Demonstration and resolution of the Gibbs paradox of the first kind

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Abstract
The Gibbs paradox of the first kind (GP1) refers to the false increase in entropy which, in statistical mechanics, is calculated from the process of combining two gas systems S1 and S2 consisting of distinguishable particles. Presented in a somewhat modified form, the GP1 manifests as a contradiction to the second law of thermodynamics. Contrary to popular belief, this contradiction affects not only classical but also quantum statistical mechanics. This paper resolves the GP1 by considering two effects. (i) The uncertainty about which particles are located in S1 and which in S2 contributes to the entropies of S1 and S2. (ii) S1 and S2 are correlated by the fact that if a certain particle is located in one system, it cannot be located in the other. As a consequence, the entropy of the total system consisting of S1 and S2 is not the sum of the entropies of S1 and S2.

1. Introduction, motivation and outline
In physics, there are two distinct paradoxes which are both known as the ‘Gibbs paradox’ and are often confused with each other. In the following, the false increase in entropy which, in statistical mechanics, is calculated from the process of combining two gases of the same kind consisting of distinguishable particles will be referred to as the Gibbs paradox of the first kind (GP1) [1–5]. The Gibbs paradox of the second kind (GP2) addresses the fact that the entropy increase, when combining two gases of different kinds, is independent of the degree of similarity between the two kinds of gases, and that this entropy increase vanishes discontinuously at the transition from similarity to sameness [6–10]. The GP2 is not the subject of this paper.

In what follows, it will be crucial to understand the meanings of the terms (non-)identical and (in)distinguishable. Roughly speaking, two particles are called identical if they agree in all their permanent properties (such as electric charge), and they are called indistinguishable if interchanging them does not alter any microstate. Clearly, non-identical particles are always distinguishable (even if they are very similar). Identical quantum particles are indistinguishable due to the symmetrization postulate [11]. Identical classical particles, by contrast, can be
assumed to be either distinguishable or indistinguishable; the two possibilities turn out to be equivalent (cf section 5.6 in [5]). For a more thorough discussion see section 2 in [5].

The GP1 is usually demonstrated and resolved as follows (e.g., in [2–4]). Two ideal gases of the same kind with equal particle number, volume and temperature are combined. (Two gases, each consisting of identical particles, are said to be of the same kind if the particles of one gas are identical to the particles of the other gas.) If the particles of the two gases are pairwise distinguishable (which implies that they are classical), then one calculates an entropy increase from the combining process. This entropy increase is considered paradoxical. If, on the contrary, the particles of the two gases are indistinguishable, then one calculates a zero entropy change, as there ought to be. On this account, quantum mechanics, in which identical particles are necessarily indistinguishable, is claimed to be the resolution of the GP1.

Both the demonstration and the resolution just outlined are unsatisfactory. The demonstration is unsatisfactory because it is not clear why, for pairwise distinguishable particles, an entropy increase during the course of combination is considered paradoxical. If, for example, the first gas is composed of the particles 1 to \(N\) and the second gas of the particles \(N+1\) to \(2N\), then the calculated entropy increase can be ascribed to the fact that, after combination, the particles 1 to \(N\) can access the volume of the second gas and, correspondingly, the particles \(N+1\) to \(2N\) can access the volume of the first gas. The resolution is unsatisfactory for two reasons. Firstly, one can conceive gases consisting of very similar but still pairwise non-identical particles. In statistical-mechanical calculations, such gases can approximately be treated as if their particles were identical but still pairwise distinguishable. As a consequence, these gases suffer from the GP1, even in quantum mechanics. (An example of such a gas, along with a quantum-mechanically valid demonstration of the GP1, is given in section 2.) Secondly, the resolution above implies that the mere concept of distinguishable identical particles is at odds with thermodynamics [12]. In the opinion of the present author, such a connection between these otherwise unrelated subjects would be rather surprising, to say the least.

In section 2, the GP1 is recast in a form which shows that, for one thing, the GP1 is indeed paradoxical (by contradicting the second law of thermodynamics) and, for another thing, the GP1 also affects quantum statistical mechanics. Instead of combining two gases, a single gas is partitioned. Thus, instead of an entropy increase, one calculates an entropy decrease which poses a clear contradiction to the second law [13]. Furthermore, instead of considering a gas of pairwise distinguishable identical (and thus, necessarily classical) particles, a gas of pairwise non-identical but very similar particles is considered, allowing the particles to be quantum-mechanical.

