entropy

MDPI

Article

Ensemble Equivalence for Distinguishable Particles

Antonio Fernández-Peralta and Raúl Toral *

Instituto de Física Interdisciplinar y Sistemas Complejos (IFISC), Consejo Superior de Investigaciones Científicas (CSIC)–Universitat de les Illes Balears (UIB), Palma de Mallorca 07122, Spain; afperalta@ifisc.uib-csic.es
* Correspondance: raul@ifisc.uib-csic.es; Tel.: +34-971-17-32-35; Fax: +34-971-17-32-48

Academic Editor: Antonio M. Scarfone
Received: 29 April 2016; Accepted: 8 July 2016; Published: 13 July 2016

Abstract: Statistics of distinguishable particles has become relevant in systems of colloidal particles and in the context of applications of statistical mechanics to complex networks. In this paper, we present evidence that a commonly used expression for the partition function of a system of distinguishable particles leads to huge fluctuations of the number of particles in the grand canonical ensemble and, consequently, to nonequivalence of statistical ensembles. We will show that the alternative definition of the partition function including, naturally, Boltzmann's correct counting factor for distinguishable particles solves the problem and restores ensemble equivalence. Finally, we also show that this choice for the partition function does not produce any inconsistency for a system of distinguishable localized particles, where the monoparticular partition function is not extensive.

Keywords: entropy; distinguishable particles; ensemble equivalence

1. Introduction

The Gibbs paradox, namely, the entropy not being extensive for a classical ideal gas, is commonly solved by adding an ad hoc term to the entropy, $-k\log(N!)$ or, using Stirling formula, $-kN\log(N/e)$, where N is the number of particles and k is Boltzmann's constant. This term appears if one divides the number of available states by $N!$, the so-called "correct Boltzmann counting". Its physical justification is usually attributed by several authors and textbooks [1,2] to quantum mechanics and the indistinguishable nature of identical particles. The inclusion or not of Boltzmann's correct counting and the correct definition of entropy for distinguishable particles has been widely discussed in the literature since the earlier works by Ehrenfest and Trkal [3] and van Kampen [4] and the more modern contributions, see, e.g., [5–14].

This topic turns out not to be just of academic interest, but appears to be relevant in current research, where the importance of distinguishable statistics has increased to a large degree. For example, when studying colloids one has to take into account that no two colloidal particles are exactly alike, with differences in the mass and shape of each particle, and they are, consequently, distinguishable between them. In such a case, the indistinguishability explanation of the Gibbs paradox fails resoundingly and we have to consider other possible alternatives [15,16] to explain experimental results with colloids. Another example is that of statistical mechanics of networks [17–19], where edges/links of the network are considered as particles, and pairs of vertices/nodes are considered as energy states, establishing a straightforward analogy with quantum physical systems. In this case, links correspond to individual identifiable actions and it seems very forced to regard them as indistinguishable [20]. This distinguishability of links becomes important for multi-edged networks (where a pair of nodes can have more than one link) when making statistics and entropy measures [21].

In this paper we want to contribute to this topic by discussing the issue of ensemble equivalence. The problem appeared to us [22] when studying the grand canonical formalism of distinguishable particles (or network links). When using the common textbook expression of the partition function [1], anomalous fluctuations of the number of particles are obtained, leading to ensemble nonequivalence between the microcanonical/canonical and the grand canonical ensembles. The nonequivalence of ensembles casts doubts on the suitability of the statistical description. We will prove that the inclusion of the $N!$ term for distinguishable particles solves the problem and restores ensemble equivalence. Although it would seem that this inclusion should give non-extensive thermodynamic potentials for localized particles, we will show that this is not the case and the definition including $N!$ is consistent in all cases.

The paper is organized as follows: in Section 2 we introduce the standard definitions of distinguishability, identical, etc., and other notation used in Statistical Mechanics, together with some simple Hamiltonian functions that will clarify those concepts. Section 3 presents the problem of ensemble equivalence for distinguishable particles that arises when using the common textbook expression for the partition function and entropy. Finally, in Section 4 we explain how the definition of entropy including Boltzmann's correct counting solves this problem for all the examples given in Section 2. We end with some conclusions in Section 5.

2. Preliminary Concepts

Indistinguishable particles are those described by a particle-exchange invariant set of microscopic states. If this invariance is not fulfilled, particles are called *distinguishable*.

In classical mechanics, a microstate for a system of N particles corresponds to a point in phase space

$$(q,p) \equiv (\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N), \tag{1}$$

of generalized coordinates $\{\vec{q}_i\}$ and momenta $\{\vec{p}_i\}$. If the generalized coordinates and momenta of any two particles are exchanged (say 1 and 2)

$$(\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N) \quad \rightarrow \quad (\vec{q}_2, \vec{q}_1, \ldots, \vec{q}_N, \vec{p}_2, \vec{p}_1, \ldots, \vec{p}_N), \tag{2}$$

we obtain a different point in phase space (except for a set of points of zero measure). Consequently, in classical mechanics particle-exchange invariance never holds and particles are always distinguishable. This is independent on whether particles are identical or not. *Identical* particles are those whose Hamiltonian is invariant under the exchange of any two particles (say 1 and 2),

$$\mathcal{H}(\vec{q}_1, \vec{q}_2, \ldots, \vec{q}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N) = \mathcal{H}(\vec{q}_2, \vec{q}_1, \ldots, \vec{q}_N, \vec{p}_2, \vec{p}_1, \ldots, \vec{p}_N). \tag{3}$$

This definition of identical particles also holds in quantum mechanics if we consider that the quantum Hamiltonian depends on operators associated to the generalized coordinates and momenta as well as on operators associated to internal degrees of freedom such as spin.

