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Revisiting Gibbs paradox: Resolving misconceptions and addressing challenges

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Abstract

The Gibbs paradox explores critical aspects of entropy in gas mixing and its implications for thermodynamics. The paradox is rooted in three key elements: the independence of entropy on the identity of gases, the extensivity puzzle, and the absence of entropy change when identical gases mix. This paper revisits the Gibbs paradox, beginning with a concise introduction to its core principles. It examines the problem of two ideal gases and explores the mixing behavior through macroscopic thermodynamic properties. Using Gibbs' methodology, the study analyzes the scenario of mixing two types of argon, which differ only subtly, and evaluates the entropy addition for an ideal gas mixture. The investigation extends to quantum mechanics, addressing challenges related to particle indistinguishability and the role of quantum statistical mechanics. This perspective provides a refined understanding of the paradox, bridging the gap between the macroscopic and microscopic interpretations. The study concludes by synthesizing insights from thermodynamics and quantum mechanics, highlighting their relevance in resolving the paradox. It emphasizes the significance of particle identity in entropy calculations and the consistency of statistical mechanics frameworks. Ultimately, this revisitation underscores the enduring importance of the Gibbs paradox in understanding entropy, particle distinguishability, and the interplay between classical and quantum domains.

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1. Introduction

The Gibbs paradox encompasses three distinct categories. Firstly, the discontinuity puzzle addresses how the entropy mixing of two gases, initially independent due to their dissimilarity, tends towards zero when they are of the same type, highlighting a peculiar shift in entropy behavior [1]. Secondly, the extensivity puzzle questions the consistent application of

entropy functions in classical mechanics across varying scales and configurations [2]. Thirdly, the non-existence puzzle examines the entropy mixing between identical samples of gas, where, despite identical microscopic motions during mixing, only approximate equivalence is achieved in terms of entropy [3]. These puzzles collectively challenge the fundamental physical interpretation of entropy, revealing interconnectedness rather than isolated phenomena. By assuming entropy mixing exists even among identical gases, these puzzles diminish in significance, unveiling the intricate layers of the Gibbs paradox [4]. Classical and quantum theories provide solutions, illustrating the evolution of the paradox from classical assumptions to quantum intricacies and underscoring the evolving understanding of entropy within different theoretical frameworks [5]. This introduction sets the stage for further exploration of the Gibbs paradox principles in subsequent sections.

2. The Gibbs Paradox

From a historical perspective on the Gibbs paradox, Boltzmann employed statistical mechanics to describe the motion of molecules and their energy distribution within a system, culminating in the formulation of the following equation:

$$S = \log W + S_0 \quad (1)$$

Where S is entropy, W represents the number of microstates, and S_0 is a constant of integration [6]. Planck subsequently amended Equation 1 by introducing the Boltzmann constant k , and without considering S_0 , which led to the final form:

$$S = k \log W \quad (2)$$

Equation 1 became a cornerstone of statistical mechanics. However, Gibbs found that when Equation 2 was applied to calculate the entropy of an ideal gas, the nature of Boltzmann's statistical entropy did not align with the classical thermodynamic entropy formulated by van Kampen [7]. This discrepancy prompted Gibbs to propose a correction method to account for particles that are indistinguishable from one another. The correction involved adjusting the calculation of the number of microstates, W , to reflect the indistinguishability of particles in the system, particularly for two ideal gases, regardless of whether their particles were distinguishable or indistinguishable from one another. Although resolving the immediate contradiction, this approach has generated debate and exploration in statistical mechanics ever since [8].