In section 3, the origin of the GP1 is identified and its resolution presented. It is shown that, when calculating the entropy of a system of distinguishable particles, one generally has to take account of two effects.

(i) If there is an uncertainty about the system’s particle composition (i.e., about which particles are located in the system), then this uncertainty contributes to the system’s entropy.

(ii) If the system consists of subsystems and there are particles which possess a non-zero probability of presence in more than one subsystem, then these subsystems are correlated (due to the fact that if such a particle is located in one subsystem, it cannot be located in another). If such correlations exist, then the system’s entropy is smaller than the sum of the entropies of the subsystems.

These two effects resolve the GP1. As a matter of fact, they are fundamental to the statistical-mechanical treatment of systems of distinguishable particles, be it systems of non-identical
particles (cf section 4 in [5]) or systems of distinguishable identical classical particles (cf section 5 in [5]).

In section 4, the GP1 in its unaltered original form is resolved by applying the insights of section 3 to systems of distinguishable identical classical particles.

This paper is accessible to undergraduates familiar with the concepts of statistical mechanics. It is particularly aimed at university teachers and textbook writers.

**Remark.** Some authors ‘resolve’ the GP1 by using tailored entropy expressions that do not agree with the standard definition used in statistical mechanics [14, 15]. Others dismiss the correspondence between statistical-mechanical and thermodynamical entropy (in order to allow violations of the statistical-mechanical version of the second law) [16]. The present resolution, by contrast, adheres (for quantum systems) to the definition

\[ S = -k \sum_{\text{all microstates } m} P(m) \ln P(m) \]  

(1)

(\( k \) is Boltzmann’s constant, \( P(m) \) denotes the probability of the microstate \( m \)) and does not question the correspondence between statistical-mechanical and thermodynamical entropy.

2. Demonstration of the GP1

Consider a C\(_{60}\) fullerene (buckyball) \( p \) made up of 30 carbon-12 atoms and 30 carbon-13 atoms. Let \( p \) be located in a vessel of volume \( V \) at temperature \( T \). The (canonical) partition function of this one-particle system has the form

\[ z(T, V, p) = z_{t.m}(T, V, p) z_{i.s}(T, p) \]  

(2)

[17], where \( z_{t.m}(T, V, p) \) denotes the partition function for \( p \)’s translational motion and \( z_{i.s}(T, p) \) denotes the partition function for \( p \)’s internal structure. As is well known,

\[ z_{t.m}(T, V, p) = V \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} \]  

(3)

[18] (\( m \) denotes the mass of \( p \)). \( z_{i.s}(T, p) \) primarily stems from \( p \)’s vibrational and rotational degrees of freedom and is independent of \( V \).

There are billions of non-equivalent ways to form a buckyball from 30 carbon-12 atoms and 30 carbon-13 atoms. All these buckyballs differ from one another by the arrangement of the carbon isotopes and, as a consequence, are pairwise non-identical. Now, let \( 2N (N \gg 1) \) of these buckyballs, \( p_1, p_2, \ldots, p_{2N} \), be confined to a vessel of volume \( 2V \) at temperature \( T \). For a sufficiently large volume, \( p_1, p_2, \ldots, p_{2N} \) form a (nearly) ideal gas \( S_0 \) with the partition function

\[ Z_0(T, 2V, p_1, p_2, \ldots, p_{2N}) \overset{\text{ideal gas}}{=} \prod_{n=1}^{2N} z(T, 2V, p_n) \]  

(2)

\[ = \prod_{n=1}^{2N} z_{t.m}(T, 2V, p_n) z_{i.s}(T, p_n). \]  

(4)

Since \( p_1, p_2, \ldots, p_{2N} \) all have the same mass \( m \), the partition functions for their translational motions agree:

\[ z_{t.m}(T, 2V, p_1) = \cdots = z_{t.m}(T, 2V, p_{2N}) = 2V \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2}. \]  