In quantum mechanics, the N particle microstate is a vector in the Hilbert space $|\psi\rangle$ which, in position representation and not considering internal degrees of freedom, is represented by a complex function $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$. A state of N identical particles must be symmetric (+, bosons) or antisymmetric (−, fermions) under particle exchange

$$\psi(\vec{r}_2, \vec{r}_1, \ldots, \vec{r}_N) = \pm\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N). \tag{4}$$

Furthermore, according to the quantum mechanics postulates, particles are indistinguishable if and only if they are identical, otherwise they are distinguishable.

Particles are called non-interacting or *ideal* when it is possible to define monoparticular Hamiltonians $h^{(i)}(\vec{q}_i, \vec{p}_i)$, depending only on the generalized coordinates and momenta of one particle, such that the N-particle Hamiltonian is $\mathcal{H} = \sum_{i=1}^{N} h^{(i)}$. In the quantum case, the monoparticular Hamiltonian might include spin and other quantum internal degrees of freedom.

For quantum systems (independently on whether particles are ideal or not), it is possible to construct the state $|\psi\rangle$ as a linear superposition of the eigenfunctions $|l_i\rangle$ of monoparticular Hamiltonians $h^{(i)}$, defined as $h^{(i)}|l_i\rangle = \epsilon_{l_i}|l_i\rangle$:

- For distinguishable particles any state can be written as an unrestricted linear combination of elements of the product basis $|l_1\rangle|l_2\rangle\dots|l_N\rangle \equiv |l_1, l_2, \dots, l_N\rangle$. For an ideal system it is:

$$\mathcal{H}|l_1, l_2, \dots, l_N\rangle = (\epsilon_{l_1} + \dots + \epsilon_{l_N})|l_1, l_2, \dots, l_N\rangle. \tag{5}$$

- For indistinguishable particles one can use instead the second-quantization basis $||n_0, n_1, n_2, \dots\rangle\rangle$ in terms of the occupation numbers n_ℓ of individual levels ℓ. In this representation, the wave function is always invariant under particle exchange, and one avoids an explicit symmetrization or anti-symmetrization process. For an ideal system it is:

$$\mathcal{H}||n_0, n_1, \dots\rangle\rangle = (n_0\epsilon_0 + n_1\epsilon_1 + \dots)||n_0, n_1, \dots\rangle\rangle. \tag{6}$$

In the ideal case, we can define the one-particle partition function $\mathcal{Z}_1^{(i)}$ associated to particle i. In the context of classical mechanics the definition is

$$\mathcal{Z}_1^{(i)} = \int \frac{d\vec{q}_i d\vec{p}_i}{h^{f_i}} e^{-\beta h^{(i)}(\vec{q}_i, \vec{p}_i)}, \qquad \beta = 1/kT, \tag{7}$$

where T is the temperature and f_i the number of degrees of freedom of particle i. The quantum counterpart is

$$\mathcal{Z}_1^{(i)} = \sum_{l_i} e^{-\beta\epsilon_{l_i}}. \tag{8}$$

Non-interacting particles are said to be *non-localized* if the monoparticular partition function $\mathcal{Z}_1$ fulfills

$$\mathcal{Z}_1(V, T) = V f(T), \tag{9}$$

and *localized* if it depends only on temperature

$$\mathcal{Z}_1(V, T) = \phi(T). \tag{10}$$

Intuitively, localized particles correspond to those for which the eigenfunctions of the monoparticular Hamiltonian are bounded in space. Examples being the infinitely-confining harmonic or infinite square well potentials in a finite region.

In order to fix ideas and to understand the concepts and definitions presented above, we will categorize the particles of four different Hamiltonians, whose statistics will be considered later. We restrict ourselves to the simplest examples (non-interacting particles) addressed in common textbooks of statistical mechanics. The results can be generalized to interacting particles as the nature of the problem addressed in this paper does not concern interactions.

(i) In the first example, we consider a non-relativistic gas of non-interacting identical particles without any internal or rotational degrees of freedom and not subject to any external field. The Hamiltonian can be written as

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}. \tag{11}$$

We will see later on that those kind of particles are non-localized. Classically, this is a system of identical, distinguishable, non-localized particles. The quantum version represents a system of identical, hence indistinguishable, non-localized particles.

(ii) The second example is the previous ideal gas but particles have different masses. This classifies the particles as non-localized, non-identical and, hence, distinguishable both in the classical and quantum versions. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i}. \tag{12}$$

It can be considered as a crude representation of a system of colloidal particles, each one with a different mass.

(iii) The third example is a set of harmonic oscillators, each one oscillating around a different position $\vec{a}_i$

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{\vec{p}_i^{\,2}}{2m} + \frac{m\omega^2}{2}(\vec{r}_i - \vec{a}_i)^2 \right]. \tag{13}$$

This constitutes a system of non-identical, distinguishable, localized particles, both in the quantum and classical cases.

(iv) The final example is the statistics of paramagnetism, where we have a set of localized particles with magnetic moments $\{\vec{\mu}_i\}$ in a magnetic field $\vec{B}$

$$\mathcal{H} = \sum_{i=1}^{N} \left[-\vec{\mu}_i \cdot \vec{B} + h_{\mathrm{loc}}^{(i)} \right]. \tag{14}$$

Here $h_{\mathrm{loc}}^{(i)}$ is an infinitely-confining Hamiltonian which localizes the particles around particular points $\vec{a}_i$ in space. Particles are then non-identical and distinguishable, both quantum and classically, despite the fact that the magnetic part of the Hamiltonian is invariant under particle exchange.