3. Problem Statement of Gibbs Paradox

Assuming two ideal gases, A and B, with molecular quantities n_A and n_B , confined in volumes V_A and V_B , separated by a diaphragm. Equation 3 represents the respective volumetric ratio between the two gases, and Equation 4 illustrates the corresponding pressures (and temperatures) of states T_A and T_B .

$$\frac{V_A}{V_B} = \frac{n_A}{n_B} \quad (3)$$

$$P_A = P_B = \frac{n_A R T_A}{V_A} \quad (4)$$

After the diaphragm's motion allows for the diffusion process between gases A and B, a molecular gas mixture reaches equilibrium, as given in Equation 5.

$$n_{mixture} = n_A + n_B \quad (5)$$

With the current uniform composition, the temperature, pressure, and total energy remain unchanged. Therefore, the entropy change due to the diffusion process between these gases is:

$$\Delta S = S_{final} - S_{initial} = nR \log(V_{mixture}) - (n_A R \log(V_A) + n_B R \log(V_B)) \quad (6)$$

$$\Delta S = -nR[f \log f + (1 - f) \log(1 - f)] \quad (7)$$

Where $f = \frac{n_A}{n_B} = \frac{V_A}{V_{mixture}}$ is the molecule's fraction of component A, and Gibbs in van Kampen [2] assumed $f = \frac{1}{2}$. Therefore, Equation 7 is rearranged as:

$$\Delta S = -nR \log 2 \quad (8)$$

3.1. Explanation of Gibbs Methodology

The respective entropy increase ($\Delta S = | -nR \log 2 |$) is independent of the nature of the gases and whether they are identical; they can still be mixed without any entropy increase. When two dissimilar gases are mixed and accompanied by an increase in entropy, these gases can be separated and returned to their original states by changing external bodies. Therefore, these changes may contribute to weight loss and heat transfer from a hot body to a cold one.

The original state does not mean the return of each molecule to its initial position but rather to an identical state from the original one in terms of observed macroscopic properties. This means the original thermodynamic state is recovered,

specifying the chemical composition, total energy, volume, and the number of gas molecules. It is essential to note that the thermodynamic assertion states that when the net entropy is zero, the original thermodynamic state is restored without any external change.

Furthermore, a thermodynamic state is related to a small number of specifications of macroscopic quantities like pressure, temperature, magnetization, and stress, denoted as $\{X_1, X_2, \dots, X_n\}$ and a thermodynamic variable could also be a microstate. Hence, the total mass and energy might be the microstate's physical properties, although entropy might not be.

The emphasis on the thermodynamic state is denoted as $X = \{X_1, \dots, X_n\}$ for a large class $C(X)$ of the microstates is compatible with Boltzmann, Planck, and Einstein, illustrating the interpretation of the entropy's microstates given by:

$$S(X) = k \log W(C) \quad (9)$$

Where $W(C)$ is the phase volume occupied by all the microstates at the chosen reference class C .

Hence, based on this formula, a large mass of correct results might be explained and deduced naturally [9]. In particular, a simple explanation of the reason for the second law as an immediate consequence of Liouville's theorem, along with a generalization of the second law of thermodynamics to non-equilibrium circumstances, finds application in the biological sciences [10]. A revisit to the gas mixing scenario is presented below.

3.2. Gas Mixing Scenarios

There is no doubt that the measurable macroscopic properties of Argon (Ar) can be described using conventional thermodynamics, including the state equation, heat capacity, vapor pressure, and heat of vaporization [11]. This approach assigns zero entropy change to mixing two argon samples at the same temperature and pressure [12]. Therefore, there are two types of Argon (A1 and A2); A2 is treatable within Whifnium (a rare superkalik element), and A1 is not treatable [13]. Therefore, a mixing experiment might be conducted, preparing bottles of pure A1 and A2 for $n_1 = fn$, ($f = \frac{n_1}{n}$) of A1 within the volume $V_1 = fV$ and for $n_2 = (1 - f)n$ moles of A2 in $V_2 = (1 - f)V$, thus the resulting actual diffusion might be identical to the precise path of each atom, with one that could have happened rarely [14]. According to the existing knowledge, the diffusion entropy increase ΔS considering the two Argon types becomes [15]:

$$\Delta S = \Delta S_1 + \Delta S_2 \quad (8)$$

Where:

$$\Delta S_1 = -nRf \log f \quad (9)$$

$$\Delta S_2 = -nR(1 - f) \log (1 - f) \quad (10)$$

The diffusion still takes place without any change in the temperature, pressure, or internal energy, but because of the greater information, it is also linked with a free energy decrease [16, 17]:

$$\Delta F = -T\Delta S \quad (11)$$

Considering the main principles of thermodynamics through the concept of uncontrolled irreversibility mixing, the same argument also applies from a reversible and isothermal perspective. Then, the work obtained is given by Equation 12, [18].