(5)
The partition functions for their internal structures, by contrast, only agree approximately because a buckyball’s arrangement of carbon isotopes slightly affects its vibrational modes and moments of inertia. In order not to base the present demonstration of the GP1 on approximations relying on the similarity between $p_1$, $p_2$, ..., $p_{2N}$, let the temperature $T$ be so low that the internal degrees of freedom of $p_1$, $p_2$, ..., $p_{2N}$ are frozen out. (The volume $2V$ is assumed so large that the buckyballs can still be treated as an ideal gas.) Furthermore, let $p_1$, $p_2$, ..., $p_{2N}$ be chosen such that they all have the same ground-state degeneracy $g$. Under these conditions, the partition functions for their internal structures become

$$z_{i,s}(T, p_n) = g \exp \left( -\frac{\epsilon_n}{kT} \right) \quad n = 1, 2, \ldots, 2N,$$

where $\epsilon_n$ denotes the ground-state energy of $p_n$. Finally, setting each buckyball’s ground-state energy to 0 eliminates the remaining differences between these partition functions and yields

$$z_{i,s}(T, p_1) = \cdots = z_{i,s}(T, p_{2N}) = g.$$  

With this, $S_0$’s partition function becomes

$$Z_0(T, 2V, 2N) = \left[ 2V \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} g \right]^{2N}.$$  

As a side note, (8) has the form of a partition function of an ideal gas of $2N$ distinguishable identical particles: for one thing, there is no indistinguishability factor $1/(2N)!$ in (8); for another thing, (8) does not depend on the particle identities $p_1$, $p_2$, ..., $p_{2N}$, but only on the particle number $2N$. Thus, as noted in section 1, one may expect that the GP1 arises.

The entropy $S(T, \ldots)$ of a system in canonical equilibrium results from its partition function $Z(T, \ldots)$ by

$$S(T, \ldots) = \frac{\partial}{\partial T} [kT \ln Z(T, \ldots)].$$  

[19]. Applying (9) to (8) yields $S_0$’s entropy

$$S_0(T, 2V, 2N) = 2Nk \left[ \ln(2V) + \ln \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} g \right] + \frac{3}{2}.$$  

Inserting a partition in the middle of $S_0$ divides $S_0$ into two equal subsystems $S_1$ and $S_2$, each with volume $V$ and each containing $N$ buckyballs. Since $S_1$ and $S_2$ are ideal gases consisting of the same particles as $S_0$, their partition functions are

$$Z_1(T, V, N) = Z_2(T, V, N) = Z_0(T, V, N)$$  

yielding the entropies

$$S_1(T, V, N) = S_2(T, V, N) = S_0(T, V, N).$$  

Thus, the entropy of the partitioned total system $S_{1+2}$ consisting of $S_1$ and $S_2$ is

$$S_{1+2}(T, 2V, 2N) = S_1(T, V, N) + S_2(T, V, N) \equiv 2S_0(T, V, N).$$  

Comparison with the entropy of the original (unpartitioned) system $S_0$ shows that the partitioning decreases the entropy by

$$S_0(T, 2V, 2N) - S_{1+2}(T, 2V, 2N) \equiv S_0(T, 2V, 2N) - 2S_0(T, V, N) \equiv 2Nk \ln 2.$$  

Since the partitioning does not perform work (see remark below), and since $S_0$’s energy equals $S_{1+2}$’s energy (see appendix A), there is, according to the first law of thermodynamics, no heat transfer to the thermal reservoir. Hence, the entropy decrease (14) contradicts the second law of thermodynamics.
Remark. The claim that the partitioning does not perform work is taken for granted here. Strictly speaking, inserting a partition in \( S_0 \) involves a tiny amount of work (because the buckyballs' wavefunctions are deformed) and it must be shown that this amount is negligible compared to \( 2NkT \ln 2 \).

3. Origin and resolution of the GP1

Two flaws are responsible for the false entropy decrease (14) calculated in the previous section. One is located in (11), the other in (13). Before pointing out and correcting these flaws, it is worthwhile to take a closer look at the term uncertainty and its use in the context of the present situation.