3. Ensemble Nonequivalence

In the canonical ensemble, thermodynamic properties follow from the calculation of the partition function. In the quantum case, this is defined as

$$\mathcal{Z}_N = \sum_m e^{-\beta E_m}, \tag{15}$$

where $|m\rangle$ are the eigenstates of the Hamiltonian and E_m the energy eigenvalues. For classical systems, the definition is

$$\mathcal{Z}_N = \int \frac{d\vec{q}_1 d\vec{p}_1}{h^{f_1}} \cdots \frac{d\vec{q}_N d\vec{p}_N}{h^{f_N}} e^{-\beta\mathcal{H}}. \tag{16}$$

For ideal systems, the usual calculation [1,2] for distinguishable particles writes the partition function as

$$\mathcal{Z}_N = \prod_{i=1}^{N} \mathcal{Z}_1^{(i)}. \tag{17}$$

Classically, this expression follows straightforwardly from $\mathcal{H} = \sum_{i=1}^{N} h^{(i)}$ and, in the quantum case, from Equation (5).

In the classical case (but not in the quantum case), if particles are identical, this expression simplifies to

$$\mathcal{Z}_N = [\mathcal{Z}_1]^N. \tag{18}$$

The extension of Equation (17) to quantum identical particles is non-trivial. While the exact calculation depends on whether the particles are fermions or bosons, an approximate result is obtained by replacing the factorial of the occupation number by $n_i! \approx 1$ [23]. This approximation is only valid at sufficiently high temperatures and low densities, where the mean occupation numbers are small. The use of this approximation leads to:

$$\mathcal{Z}_N \approx \frac{[\mathcal{Z}_1]^N}{N!}. \tag{19}$$

Quite generally, the partition function might depend on volume V, (inverse) temperature β and number of particles N. Helmholtz's free energy is $F(N, V, T) = -kT \log \mathcal{Z}_N$ and its derivatives provide the internal energy U, entropy S, pressure P and chemical potential μ:

$$\begin{aligned} U &= -\left(\frac{\partial \log \mathcal{Z}_N}{\partial \beta}\right)_{N,V}, && (20)\\ S &= k\left(\frac{\partial (T \log \mathcal{Z}_N)}{\partial T}\right)_{N,V}, && (21)\\ P &= kT\left(\frac{\partial \log \mathcal{Z}_N}{\partial V}\right)_{\beta,N}, && (22)\\ \mu &= -kT\left(\frac{\partial \log \mathcal{Z}_N}{\partial N}\right)_{\beta,V}. && (23) \end{aligned}$$

In the grand canonical ensemble, the number of particles is allowed to fluctuate. The probability of finding N particles is given by

$$p(N) = \frac{z^N \mathcal{Z}_N}{\Xi(z, V, \beta)}, \tag{24}$$

with a grand canonical partition function defined as

$$\Xi(z, V, \beta) = \sum_{N=0}^{\infty} z^N \mathcal{Z}_N, \tag{25}$$

and $z = e^{\beta\mu}$. The average (observable) number of particles is

$$\langle N \rangle = \sum_{N=0}^{\infty} N p(N). \tag{26}$$

The J (Landau) potential is $J(\mu, T, V) = kT \log \Xi$ and its derivatives yield:

$$\begin{aligned} U &= -\left(\frac{\partial \log \Xi}{\partial \beta}\right)_{V,z}, && (27)\\ S &= k\left(\frac{\partial (T \log \Xi)}{\partial T}\right)_{\mu,V}, && (28)\\ P &= kT\left(\frac{\partial \log \Xi}{\partial V}\right)_{\beta,z}, && (29)\\ \langle N \rangle &= z\left(\frac{\partial \log \Xi}{\partial z}\right)_{\beta,V}. && (30) \end{aligned}$$

Ensemble equivalence tells us that we can use either the canonical or the grand canonical formalism and still obtain the same functional form for $U(N, V, T), S(N, V, T), P(N, V, T), \mu(N, V, T)$, provided we identify N with $\langle N \rangle$ and take the limit $N \to \infty$. The physical basis of this equivalence relies on the fact that the probability $p(N)$ is heavily concentrated around its mean value $\langle N \rangle$ and hence this number can be identified as the physically measurable number of particles N. Otherwise, ensemble equivalence is not justified and the whole building of Statistical Mechanics falls apart. A necessary condition for ensemble equivalence is that the fluctuations of the number of particles in the grand canonical ensemble, measured by the root-mean-square $\sigma[N]$, are vanishingly small compared to the average value $\langle N \rangle$. This usually requires the thermodynamic limit: $\lim_{\langle N \rangle \to \infty} \frac{\sigma[N]}{\langle N \rangle} = 0$.

We will now show that ensemble equivalence does not hold if one uses the partition function given by Equation (17) or (18), thus showing that those partition functions are not acceptable.