$$W = \Delta F = -T\Delta S \quad (12)$$

Assuming that the diaphragm between the two argon types (A1, A2), then A2 is expected to be diffused via the piston until the partial pressure is the same on both sides, after the slow motion of the piston in the direction of increasing V_1 . Hence, for this expansion, the obtained work is given by Equation 13 and W_1 is given by Equation 14, [19]:

$$W_1 = \int_{V_1}^V p_1 dV = n_1 RT \log \left(\frac{V}{V_1} \right) \quad (13)$$

$$W_1 = T\Delta S_1 \quad (14)$$

Where ΔS_1 is the entropy mixing, indicating the work obtained from the reversible isothermal expansion of A1 within the full volume:

$$V = V_1 + V_2 \quad (15)$$

The initial diffusion of A2 represents the increase in irreversible entropy S_2 , whereas no work is obtained [20, 21]. In the case of using the other superkalik element, Whafnium, it presents an opposite property since it is permeable to A1 and not to A2. Thus, an apparatus of two superkalic pistons can be developed. Hence, the Whifnium goes in the right direction in producing work:

$$W_1 = T\Delta S_1 \quad (16)$$

While moving to the left, it yields:

$$W_2 = T\Delta S_2 \quad (17)$$

Therefore, mixing entropy represents human information that predicts the available work from mixing. The discovery of the superkalic elements contributes to different entropy changes related to the identical physical process down to the exact path of each atom. Furthermore, possessing a superkalic piston provides the ability to control a new thermodynamic degree of freedom X_{n+1} .

After the discovery of superkalic elements, there is still the option not to use them but to stick at the old macro variables $\{X_1, \dots, X_n\}$ of the previous century (20th). Then, there is still zero mixing entropy associated with the interdiffusion of A1 and A2; thus, these thermodynamic measurements of the Argon (A1, A2) are made without utilizing the new technology. An extensive addition of the entropy of the ideal gases is illustrated in the succeeding section.

3.3. Addition of Entropy of An Ideal Gas

The addition of properties such as mass, heat capacity, and a few additional substances is experimentally tested based on measurements of the respective values for a specific amount of the substance [11]. The addition of entropy substances cannot be verified experimentally, as entropy cannot be evaluated directly, although it is considered a characteristic of a functioning state [13]. If the entropy is evaluated in terms of the formula's parameters, it becomes possible to determine whether a property belongs to the category of an additive quantity. Thus, the calculation of the entropy result for the thermodynamic system is compared with the sum of the entropy values within the system. Furthermore, considering that the additive properties are also related to the additive functions of the amounts of the substances, the amount of added entropy can be inferred from the form of the entropy's dependence on the substance [22]. Various expressions of the ideal gases and in thermodynamics handbooks have been derived to express the Gibbs paradox, such as:

$$S_i = n_i(C_{vi}\ln T + R\ln \frac{V_i}{n_i} + S_{o,vi}) \quad (18)$$

$$S_i = n_i(f(T) + K\ln \frac{V_i}{n_i}) \quad (19)$$

According to Equations 18 and 19, the respective entropy of the ideal gas is a non-homogeneous linear function of the additive quantity n_i . Thus, it is not an additive function and, consequently, not an additive quantity. Consequently, the entropy of an ideal gas will not be equal to the sum of the entropies of the individual parts of the gas, even if the gas is not partitioned into separate parts. An examination of the entropy of an ideal gas reveals that it equals the sum of the entropies of the parts when certain restrictions are considered when partitioning the gas into parts. Therefore, the calculation of the entropy values for n moles of the i -th-ideal gas and the sum of the individual entropies for both methods of partitioning the gas into two parts (n_1, n_2) are considered. Hence in the first partition method, the parts of the gas are located in different places in space with equal temperature and pressure values, equal to the gas values. Thus, the volume of the gas is the sum of the volumes of each part:

$$V = V_1 + V_2 \quad (20)$$

In the second partition method, the parts are at the same place, forming a mixture, and the volumes of the gas and the parts are:

$$V = V_1 = V_2 \quad (21)$$

The entropy of the gases to be considered is related to a certain amount of the i -th, first and second gas as a function of quantities: $S_i(n_i, V, T)$, $S_i(n, V_1, T)$, $S_i(n_2, V_2, T)$, $S_i(n_1 + n_2, V, T)$, $S_i(n_1, V_1, T)$, $S_i(n_2, V, T)$. More information about the theoretical derivation can be found in Zhang and Liu [23]. Special attention is paid to the difference between the non-additivity of the entropy of the ideal gas from the parts of a mixture by means of the non-additivity of the properties from the substances in case of the formation of non-ideal mixtures [15]. Further deviations from the additivity in non-ideal mixtures come out, when a comparison between the values of these properties obtained by measurements takes place. These deviations encompass the entire scope of molecular theory, as non-ideal mixtures exhibit interactions between molecules that are absent in ideal mixtures. A description of the Gibbs paradox in Quantum Mechanics is illustrated in the following section.

3.4. Revisit of Gibbs Paradox in Quantum Mechanics

A new paradox is also demonstrated in quantum mechanics through the identification of indistinguishable particles, which is very significant, given the symmetrization proposal [24]. These suggested particles are related to all these particles of the same sign, and permutations are considered either invariant (bosons) or with a different sign (fermions). These symmetrization postulates are valid, holding regardless of the anomalies, and the situation is considered. In the context of

quantum mechanics, the division by $N!$ is justified and even mandatory in cases where the number of microstates is also being evaluated [25].

The paradox in the current case (quantum mechanics) is related to the treatment of gas mixing, which reproduces the results of a classical limiting situation, yielding the value of $2kN \log 2$, despite following individual particle trajectories, which seems impossible. Therefore, the quantum mechanics description of spatially one-particle wave packets presents an identical attitude to that of classical particles [23]. A quantum description of a diluted ideal gas is identical to the description of the classical theory. This justifies the substitution of small wave particles for classical particles, as they comply with the same dynamical principles and follow the same trajectories. This prediction occurs in the classical limit situation, whereas predictions made by quantum mechanics follow classical mechanics [26]. In the case of the two-particle quantum system, this is clearer, where the wave functions do not overlap spatially, and the quantum state of the system is expressed as:

$$\langle |\Psi\rangle = \frac{1}{\sqrt{2}} (|\phi_1\rangle |\psi_2\rangle + |\psi_1\rangle |\phi_2\rangle) \quad (22)$$

where $|\phi\rangle$, $|\psi\rangle$ are the non-overlapping wave packets of particles 1 and 2.

This state is symmetrical, and indices 1 and 2 are assumed to be invariant, with no distinct difference between them. In summary, although this argument of the symmetrization of each index is valid in N particles, the quantum states become:

$$\langle |\Psi\rangle = \frac{1}{\sqrt{N!}} \sum \Pi (|\phi_{i1}\rangle |\psi_{i2}\rangle |\chi_{i3}\rangle |\tau_{i4}\rangle \dots \quad (23)$$

The expressions $|\phi\rangle$, $|\psi\rangle$, $|\chi\rangle$, $|\tau\rangle$ are the distinguishable particles in the classical limit when these particles do not overlap. Consequently, the indices of the quantum mechanical formalism, where anti-symmetry occurs, are not reported as those of classical Physics particles. As a result, this observation is key to resolving the paradox. Although the indices present symmetrical roles, they do not correspond to any differences without ordinarily exchanging the two particles. Accordingly, the symmetrization postulates are still identified, and entropy depends on the distinguishability of the particles [15]. The following section is devoted to the challenges of the Gibbs paradox.

4. Challenges of Gibbs Paradox

A few facts about classical thermodynamics have been understood by various scientists, including Gibbs, over the last 100 years, and this effort has contributed to the increase and decrease of the scientific community's confidence level regarding the future of the second law of thermodynamics. This means that if an expert experimentalist observes a violation of the second law of thermodynamics, instead of issuing a sensational announcement, it would be advisable to investigate the unobserved degree of freedom. This is also related to the connection between entropy working in both directions, where the apparent entropy decrease signifies ignorance of the respective macro variables.

