. First, notice that

$$\begin{aligned} f(\beta_N) &= 2(1 - (1 - q)\beta_N U)^{\frac{1}{q-1}} U + \sum_{n=2}^k 2n^2(1 - (1 - q)\beta_N |E_n|)^{\frac{1}{q-1}} |E_n| \\ &= 2((1 - q)\delta_N U)^{\frac{1}{q-1}} U + \sum_{n=2}^k 2n^2(1 - (1 - q)\beta_N |E_n|)^{\frac{1}{q-1}} |E_n| \\ &= 2(1 - q)^{\frac{1}{q-1}} \delta_N^{\frac{1}{q-1}} U^{\frac{q}{q-1}} \left(1 + \delta_N^{\frac{1}{1-q}} \sum_{n=2}^k \frac{n^2 |E_n| (1 - q)^{\frac{1}{1-q}} U^{\frac{q}{1-q}}}{(1 - (1 - q)\beta_N |E_n|)^{\frac{1}{1-q}}} \right), \end{aligned} \quad (64)$$

and, since $\lim_{N \rightarrow \infty} \delta_N = 0$, we have

$$\lim_{N \rightarrow \infty} \delta_N^{\frac{1}{1-q}} \sum_{n=2}^k \frac{n^2 |E_n| (1 - q)^{\frac{1}{1-q}} U^{\frac{q}{1-q}}}{(1 - (1 - q)\beta_N |E_n|)^{\frac{1}{1-q}}} = 0. \quad (65)$$

Also,

$$\begin{aligned} g_N(\beta_N) &= \sum_{n=k+1}^N 2n^2(1 + (1 - q)\beta_N |E_n|)^{\frac{1}{q-1}} |E_n| \\ &= (1 - q)^{\frac{1}{q-1}} \sum_{n=k+1}^N 2n^2(U\delta_N + \beta_N e_n)^{\frac{1}{q-1}} \left(e_{ion} - U - \frac{e_{ion}}{n^2} \right) \\ &= (1 - q)^{\frac{1}{q-1}} (e_{ion} - U) \sum_{n=k+1}^N 2n^2(U\delta_N + \beta_N e_n)^{\frac{1}{q-1}} - 2(1 - q)^{\frac{1}{q-1}} e_{ion} \sum_{n=k+1}^N (U\delta_N + \beta_N e_n)^{\frac{1}{q-1}}. \end{aligned}$$

for $N \geq k + 1$. Next, notice that

$$\frac{(N-k)}{N^3}(U + \beta_N)^{\frac{1}{q-1}} \leq \frac{\sum_{n=k+1}^N (U\delta_N + \beta_N e_n)^{\frac{1}{q-1}}}{N^3} \leq \frac{(N-k)}{N^3}(\beta_N e_{k+1})^{\frac{1}{q-1}},$$

and, therefore,

$$\lim_{N \rightarrow \infty} \frac{\sum_{n=k+1}^N (U\delta_N + \beta_N e_n)^{\frac{1}{q-1}}}{N^3} = 0. \quad (66)$$

Since $\beta = 1/(1-q)U$, we have

$$\begin{aligned} \sum_{n=k+1}^N 2n^2 (U\delta_N + \beta_N e_n)^{\frac{1}{q-1}} &= \sum_{n=k+1}^N 2n^2 \left(\beta e_{ion} + U\delta_N + (\beta_N - \beta)e_n - \frac{\beta e_{ion}}{n^2} \right)^{\frac{1}{q-1}} \\ &= \sum_{n=k+1}^N 2n^2 (\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}}, \end{aligned}$$

with

$$\sigma(n, N) = U\delta_N + (\beta_N - \beta)e_n - \frac{\beta e_{ion}}{n^2},$$

for $k+1 \leq n \leq N$. For $0 < \varepsilon < \beta e_{ion}/2$, let $M_1 \geq t+1$ be such that $n, N \geq M_1$ implies $|\sigma(n, N)| < \varepsilon$. Then, for $N \geq M_1$,