Let us take, for example, Equation (18). The grand canonical partition function reads (see, e.g., Chapter 4 of [1]):

$$\Xi = \sum_{N=0}^{\infty} z^N \mathcal{Z}_1^N = \frac{1}{1 - z\mathcal{Z}_1}. \tag{31}$$

The geometric sum is convergent as, using Equation (30) we obtain

$$z\mathcal{Z}_1 = \frac{\langle N \rangle}{\langle N \rangle + 1} < 1. \tag{32}$$

Indeed, using both sets of Equations (20)–(23) or Equations (27)–(30) we obtain equivalent expressions (identifying $\langle N \rangle$ and N and taking $N \to \infty$):

$$U = -N \left(\frac{\partial \log \mathcal{Z}_1}{\partial \beta} \right)_V, \tag{33}$$

$$S = Nk \left(\frac{\partial (T \log \mathcal{Z}_1)}{\partial T} \right)_V, \tag{34}$$

$$P = kTN \left(\frac{\partial \log \mathcal{Z}_1}{\partial V} \right)_\beta, \tag{35}$$

$$\mu = -kT \log \mathcal{Z}_1. \tag{36}$$

However, when calculating the probability of the number of particles N in the grand canonical ensemble, we obtain a geometric distribution with mean value and fluctuations:

$$p(N) = (z\mathcal{Z}_1)^N (1 - z\mathcal{Z}_1), \tag{37}$$

$$\langle N \rangle = \frac{z\mathcal{Z}_1}{1 - z\mathcal{Z}_1}, \tag{38}$$

$$\frac{\sigma[N]}{\langle N \rangle} = \sqrt{\frac{\langle N \rangle + 1}{\langle N \rangle}} \xrightarrow[\langle N \rangle \to \infty]{} 1. \tag{39}$$

These huge fluctuations, as big as the average value, imply that the number of particles of the system is not well defined and, according to the discussion above, that the partition function Equation (17) is incorrect and cannot represent a macroscopic state of a physical system.

On the other hand, if one redoes these calculations with the approximate partition function for indistinguishable particles Equation (19), we still obtain equality of results, with the same functional forms Equations (33) and (35) for the internal energy U and pressure P, and a chemical potential $\mu = -kT \log(\mathcal{Z}_1 / N)$ and entropy $S = Nk \left(\frac{\partial (T \log(\mathcal{Z}_1 e/N))}{\partial T} \right)_V$. Furthermore, we obtain a Poisson distribution for the number of particles, with mean value and fluctuations:

$$p(N) = e^{-z\mathcal{Z}_1} \frac{(z\mathcal{Z}_1)^N}{N!}, \tag{40}$$

$$\langle N \rangle = z\mathcal{Z}_1, \tag{41}$$

$$\frac{\sigma[N]}{\langle N \rangle} = \langle N \rangle^{-1/2} \xrightarrow[\langle N \rangle \to \infty]{} 0. \tag{42}$$

Note that the relative fluctuations now vanish in the thermodynamic limit. Although this result has been obtained using the high temperature limit Equation (19), it can be shown that the exact treatment of indistinguishable particles also leads to vanishing fluctuations and ensemble equivalence [1]. Then, apparently, if we follow the usual textbook procedure we obtain ensemble equivalence only for indistinguishable particles.

The validity of Equation (17) for classical non-localized particles (e.g., an ideal gas) where $\mathcal{Z}_1 \propto V$, is typically questioned because of the absence of extensiveness of the entropy Equation (34), or intensiveness of the chemical potential, Equation (36), and a term $1/N!$ is added ad hoc to the partition function Equation (16) or, by arguing that it originates as a consequence of quantum indistinguishability of identical particles in the approximation Equation (19), also known as classical limit. The failure of this explanation is that it implies that for quantum non-identical, and consequently distinguishable, particles the correct partition function should be Equation (17), leading to an entropy which is not extensive. Here, we have shown that Equation (17) leads for all cases to ensemble nonequivalence, an unacceptable result from a statistical point of view. The question now is, which partition function is correct for each classification of particles?

4. Correct Partition Function

The answer to the previous question concerns very fundamental aspects of statistical mechanics, from the definition of entropy to the selection of a macrostate that only captures measures of macroscopic variables and we refer to the bibliography cited in the introduction for a detailed discussion. The standard statistical expression of entropy is derived by considering one isolated system of N particles and internal energy E formed by two subsystems, 1 and 2, that can exchange energy and particles amongst them. The equilibrium condition is postulated to be that of a maximum for the probability for system 1 to have energy E_1 and number of particles N_1. In order to recover the usual thermodynamic conditions for equilibrium, namely, equality of temperature, pressure and chemical potential, the entropy is defined (quantum) as

$$S = k\log\Omega, \qquad \Omega = \sum_{m\left|\substack{E_m=E\\N_m=N}\right.} 1, \tag{43}$$

where $|m\rangle$ is a microstate, eigenfunction of the Hamiltonian and the number operator with energy E_m and number of particles N_m. $\Omega(E,N)$ is the total number of those microstates with N particles and energy equal to E. In classical mechanics, the definition of entropy replaces the sum over microstates by an integral over phase space. The partition function for the canonical $\mathcal{Z}_N$ and grand canonical Ξ ensembles follow from the definition of entropy [1]:

$$\mathcal{Z}_N = \sum_{m|N_m=N} e^{-\beta E_m}, \tag{44}$$

$$\Xi = \sum_{N=0}^{\infty} z^N \mathcal{Z}_N. \tag{45}$$

However, it has been argued [5,8,9,11,13] that expressions Equation (43), and consequently Equation (44), are incorrect for distinguishable particles and that a different expression for the entropy is needed. The argument, correct in our opinion, is that when writing the probability for system 1 to have energy E_1 and number of particles N_1 and equivalent E_2, N_2 for system 2, one has to consider a multiplying factor $\binom{N}{N_1} = \frac{N!}{N_1!N_2!}$, that counts the number of ways of selecting N_1 distinguishable particles out of $N = N_1 + N_2$. In simple words, the macrostate specifies that you have N_1 distinguishable particles in the system but, since particles can be exchanged, it is not possible to know the identity of the particles.