The main challenge to be mentioned in future notices is related to whether classical mechanics is comparable to quantum mechanics in terms of the entropy concept, which should be reopened or reinvestigated by the worldwide scientific community. Therefore, it is not surprising that the concept of entropy has been a persistent and controversial issue since Clausius first discovered it. Different people are examining different aspects, as there are still uncompleted tasks from both phenomenological and statistical perspectives. This implies that further theoretical work needs to be conducted before the claim of understanding entropy can be made [27, 28].

Another investigation revealed that the respective gas particles are not assumed to be indistinguishable; thus, the Gibbs paradox is resolved, and the extensive thermodynamics entropy results from subtracting two probabilistic entropies [29]. Therefore, considering that the particles obey the fundamental laws of quantum mechanics and also possess indistinguishable properties, although this concept is not directly related to *real Physics*. Hence, by means of the particle's concept, they do belong at the same state, but rather as signals with unused indices as particle names.

Furthermore, since the particle concept is not directly related to particles or completely distinguishable particles, this quantum approach is assumed not to be the best way to solve the Gibbs Paradox, and the existence of these particles is not established. The opposing concept in quantum mechanics presents an alternative perspective, as particles are represented by wave packets that emerge from the nonlinearity of quantum mechanics. Thus, they also become familiar with classical particles in the classical limit, presenting distinguishable properties (location) and trajectories. The primary difference between the particle concept and the classical particle concept lies in the distinct geometric configurations of the wave packets. Hence, the shape is represented by very narrow packets instead of impenetrable spheres [30]. Therefore, the quantum mechanical particle concept does not significantly contribute to Gibbs classical paradox. The conclusions of this interesting revisit are depicted in the following section.

5. Conclusions

In the Gibbs paradox, the respective energy function of the mixture depends on the applied pressure, volume, and temperature. Thus, the system is described in terms of momentum space by statistical mechanics from a macroscopic point of view, contributing to the extension of entropy. Thus, the mixing of entropy in case two equal gases mix has been an established fact, indicating the level of statistical mechanics by means of the microscopic constitution of the considered gases that should not make any difference when the gas particles originate from one state to another of the initially separated gases, although this interpretation might be mistaken. Hence, when non-thermodynamic microscopic separation and mixing

processes occur, there is also a corresponding effect on the level of statistical mechanics, taking into account the microscopic constitution of the gases. Thus, this should not make any difference in the origination of the gas particles from one or the other of the initially separated gases. Considering the allowance for processes such as non-thermodynamic and microscopic separation, it is concluded that, in the case of equal gases, the annotated value of $2kN\log 2$ for the mixing entropy and other mixing effects is experimentally verified.

From a quantum mechanics point of view, there is a need to find an argument to consider the particles indistinguishable. In the first particle concept, the quantum mechanical formalism obeys its symmetrization postulates; it is a very abstract particle concept, and the indices used in this approach are not linked to real objects. Thus, this approach is not applicable when we talk about mixing gases of particles. In the second particle concept, individual particles are represented by small wave packets that become wave packets fully localized as the well-known classical particles. The advantage of this particle concept is that these particles refer to *real* entities, as opposed to the first quantum mechanical particle concept. However, because these wave packets resemble classical particles, they even have trajectories, and they are assumed to be distinguishable as *normal* classical particles. Thus, neither of the two quantum particle concepts justifies the reduced entropy.

The Gibbs Paradox does not truly consider quantum mechanics to be verified because none of the quantum particle concepts add anything useful to the classical and philosophical solutions formulated. Therefore, the Gibbs Paradox cannot provide reliable solutions and is not applicable without certain constraints.

Nomenclatures

C_{vi}		constant thermodynamic capacity of the i -th ideal gas under constant volume
$f(T)$		function of the temperature
S	[Kj/kg]	system's entropy
S_o	[Kj/kg]	entropy at 0 K
	S_i	[Kj/kg] entropy of the same amount of the i -th ideal gas
	n_i	number of molecules
	K	Boltzmann's constant
	T	thermodynamic (absolute) temperature of the gas
	W	probability of a Microscopic state
	I	Permutation indices over the entire sum

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