$$\begin{aligned} \left| \sum_{n=N_1}^N 2n^2 ((\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}} - (\beta e_{ion})^{\frac{1}{q-1}}) \right| &\leq \sum_{n=N_1}^N 2n^2 |(\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}} - (\beta e_{ion})^{\frac{1}{q-1}}| \\ &\leq \sum_{n=N_1}^N 2n^2 \left| \int_{\beta e_{ion}}^{\beta e_{ion} + \sigma(n, N)} \frac{1}{(q-1)s^{\frac{2-q}{1-q}}} ds \right| \\ &\leq \frac{\varepsilon}{(1-q)(\beta e_{ion} - \varepsilon)^{\frac{2-q}{1-q}}} \sum_{n=N_1}^N 2n^2 \\ &= \frac{\varepsilon}{(1-q)(\beta e_{ion} - \varepsilon)^{\frac{2-q}{1-q}}} \left(\frac{2N^3}{3} + o(N^3) \right). \end{aligned}$$

Notice that

$$\lim_{N \rightarrow \infty} \frac{|\sum_{n=k+1}^{M_1} 2n^2 ((\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}} - (\beta e_{ion})^{\frac{1}{q-1}})|}{N^3} = 0,$$

and, therefore,

$$\lim_{N \rightarrow \infty} \frac{|\sum_{n=k+1}^N 2n^2 ((\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}} - (\beta e_{ion})^{\frac{1}{q-1}})|}{N^3} \leq \frac{2\varepsilon}{3(1-q)(\beta e_{ion} - \varepsilon)^{\frac{2-q}{1-q}}}. \quad (67)$$

Since (67) is valid for arbitrarily small $\varepsilon > 0$, we conclude that

$$\lim_{N \rightarrow \infty} \frac{\sum_{n=k+1}^N 2n^2(\beta e_{ion} + \sigma(n, N))^{\frac{1}{q-1}}}{N^3} = \lim_{N \rightarrow \infty} \frac{\sum_{n=k+1}^N 2n^2(\beta e_{ion})^{\frac{1}{q-1}}}{N^3} = \frac{2(\beta e_{ion})^{\frac{1}{q-1}}}{3}. \quad (68)$$

Furthermore, (66) and (68) imply

$$\lim_{N \rightarrow \infty} \frac{g_N(\beta_N)}{N^3} = \frac{2(e_{ion} - U)}{3(1-q)^{\frac{1}{1-q}} \beta^{\frac{1}{1-q}}} = \frac{2(e_{ion} - U)U^{\frac{1}{1-q}}}{3e_{ion}^{\frac{1}{1-q}}}.$$

Finally, (64) and (65) imply

$$\begin{aligned} 1 &= \lim_{N \rightarrow \infty} \frac{f(\beta_N)}{g_N(\beta_N)} \\ &= \lim_{N \rightarrow \infty} \frac{N^3}{g_N(\beta_N)} \frac{f(\beta_N)}{N^3} \\ &= \frac{3e_{ion}^{\frac{1}{1-q}}}{2(e_{ion} - U)U^{\frac{1}{1-q}}} \frac{1}{(1-q)^{\frac{1}{1-q}} U^{\frac{q}{1-q}}} \lim_{N \rightarrow \infty} \frac{1}{\delta_N^{\frac{1}{1-q}} N^3} \\ &= \frac{3e_{ion}^{\frac{1}{1-q}}}{2(1-q)^{\frac{1}{1-q}} (e_{ion} - U)U^{\frac{1+q}{1-q}}} \left(\lim_{N \rightarrow \infty} \frac{1}{\delta_N N^{3(1-q)}} \right)^{\frac{1}{1-q}}, \end{aligned}$$

so that

$$\lim_{N \rightarrow \infty} N^{3(1-q)} \delta_N = \frac{3^{1-q} e_{ion}}{2^{1-q} (1-q) (e_{ion} - U)^{1-q} U^{1+q}}.$$

Q.E.D.

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