Explicitly, the probability function for distinguishable particles reads

$$p_1^{\text{dist}}(E_1, N_1) = \binom{N}{N_1}\frac{\Omega_1(E_1,N_1)\Omega_2(E_2,N_2)}{\Omega(E,N)} = \frac{\Omega_1}{N_1!}\cdot\frac{\Omega_2}{N_2!}\cdot\frac{N!}{\Omega}, \tag{46}$$

while for indistinguishable particles, it is

$$p_1^{\text{indist}}(E_1, N_1) = \frac{\Omega_1(E_1,N_1)\Omega_2(E_2,N_2)}{\Omega(E,N)}. \tag{47}$$

Note how, one cannot apply Equation (47) for distinguishable particle or it would be undercounting the number of combinations in which distinguishable particles might enter or leave the system. Comparing Equations (46) and (47), it is clear now that $\Omega(E,N)/N!$ in the case of distinguishable particles plays the same role as $\Omega(E,N)$ for indistinguishable particles, as far as the calculation of the probability $p_1(E_1, N_1)$ is concerned. Consequently, the correct relation between statistics and thermodynamics for distinguishable quantum particles is

$$S = k\log\left[\frac{\Omega}{N!}\right], \qquad \Omega = \sum_{m\left|\substack{E_m=E\\N_m=N}\right.} 1, \tag{48}$$

$$F = -kT\log\mathcal{Z}_N, \qquad \mathcal{Z}_N = \frac{1}{N!}\sum_{m|N_m=N} e^{-\beta E_m}, \tag{49}$$

$$J = kT\log\Xi, \qquad \Xi = \sum_{N=0}^{\infty} z^N \mathcal{Z}_N, \tag{50}$$

whereas for distinguishable (identical or not) classical particles the canonical partition function is computed as:

$$\mathcal{Z}_N = \frac{1}{N!}\int \frac{d\vec{q}_1 d\vec{p}_1}{h^{f_1}}\cdots\frac{d\vec{q}_N d\vec{p}_N}{h^{f_N}} e^{-\beta\mathcal{H}}. \tag{51}$$

We have shown in the previous section that when one applies Equations (44) and (45) to distinguishable particles, non physical results are obtained, both from the thermodynamic (non-extensiveness of the entropy for non-localized particles) and statistical (non-vanishing fluctuations) points of view. A macrostate of distinguishable particles with expression given by Equation (43) would imply that you know exactly which particles are forming the system, which is incompatible from the very definition of a macrostate, and this is exactly what the binomial coefficient $\binom{N}{N_1}$ is preventing.

Let us now work out the implications of the definitions Equations (48)–(51) for each one of the Hamiltonians introduced in Section 2.

4.1. Ideal Gas of Identical Non-Localized Particles

Using Equation (51), the partition function of an ideal gas of classical distinguishable identical particles Equation (11) is

$$\mathcal{Z}_N = \frac{[\mathcal{Z}_1]^N}{N!}, \qquad \mathcal{Z}_1 = Vf(T), \qquad f(T) = \frac{(2\pi mkT)^{3/2}}{h^3}. \tag{52}$$

Note that the Gibbs paradox and huge fluctuations disappear immediately and classical distinguishability does not produce any incorrect prediction.

4.2. Ideal Gas of Non-Identical Non-Localized Particles

Similar ideas can be extended to the ideal gas composed by non-identical particles. A simple extension of the previous arguments leads to the fact that, again, the presence of the $N!$ factorial term in the definition of the partition function is necessary if one wants a consistent statistical description. For the sake of concreteness, we consider a system in which particles are not identical because they have different masses, e.g., a system described by the Hamiltonian Equation (12). As the number of particles N is macroscopic it is not feasible to specify the masses of each and everyone of the particles. Instead, we introduce a probability density function (pdf) $\rho(m)$ constructed from the histogram of all masses $\{m\} \equiv (m_1, \ldots, m_N)$ in the system.

In the statistical-mechanics derivation of entropy we consider a situation in which particles can be exchanged between systems 1 and 2. We use the label $n = 1, \ldots, \binom{N}{N_1}$ for each one of the different choices for N_1 particles in system 1 and N_2 in 2, and call $\{m\}_1^n = (m_{i_1}, \ldots, m_{i_{N_1}})$, $\{m\}_2^n = (m_{i_{N_1+1}}, \ldots, m_{i_N})$ the corresponding list of masses taken from $\{m\} = (m_1, \ldots, m_N)$. Again, as both N_1 and N_2 are macroscopic, we construct the pdf's $\rho_1^n(m)$ and $\rho_2^n(m)$ from the lists $\{m\}_1^n$ and $\{m\}_2^n$, respectively. The probability for system 1 to have energy E_1 and number of particles N_1 is

$$p_1(E_1, N_1) = \sum_{n=1}^{\binom{N}{N_1}} \frac{\Omega_1(E_1, N_1, \rho_1^n(m))\Omega_2(E_2, N_2, \rho_2^n(m))}{\Omega(E, N, \rho(m))}. \tag{53}$$