Each microstate of a system in canonical equilibrium possesses a certain non-zero probability. Hence, if the microstates of such a system differ in a specific property, then there is an uncertainty about this property. For example, in \( S_0 \) there is, classically speaking, an uncertainty about the position of particle \( p_1 \) because there are microstates in which \( p_1 \) is located in the first half of the vessel and other microstates in which \( p_1 \) is located in the second half. Accordingly, after partitioning, there is an uncertainty in \( S_1 + S_2 \) about whether \( p_1 \) is located in \( S_1 \) or \( S_2 \). From \( S_1 \)'s perspective, there is an uncertainty about whether \( p_1 \) is located within the system at all. Since the same uncertainty exists with regard to the other particles \( p_2, p_3, \ldots, p_{2N} \), there is an uncertainty about the particle composition of \( S_1 \), i.e., the set of particles located in \( S_1 \). In short, the uncertainty about the particle positions in \( S_0 \) results, after partitioning, in an uncertainty about which particles are located in \( S_1 \).

By definition, there is no uncertainty about \( S_0 \)'s particle composition \( \{p_1, p_2, \ldots, p_{2N}\} \). In contrast, as just explained, \( S_1 \)'s particle composition might be \( \{p_1, p_2, \ldots, p_{2N}\} \) in one microstate and, e.g., \( \{p_2, p_3, \ldots, p_{2N+1}\} \) in another. Provided that \( S_1 \) consists of \( N \) particles (cf second remark below), there are \( \binom{2N}{N} \) possible particle compositions \( \xi_1, \xi_2, \ldots, \xi_{\binom{2N}{N}} \) of \( S_1 \), namely, all \( N \)-element subsets of \( S_0 \)'s particle composition:

\[
\xi_1, \xi_2, \ldots, \xi_{\binom{2N}{N}} \subset \{p_1, p_2, \ldots, p_{2N}\} \tag{15}
\]

\[
|\xi_1| = |\xi_2| = \cdots = |\xi_{\binom{2N}{N}}| = N. \tag{16}
\]

Now, consider the hypothetical system \( S_1^\xi \) which is thought to be in all respects the same as \( S_1 \) except that there is no uncertainty about its particle composition \( \xi \in \{\xi_1, \xi_2, \ldots, \xi_{\binom{2N}{N}}\} \). The partition function of \( S_1^\xi \) is

\[
Z_1(T, V, N | \xi) = \prod_{q \in \xi} z(T, V, q) \equiv \prod_{q \in \xi} \xi_{i,m}(T, V, q) \zeta_{s.t.}(T, q) \equiv V \left( \frac{m k T}{2 \pi \hbar^2} \right)^{3/2} g \equiv Z_0(T, V, N). \tag{17}
\]

This shows that setting \( S_1 \)'s partition function equal to \( S_0 \)'s partition function, as was done in (11), amounts to ignoring the uncertainty about \( S_1 \)'s particle composition. The correct
calculation of $S_1$’s partition function, by contrast, takes all possible particle compositions of $S_1$ into account:

$$Z_1(T, V, N) = \sum_{i=1}^{(2^N)} \sum_{\text{all microstates } m \text{ of } S_1 \text{ in which the particle composition of } S_1 \text{ is } \zeta_i} \exp \left( -\frac{E_m}{kT} \right)$$

$$= \sum_{i=1}^{(2^N)} Z_1(T, V, N | \zeta_i)$$

$$\equiv (17) \frac{(2N)}{N} Z_0(T, V, N) \quad (18)$$

($E_m$ denotes the energy of the microstate $m$). From (18), one obtains $S_1$’s entropy

$$S_1(T, V, N) = S_0(T, V, N) + k \ln \left( \frac{2N}{N} \right). \quad (19)$$

Compared to (12), there is an additional term $k \ln \left( \frac{2N}{N} \right)$ reflecting the uncertainty about the particle composition of $S_1$.

Applying the above reasoning to $S_2$ yields

$$S_2(T, V, N) = S_1(T, V, N), \quad (20)$$

as required by symmetry.