For large N_1, N_2, N it is legitimate to assume that a vast majority of combinations n will lead to the same distributions $\rho_1^n(m) = \rho_2^n(m) = \rho(m)$ and all the terms of sum Equation (53) contribute equally:

$$\begin{aligned} p_1(E_1, N_1) &= \binom{N}{N_1} \frac{\Omega_1(E_1, N_1, V_1, \rho(m))\Omega_2(E_2, N_2, V_2, \rho(m))}{\Omega(E, N, V, \rho(m))} \\ &= \frac{\Omega_1}{N_1!} \cdot \frac{\Omega_2}{N_2!} \cdot \frac{N!}{\Omega}, \end{aligned} \tag{54}$$

leading to definitions Equations (48) and (49). This method can be generalized for whatever Hamiltonian of heterogeneous particles (such as colloids), that could depend on properties such as moment of inertia, shape of the molecules, etc. The correct partition function for non-identical distinguishable particles reads

$$\mathcal{Z}_N = \frac{[\mathcal{Z}_1]^N}{N!}, \qquad \mathcal{Z}_1 = V f(T), \qquad f(T) = \frac{(2\pi k T)^{3/2}}{h^3} \exp\left[\int \rho(m) \log(m^{3/2}) dm\right], \tag{55}$$

which has extensive entropy and vanishing fluctuations. Note here that Equation (55) is exact for classical and quantum mechanics, and there is no need to resort to the Boltzmann approximation. If we choose $\rho(x) = \delta(x - m)$, we recover (52) which is known to be exact for classical particles, but only an approximation for quantum systems. The limit of identical quantum particles is a singular one. By this we mean that, for quantum mechanics there is a discontinuity in considering the masses of the particles identical or non-identical, as the Hamiltonian of the system is invariant or not, respectively, under particle exchange.

Special attention deserves the case of a system with two (or more) macroscopically observable types of particles, A and B. This is naturally represented by a bimodal distribution of masses:

$$\rho(m) = \frac{N_A}{N} \rho_A(m) + \frac{N_B}{N} \rho_B(m), \qquad N_A + N_B = N, \tag{56}$$

where N_A is the number of particles of type A and N_B of type B. Here $\rho_A(m)$ and $\rho_B(m)$ are non-overlapping distributions, peaked, respectively, around masses m_A and m_B. Note that distinguishability of particles is a property of symmetry in the set of microscopic states, while what categorizes types is a determined property of particles (such as a mass distribution $\rho(m)$). In this way, particles can be distinguishable and of the same type. By this we mean that, particles can be heterogeneous in their microscopic physical properties but at the same time be considered as a same type in the thermodynamic description, by only measuring the total number of them N.

The probability Equation (54) and the partition function Equation (55) describe a system with a constant proportion of particles A and B. This means that when the number of particles N_1 in subsystem 1 is fixed, we automatically fix the number of particles of A and B in this subsystem as $N_{1A} = N_1 \cdot \dfrac{N_A}{N}$, $N_{1B} = N_1 \cdot \dfrac{N_B}{N}$. This is the situation for a system that, macroscopically, is not allowed to exchange particles selectively, i.e., no selective membranes. If one is interested in a situation in which the number of particles N_{1A} and N_{1B} can change independently at the macroscopic level, it is necessary to consider a macrostate that specifies not only the total number of particles of the system N_1, but the number of each type N_{1A}, N_{1B}, keeping $N_{1A} + N_{1B} = N_1$, and calculate its probability $p_1(E_1, N_{1A}, N_{1B})$. Rewriting $\Omega_1(E_1, N_1, \rho_1^n(m)) = \Omega_1(E_1, N_{1A}, N_{1B}, \rho_A(m), \rho_B(m))$ (we again assume that each one of the possible combinations n leads to a same distribution of masses for A and B), and splitting the $\binom{N}{N_1}$ configurations according to the value of N_{1A}, $\binom{N}{N_1} = \sum_{N_{1A}=0}^{N_1} \binom{N_A}{N_{1A}}\binom{N_B}{N_{1B}}$, Equation (53) becomes

$$p_1(E_1, N_1) = \sum_{N_{1A}=0}^{N_1} \binom{N_A}{N_{1A}} \binom{N_B}{N_{1B}} \frac{\Omega_1 \Omega_2}{\Omega} = \sum_{N_{1A}=0}^{N_1} p_1(E_1, N_{1A}, N_{1B}). \tag{57}$$

Using the probability function $p_1(E_1, N_{1A}, N_{1B})$ to derive the appropriate expression for the entropy and the partition function, we obtain

$$\begin{aligned} \mathcal{Z}_{N_A,N_B} &= \frac{[\mathcal{Z}_{1A}]^{N_A}}{N_A!} \frac{[\mathcal{Z}_{1B}]^{N_B}}{N_B!}, \\ \mathcal{Z}_{1A} &= V f_A(T), \qquad f_A(T) = \frac{(2\pi k T)^{3/2}}{h^3} \exp\left[\int \rho_A(m) \log(m^{3/2}) dm\right], \\ \mathcal{Z}_{1B} &= V f_B(T), \qquad f_B(T) = \frac{(2\pi k T)^{3/2}}{h^3} \exp\left[\int \rho_B(m) \log(m^{3/2}) dm\right]. \end{aligned} \tag{58}$$

Note the presence of the terms $N_A!$, $N_B!$, which will ensure that fluctuations of the number of particles N_A and N_B in the grand canonical ensemble vanish in the thermodynamic limit.

One might wonder the validity of Equation (55) for a general distribution of masses $\rho(m)$. When we use Equation (55) we are considering only one type of particles, independently on the functional form of $\rho(m)$. This choice will be consistent with the thermodynamic description of a process as long as the distribution $\rho(m)$ does not to change during the process, i.e., that the same thermodynamic variables are used in both, initial and final, equilibrium states. On the other hand, the intention of Equation (58) is to describe a system that can exchange two types of particles particles selectively, due to the presence of selective membranes or some other ingredient, like chemical reactions, that may change the composition and mass distribution of the system, but again assuming the particular $\rho_A(m)$ and $\rho_B(m)$ to be invariant, while $\rho(m) = \frac{N_A}{N}\rho_A(m) + \frac{N_B}{N}\rho_B(m)$, N_A and N_B being independent variables. In general, the number of types of particles is determined by the small number of macroscopic variables that one chooses to measure in an experiment or particular thermodynamic process. In other words, the thermodynamic potentials depend on the macroscopic variables that one considers to properly describe the system [7].

4.3. Localized Particles

It would seem that the proposed definition brings problems in the case of localized distinguishable particles since the entropy and other thermodynamic potentials derived from

Equations (49)–(51) appear to be non-extensive, at least in the ideal case where $\mathcal{Z}_1 \propto V^0$. We will now argue that this is not the case.

For localized particles, e.g., those described by the Hamiltonians Equations (13) and (14), we face the same conceptual problem than before: a macrostate cannot include the detailed location of each and every particle $\{\vec{a}_i\}$. Let us assume that there exists a set $M \geq N$ of available locations. A microstate of the system can be written as linear combination of the basis

$$|m\rangle = |\ell_1, \vec{a}_1\rangle |\ell_2, \vec{a}_2\rangle \dots |\ell_N, \vec{a}_N\rangle, \tag{59}$$

where $\vec{a}_i$ is the actual location of the particle for this microstate, and ℓ_i is its monoparticular level. The energy of each level can be obtained solving $h^{(i)}|\ell_i\rangle = \epsilon_{\ell_i}|\ell_i\rangle$

$$\begin{aligned} \epsilon_\ell = \left(\ell + \frac{1}{2}\right)\hbar\omega, \qquad \ell &= 0, 1, \dots \qquad \text{(Harmonic oscillators 1d)}, \\ \epsilon_\ell = -g\mu_B B \ell, \qquad \ell &= -J, -J+1, \dots, J \qquad \text{(Paramagnetism)}, \end{aligned} \tag{60}$$

where μ_B is the Bohr magneton, g is the Landé g-factor and J is the total angular momentum of the particles and, in the paramagnetic case, we have neglected the contribution from $h^{(i)}_{\text{loc}}$ to the energy. The macroscopic description can not specify the location of each particle. Therefore, when calculating the partition function Equation (49), we have to consider the count over the ways N distinguishable particles can be placed in M locations, i.e., $\frac{M!}{(M-N)!}$, obtaining

$$\mathcal{Z}_N = \frac{1}{N!} \sum_{m|N_m=N} e^{-\beta E_m} = \frac{1}{N!} \frac{M!}{(M-N)!} [\mathcal{Z}_1]^N = \binom{M}{N} [\mathcal{Z}_1]^N. \tag{61}$$

The monoparticular partition function for the cases of interest is

$$\mathcal{Z}_1 = \phi(T) = \begin{cases} \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1} & \text{(harmonic oscillators)}, \\ \sinh\left[\left(1 + \frac{1}{2J}\right)x\right] / \sinh\left[\frac{1}{2J}x\right] & \text{(paramagnetism)}, \end{cases} \tag{62}$$

where $x = \beta g \mu_B J B$. The partition function in the grand canonical ensemble is

$$\Xi = \sum_{N=0}^{M} z^N \mathcal{Z}_N = \sum_{N=0}^{M} \binom{M}{N} [z\mathcal{Z}_1]^N = (1 + z\mathcal{Z}_1)^M. \tag{63}$$

We can now prove ensemble equivalence. Using the standard relations, both the canonical and grand canonical ensembles (identifying N and $\langle N \rangle$) lead to

$$\begin{aligned} U &= -N\frac{\partial \log \mathcal{Z}_1}{\partial \beta}, \\ S &= Nk\left[\frac{\partial(T\log\mathcal{Z}_1)}{\partial T} + (1 - 1/\alpha)\log(1-\alpha) - \log\alpha\right], \\ P &= kTN\frac{\partial \log \mathcal{Z}_1}{\partial V}, \\ \mu &= -kT\log\left(\frac{1-\alpha}{\alpha}\mathcal{Z}_1\right), \end{aligned} \tag{64}$$

where $\alpha = N/M$. Note that despite being $\mathcal{Z}_1 \propto V^0$, the entropy is extensive while the chemical potential keeps its intensiveness if we consider that the number of available locations M

is itself extensive and thus $\alpha = O(1)$. The probability of the number of particles follows now a binomial distribution

$$\begin{aligned} p(N) &= \binom{M}{N}\alpha^N (1-\alpha)^{M-N}, \\ \frac{\sigma[N]}{\langle N\rangle} &= \langle N\rangle^{-1/2}\sqrt{1-\alpha} \xrightarrow[\langle N\rangle\to\infty]{} 0, \end{aligned} \tag{65}$$

whose fluctuations vanish in the thermodynamic limit, restoring ensemble equivalence.

The particular case typically considered in textbooks is $N = M$, i.e., the number of available locations equal to the number of particles, brings no further problems as in this case, we simply recover Equations (33)–(35). Note, however, that in such a case, it is impossible for the system to include more particles and, consequently the chemical potential $\mu \to \infty$ as $\alpha \to 1$. In the same limit in the grand-canonical ensemble it is $p(N) \to \delta(N-M)$ and fluctuations become exactly zero $\sigma[N]/\langle N\rangle = 0$.

5. Conclusions

We have shown that the common textbook expression of the partition function of a system of distinguishable particles which does not include the $N!$ term, leads to abnormally large fluctuations of the number of particles in the grand canonical ensemble. This occurs independently on whether particles are classical or quantum, localized or non-localized. The large fluctuations go against the postulates of statistical mechanics, which require that the relative fluctuations of the number of particles in the grand canonical ensemble vanish in the thermodynamic limit, such that it is possible to identify the mean value of the number of particles as the physically measurable N and ensure ensemble equivalence.