Each microstate of the partitioned total system $S_{1+2}$ is the tensor product $m \otimes n$ of a microstate $m$ of $S_1$ and a microstate $n$ of $S_2$. Since there is no interaction between $S_1$ and $S_2$,

$$E_{m \otimes n} = E_m + E_n. \quad (21)$$

However, not every microstate $n$ of $S_2$ is compatible with every microstate $m$ of $S_1$. If in $m$ a certain particle is located in $S_1$, and in $n$ the same particle is located in $S_2$, then the tensor product $m \otimes n$ is not well-defined because the same particle appears twice in it. On the other hand, if in $m$ a certain particle out of $p_1, p_2, \ldots, p_{2N}$ is not located in $S_1$, and in $n$ the same particle is not located in $S_2$, then $m \otimes n$ is inadmissible for $S_{1+2}$ because it does not include all particles of $S_{1+2}$. Thus, for $n$ to be compatible with $m$, the particle composition of $S_2$ in $n$ must be complementary to the particle composition of $S_1$ in $m$. For example, if the particle composition of $S_1$ in $m$ is $\{p_1, p_2, \ldots, p_N\}$, then the particle composition of $S_2$ in a microstate $n$ compatible with $m$ must be $\{p_{N+1}, p_{N+2}, \ldots, p_{2N}\}$. If this complementary relationship between compatible microstates of $S_1$ and $S_2$ is taken into account, one obtains

$$Z_{1+2}(T, 2V, 2N) = \sum_{i=1}^{(2^N)} \sum_{\text{all microstates } m \text{ of } S_1 \text{ in which the particle composition of } S_1 \text{ is } \zeta_i} \sum_{\text{all microstates } n \text{ of } S_2 \text{ which are compatible with } m} \exp \left( -\frac{E_{m \otimes n}}{kT} \right)$$

$$\equiv (21) \sum_{i=1}^{(2^N)} \sum_{\text{all microstates } m \text{ of } S_1 \text{ in which the particle composition of } S_1 \text{ is } \zeta_i} \exp \left( -\frac{E_m}{kT} \right) \sum_{\text{all microstates } n \text{ of } S_2 \text{ in which the particle composition of } S_2 \text{ is } \zeta_i^c} \exp \left( -\frac{E_n}{kT} \right)$$

$$= \sum_{i=1}^{(2^N)} Z_1(T, V, N | \zeta_i) Z_2(T, V, N | \zeta_i^c), \quad (22)$$
where $\xi^c$ denotes the particle composition that is complementary to $\xi$ and $Z_2(T, V, N | \xi^c)$
denotes the partition function of a (hypothetical) system which is in all respects the same as
$S_2$ except that its particle composition is $\xi^c$. As in (17), one has

$$Z_2(T, V, N | \xi^c) = Z_0(T, V, N).$$

(23)

With this, $S_{1+2}$’s partition function becomes

$$Z_{1+2}(T, 2V, 2N) \overset{(22), (21)}{=} \left(\frac{2N}{N}\right)^2 [Z_0(T, V, N)]^2
$$

(24)

yielding the entropy

$$S_{1+2}(T, 2V, 2N) \overset{(9), (24)}{=} 2S_0(T, V, N) + k \ln \left(\frac{2N}{N}\right).
$$

(25)

$S_{1+2}(T, 2V, 2N)$ is smaller than

$$S_1(T, V, N) + S_2(T, V, N) \overset{(19), (20)}{=} 2 \left[ S_0(T, V, N) + k \ln \left(\frac{2N}{N}\right) \right]
$$

(26)

by $k \ln \left(\frac{2N}{N}\right)$, reflecting the fact that $S_1$ and $S_2$ are correlated by their complementary particle compositions. This correlation was ignored in section 2 when, in (13), the entropy of $S_{1+2}$ was set to the sum of the entropies of $S_1$ and $S_2$.

Comparison of the entropies of $S_0$ and $S_{1+2}$ shows that the partitioning does not change the entropy:

$$S_0(T, 2V, 2N) - S_{1+2}(T, 2V, 2N) \overset{(25)}{=} S_0(T, 2V, 2N) - 2S_0(T, V, N) - k \ln \left(\frac{2N}{N}\right)
$$

$$\overset{(10)}{=} 2Nk \ln 2 - k \left[ \ln (2N)! - 2 \ln N! \right]
$$

(27)

Thus, the GP1 is resolved.

Remarks.