As argued by some authors, the correct partition function (including the $N!$ term) for distinguishable particles is obtained from the statistical derivation of entropy and the selection of a macrostate that only captures macroscopic measurements. We have tested this expression of the partition function with some common examples of distinguishable particles that include: an ideal gas of classical identical particles, an ideal gas of classical or quantum non-identical particles (where particles hold different masses), a set of harmonic oscillators and the statistics of paramagnetism. For the ideal gas of non-identical particles, we have discussed the derivation of the correct partition function for both unimodal and bimodal distributions of masses. We have also shown that the proposal for the partition function including the $N!$ term does not produce any inconsistency for a system of localized particles, where the monoparticular partition function is not extensive $\mathcal{Z}_1 \propto V^0$. The thermodynamic potentials obtained in all examples fulfill the corresponding extensiveness properties and the fluctuations of the number of particles in the grand canonical ensemble vanish in the thermodynamic limit, restoring ensemble equivalence.

Acknowledgments: We acknowledge useful discussions with O. Sagarra and C.J. Pérez-Vicente concerning the issue of distinguishability in networks. This work was supported by FEDER (Fondo Europeo de Desarrollo Regional) (EU) and MINECO (Ministerio de Economía y Competitividad) (Spain) under Grant ESoTECoS (FIS2015-63268-C2-2-R). Antonio Fernández-Peralta acknowledges support by the FPU (Formación de Profesorado Universitario) program of MECD (Ministerio de Educación, Cultura y Deporte) (Spain).

Author Contributions: Antonio Fernández-Peralta and Raúl Toral conceived the problem of ensemble equivalence. Antonio Fernández-Peralta reviewed and interpreted the relevant literature. Antonio Fernández-Peralta and Raúl Toral wrote and revised the manuscript. Both authors have read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pathria, R.K.; Beale, P.D. *Statistical Mechanics*, 3rd ed.; Butterworth-Heinemann: Oxford, UK, 2011.

2. Huang, K. *Statistical Mechanics*; John Wiley & Sons: New York, NY, USA, 1963.
3. Ehrenfest, P.; Trkal, V. Deduction of the dissociation-equilibrium from the theory of quanta and a calculation of the chemical constant based on this. *Proc. K. Ned. Akad. Wet.* **1921**, *23*, 162–183.
4. Van Kampen, N. The Gibbs Paradox. In *Essays in Theoretical Physics*; Parry, W., Ed.; Pergamon Press: Bergama, Turkey, 1984; pp. 303–312.
5. Swendsen, R.H. Statistical Mechanics of Classical Systems with Distinguishable Particles. *J. Stat. Phys.* **2002**, *107*, 1143–1166.
6. Nagle, J.F. Regarding the Entropy of Distinguishable Particles. *J. Stat. Phys.* **2004**, *117*, 1047–1062.
7. Swendsen, R.H. Response to Nagle's Criticism of My Proposed Definition of the Entropy. *J. Stat. Phys.* **2004**, *117*, 1063–1070.
8. Swendsen, R.H. Gibbs' Paradox and the Definition of Entropy. *Entropy* **2008**, *10*, 15–18.
9. Cheng, C. Thermodynamics of the System of Distinguishable Particles. *Entropy* **2009**, *11*, 326–333.
10. Nagle, J.F. In Defense of Gibbs and the Traditional Definition of the Entropy of Distinguishable Particles. *Entropy* **2010**, *12*, 1936–1945.
11. Peters, H. Statistics of Distinguishable Particles and Resolution of the Gibbs Paradox of the First Kind. *J. Stat. Phys.* **2010**, *141*, 785–828.
12. Versteegh, M.A.M.; Dieks, D. The Gibbs paradox and the distinguishability of identical particles. *Am. J. Phys.* **2011**, *79*, 741–746.
13. Swendsen, R.H. Choosing a definition of entropy that works. *Found. Phys.* **2012**, *42*, 582–593.
14. Dieks, D. Is There a Unique Physical Entropy? Micro versus Macro. In *New Challenges to Philosophy of Science*; Springer: Dordrecht, The Netherlands, 2013; Volume 4, pp. 23–34.
15. Swendsen, R.H. Statistical mechanics of colloids and Boltzmann's definition of the entropy. *Am. J. Phys.* **2006**, *74*, 187–190.
16. Cates, M.E.; Manoharan, V.N. Celebrating Soft Matter's 10th Anniversary: Testing the Foundations of Classical Entropy: Colloid Experiments. *Soft Matter* **2015**, *11*, 6538–6546.
17. Park, J.; Newman, M.E.J. Statistical mechanics of networks. *Phys. Rev. E* **2004**, *70*, 066117.
18. Bianconi, G. Entropy of network ensembles. *Phys. Rev. E* **2009**, *79*, 036114.
19. Bianconi, G. The entropy of randomized network ensembles. *Europhys. Lett.* **2008**, *81*, 28005.
20. Sagarra, O.; Pérez Vicente, C.J.; Díaz-Guilera, A. Statistical mechanics of multiedge networks. *Phys. Rev. E* **2013**, *88*, 062806.
21. Sagarra, O.; Pérez Vicente, C.J.; Díaz-Guilera, A. Role of adjacency-matrix degeneracy in maximum-entropy-weighted network models. *Phys. Rev. E* **2015**, *92*, 052816.
22. Fernández-Peralta, A. Statistical Mechanics of Multilayer Networks. Master's Thesis, University of the Balearic Islands, Palma, Spain, 2015.
23. Balescu, R. *Equilibrium and Non-Equilibrium Statistical Mechanics*; John Wiley & Sons: New York, NY, USA, 1975.