- Traditionally, the GP1 is demonstrated by combining two gas systems and not by partitioning a single one. In order to resolve the GP1 in its traditional form, it is crucial to carefully specify the initial bipartite system. If this initial system is, e.g., $S_{1+2}$, then combining its subsystems $S_1$ and $S_2$ yields $S_0$ and, according to (27), a zero entropy change. If, on the other hand, the initial system consists of, e.g., two subsystems $S_3$ and $S_4$, where $S_3$’s particle composition is $\{p_1, p_2, \ldots, p_N\}$ and $S_4$’s particle composition is $\{p_{N+1}, p_{N+2}, \ldots, p_{2N}\}$, then combining $S_3$ and $S_4$ increases the entropy. However, as with two gases of different kinds, this entropy increase is not paradoxical; it reflects the fact that the combining process cannot be reversed by reinserting the partition, since, after reinsertion, there is no longer certainty that the particle compositions of the subsystems are $\{p_1, p_2, \ldots, p_N\}$ and $\{p_{N+1}, p_{N+2}, \ldots, p_{2N}\}$, respectively.

- The assumed certainty about $S_0$’s particle composition $\{p_1, p_2, \ldots, p_{2N}\}$ is a special case. In the general case, where there is an uncertainty about $S_0$’s and thus also about $S_{1+2}$’s particle composition, the particle compositions of $S_1$ and $S_2$ need no longer be complementary but only disjoint (cf section 4.3.2 in [5]).

- In addition to the uncertainty about which particles are located in $S_1$ and $S_2$, respectively, there is also an uncertainty about how many particles are located in each subsystem. However, the latter uncertainty contributes only negligibly to the entropies of $S_1$, $S_2$ and $S_{1+2}$ [20, 21]. It is therefore acceptable to disregard this uncertainty by assuming the particle number $N$ for $S_1$ and $S_2$. As an aside, this disregard is responsible for the
small discrepancy between $S_0(T, 2V, 2N)$ and $S_{1+2}(T, 2V, 2N)$ expressed by the Stirling approximation in (27).

- The concept of the canonical partition function is based on the assumption that the probability of any microstate $m$ of a system in canonical equilibrium is given by
  \[ P(m) = C \exp \left( -\frac{E_m}{kT} \right), \]
  where the normalization constant $C$ may depend on the equilibrium macrostate, but not on the microstate $m$. Non-ergodic systems, such as $S_1$, generally do not satisfy this assumption. ($S_1$ is non-ergodic because a microstate $m$ cannot dynamically evolve to a microstate $n$ if $S_1$’s particle composition in $m$ differs from that in $n$.) Therefore, using $S_1$’s partition function (18) requires justification. This justification is provided appendix B. (The justifications for using the partition functions of $S_2$ and $S_{1+2}$ are similar.)

4. Resolution of the GP1 for distinguishable identical classical particles

Consider a structureless classical particle $q_1$ of mass $m$ confined to a vessel of volume $V$ at temperature $T$. Assuming an elementary phase space volume of $(2\pi\hbar)^3$, the partition function of this one-particle system is
  \[ z(T, V, q_1) = V \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \]  
[22]. Now, let the vessel be filled with $N$ ($N \gg 1$) distinguishable identical particles $q_1, q_2, \ldots, q_N$. For a sufficiently large volume, $q_1, q_2, \ldots, q_N$ form a (nearly) ideal gas $S_1$ with the partition function
  \[ Z_1(T, V, q_1, q_2, \ldots, q_N) = [z(T, V, q_1)]^N \equiv \left[ V \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right]^N. \]

Let $q_1, q_2, \ldots, q_N$ be all the particles in the universe that are identical to the particles in $S_1$ and assume $\mathcal{N} \gg N$. Since, by definition, $q_1, q_2, \ldots, q_N$ agree in all their permanent properties, there is, as a matter of principle, no way to be sure that really $q_1, q_2, \ldots, q_N$ are located in $S_1$ and not, e.g., $q_2, q_1, \ldots, q_{N+1}$. Therefore, $\{q_1, q_2, \ldots, q_N\}$ is just one of $\binom{\mathcal{N}}{N}$ possible particle compositions of $S_1$. Taking this uncertainty about $S_1$’s particle composition into account results, as with (18), in an $\binom{\mathcal{N}}{N}$ times larger partition function. Thus, $S_1$’s true partition function is
  \[ Z_1(T, V, N) \equiv \binom{\mathcal{N}}{N} \left[ V \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right]^N \]  
(30)
yielding the entropy
  \[ S_1(T, V, N) \equiv Nk \left( \ln N + \frac{3}{2} \ln \left( \frac{mkT}{2\pi\hbar^2} \right) + \frac{3}{2} \right) + k \ln \left( \frac{\mathcal{N}}{N} \right). \]

Now, consider a second system $S_{II}$ of volume $V$ which is separated from $S_1$ by a removable partition. Let $S_{II}$, at temperature $T$, contain $N$ particles identical to the particles in $S_1$. Then, of course, the entropies of $S_1$ and $S_{II}$ agree:
  \[ S_{II}(T, V, N) = S_1(T, V, N). \]  
(33)
Since \( N \gg N \), \( S_I \) and \( S_{II} \) are nearly uncorrelated (see first remark below) and, as a consequence, the entropy of the total system \( S_{I+II} \) is approximately the sum of the entropies of its subsystems \( S_I \) and \( S_{II} \):

\[
S_{I+II}(T, 2V, 2N) \approx S_I(T, V, N) + S_{II}(T, V, N) \quad (33) = 2S_I(T, V, N). \tag{34}
\]

By removing the partition between \( S_I \) and \( S_{II} \), one obtains the combined system \( S_{III} \) with the entropy:

\[
S_{III}(T, 2V, 2N) = S_I(T, 2V, 2N). \tag{35}
\]

Comparison of the entropies of \( S_{I+II} \) and \( S_{III} \) shows that the combination does not change the entropy:

\[
S_{I+II}(T, 2V, 2N) - S_{III}(T, 2V, 2N) \\
\approx 2S_I(T, V, N) - S_I(T, 2V, 2N) \quad (34) \tag{36}
\]

\[
\approx 2k \ln \left( \frac{\Omega}{N} \right) - 2Nk \ln 2 - k \ln \left( \frac{\Omega}{2N} \right) \quad \text{(32)}
\]

\[
\approx k[2 \ln \Omega - 2N \ln N - 2N \ln 2 - \ln \Omega^{2N} + \ln(2N)!] \quad \text{(37)}
\]

\[
\approx 0. \quad \text{Stirling}
\]

Remarks.

- The resolution above is based on the assumption \( \Omega \gg N \). The absence of the GP1 in this limiting case was found before by van Kampen [23]. If the assumption \( \Omega \gg N \) is not satisfied, then the correlation between \( S_I \) and \( S_{II} \) arising from their disjoint particle compositions is no longer negligible (see section 5.4 in [5]). The general resolution which does not rely on \( \Omega \gg N \) is given in section 6.1.2 in [5].

- One might expect that \( \Omega \) is necessarily an unknown and very large number and, as a consequence, that entropy expressions containing \( \Omega \), such as (32), are of little value. Indeed, for a system containing \( N \) (out of \( \Omega \)) distinguishable identical classical particles, the entropy \( S(N, \ldots) \), as a thermodynamic potential, must be replaced by the reduced entropy

\[
R(N, \ldots) = S(N, \ldots) - k \ln \frac{\Omega!}{(\Omega - N)!} \quad (37)
\]

(defined in section 5.5 in [5]) which, unlike \( S(N, \ldots) \), does not depend on \( \Omega \) but instead happens to agree with the entropy of indistinguishable particles (cf section 5.6.6.2 in [5]). This being said, \( \Omega \) is not necessarily unknown and large compared to \( N \); by exploiting some leeway in the choice of what properties are regarded as permanent (cf section 2.6.2 in [5]), it is, for example, possible to achieve \( \Omega = 2N \) in the above situation.

5. Summary

In section 1, a distinction was made between the Gibbs paradox of the first kind (GP1) and that of the second kind. The meanings of the terms identical and indistinguishable were outlined. It was explained why the usual demonstration and resolution of the GP1 are unsatisfactory. In section 2, an entropy decrease was calculated from the partitioning of an ideal gas consisting...
of pairwise distinct buckyballs, each individually made up of the isotopes carbon-12 and carbon-13. This specific example demonstrates that the GP1 poses a clear contradiction to the second law of thermodynamics and that not only classical but also quantum systems can suffer from the GP1. In section 3, it was shown that, after partitioning, the uncertainty about which buckyballs are located in which subsystem, for one thing, increases the entropies of the subsystems and, for another thing, causes a correlation between the subsystems which deprives the entropy of its additivity. These two effects compensate for the paradoxical entropy decrease calculated in section 2. In section 4, the concepts of section 3 were used to resolve the GP1 in its original classical form.

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Appendix A

As a general rule, one obtains the energy \( E(T, \ldots) \) of a system in canonical equilibrium from its partition function \( Z(T, \ldots) \) by

\[
E(T, \ldots) = kT^2 \frac{\partial}{\partial T} \ln Z(T, \ldots) \tag{A.1}
\]

[19]. Applying (A.1) to (8) yields \( \mathcal{S}_0 \)'s energy

\[
E_0(T, 2V, 2N) = 3NkT, \tag{A.2}
\]

and applying it to (11) yields the same energy for \( \mathcal{S}_{1+2} \):

\[
E_{1+2}(T, 2V, 2N) = E_1(T, V, N) + E_2(T, V, N) = 2E_0(T, V, N) \overset{(A.2)}{=} 3NkT. \tag{A.3}
\]

Appendix B

Let \( m \) be a microstate of \( \mathcal{S}_1 \) and let \( \zeta \) be \( \mathcal{S}_1 \)'s particle composition in \( m \). The conditional probability of \( m \) given that \( \mathcal{S}_1 \)'s particle composition is \( \zeta \) is defined as

\[
P(m|\zeta) = \frac{P(m)}{P(\zeta)}, \tag{B.1}
\]

where

\[
P(\zeta) = \sum_{\text{all microstates } n \text{ of } \mathcal{S}_1 \text{ in which the particle composition of } \mathcal{S}_1 \text{ is } \zeta} P(n) \tag{B.2}
\]

is the probability that \( \mathcal{S}_1 \)'s particle composition is \( \zeta \). The assumption that \( \mathcal{S}_1 \) contains \( N \) particles (cf second remark of section 3) guarantees

\[
\zeta \in \{\zeta_1, \zeta_2, \ldots, \zeta_{(2N)}\} \tag{B.3}
\]
and yields the normalization condition
\[
\sum_{i=1}^{(2N)} P(\xi_i) = \sum_{n \text{ all microstates of } S_1} P(n) = 1. \quad \text{(B.4)}
\]
For reasons of symmetry, all possible particle compositions are equiprobable, that is,
\[
P(\xi_1) = P(\xi_2) = \cdots = P(\xi_{(2N)}) = \frac{1}{(2N)}. \quad \text{(B.5)}
\]
(In the terminology of [5], \(S_1\) is called harmonic.) Furthermore, in canonical equilibrium, the conditional probability \(P(m | \xi)\) is equal to \(m\)’s probability in the hypothetical system \(S_\xi\).

Expressing \(m\)’s probability in \(S_\xi\) by the partition function of \(S_\xi\) yields
\[
P(m | \xi) = \frac{1}{Z_\xi(T, V, N | \xi)} \exp \left( -\frac{E_m}{kT} \right). \quad \text{(B.6)}
\]
Note that using the partition function of \(S_\xi\) is justified because, since there is no uncertainty about the particle composition of \(S_\xi\), \(S_\xi\) does not suffer from \(S_1\)’s non-ergodicity. Finally,
\[
P(m) = \frac{P(\xi) P(m | \xi)}{\sum_{\xi} P(\xi) Z_1(T, V, N | \xi) \exp \left( -\frac{E_m}{kT} \right)} = \frac{1}{\sum_{\xi} \frac{1}{Z_1(T, V, N | \xi)} \exp \left( -\frac{E_m}{kT} \right)} \quad \text{(B.3), (B.1), (B.6)}
\]
shows that \(S_1\) satisfies assumption (28) despite the fact that it is non-ergodic.

As a side note, if microstates of \(S_\xi\) with particle numbers other than \(N\) were not ignored (cf second remark of section 3) or if the ground-state energies of the buckyballs were not set to the same value, then \(S_\xi\) would not satisfy assumption (28) and, as a consequence, using \(S_1\)’s partition function (e.g., to calculate \(S_1\)’s entropy) would lead to incorrect results.

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