

Gibbs' Paradox according to Gibbs and slightly beyond

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The so-called Gibbs paradox is a paradigmatic narrative illustrating the necessity to account for the $N!$ ways of permuting N identical particles when summing over microstates. Yet, there exist some mixing scenarios for which the expected thermodynamic outcome depends on the viewpoint one chooses to justify this combinatorial term. After a brief summary on the Gibbs' paradox and what is the standard rationale used to justify its resolution, we will allow ourself to question from a historical standpoint whether the Gibbs paradox has actually anything to do with Gibbs' work. In so doing, we also aim at shedding a new light with regards to some of the theoretical claims surrounding its resolution. We will then turn to the statistical thermodynamics of discrete and continuous mixtures and introduce the notion of composition entropy to characterise these systems. This will enable us to address, in a certain sense, a "curiosity" pointed out by Gibbs in a paper published in 1876. Finally, we will finish by proposing a connexion between the results we propose and a recent extension of the Landauer bound regarding the minimum amount of heat to be dissipated to reset one bit of memory.

I. INTRODUCTION

The *Gibbs paradox* appears with various degrees of emphasis — ranging from simple comments or practice questions to dedicated chapters — in most physics textbooks involved with thermodynamics and statistical mechanics [1–28]. It is often presented as the theoretical inability of classical statistical mechanics, as initially developed by Gibbs, to be fully compatible with thermodynamics which it has yet set out to retrieve in the large system limit. The standard exposition usually starts with the classical *canonical* partition function following, in essence, Gibbs' 1902 treatment [29]:

$$Q(N, V, \beta) = \int \prod_{i=1}^N \left(\frac{d^3 r_i d^3 p_i}{\xi^3} \right) e^{-\beta H(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)} \quad (1)$$

In Eq. (1), $Q(N, V, \beta)$ is the partition function of a system of N identical particles confined in a volume V at fixed inverse temperature $\beta = 1/k_B T$, \mathbf{r}_i , \mathbf{p}_i and $d^3 r_i d^3 p_i$ are respectively the position, momentum and phase space measure of particle i and H is the hamiltonian of the system. The parameter ξ , initially introduced by Gibbs, has the dimension of an action so as to ensure that the partition function is dimensionless. Although it is often identified to the Planck constant h , it doesn't play any role in the thermodynamic properties derivable from Eq. (1) and, as a consequence, its actual value matters not here. In the case of a monoatomic ideal gas the partition function (1) reads:

$$Q_{IG}(N, V, \beta) = V^N \left(\frac{2\pi m}{\beta \xi^2} \right)^{3N/2} \quad (2)$$

from which one derives the corresponding free energy in the thermodynamic limit (where the Stirling approxima-

tion is being used):

$$\begin{aligned} \beta A_{IG}(N, V, \beta) &\equiv -\ln Q_{IG}(N, V, \beta) = -\frac{S_{IG}(N, V, \beta)}{k_B} \\ &= -N \ln V - \frac{3}{2} N \ln \frac{2\pi m k_B T}{\xi^2} \end{aligned} \quad (3)$$

From Eq. (3) one can find an *anomaly* in the paradigmatic case of the mixing of two ideal gases in the same conditions of pressure and temperature.

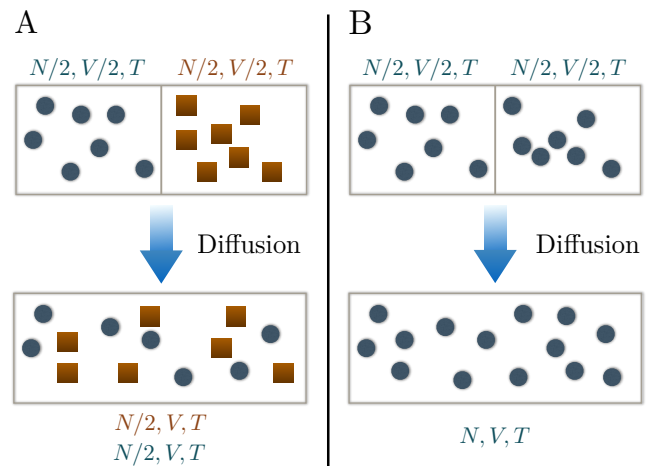


Figure 1. *Mixing of gases.* Schematic representation of the mixing by diffusion between two gases. Case A: mixing of two gases each made of different particle species. Case B: mixing of two gases made of the same particle species.

Indeed, as illustrated in Fig. 1, two cases can a priori be distinguished: either the gases to be mixed are *different* (case A in Fig. 1) or they are *identical* (case B in Fig. 1). In either case, one finds that, according to Eq.

(3), the entropy of mixing reads:

$$\begin{aligned}\Delta S_{IG} &= S_f - S_i = 2\frac{N}{2}k_B \ln \frac{V_{fin}}{V_{in}} \\ &= Nk_B \ln 2\end{aligned}\quad (4)$$

where the final volume V_{fin} of the box for each gas is double that of the initial volume V_{in} they were in $V_{fin} = 2V_{in}$. In case A, the result of Eq. (4) is consistent with the standard thermodynamics result one can obtain by considering the mixing process as a free expansion of either gas into a volume of double its initial size [19]. In case B, however, we see from Fig. 1B that there is no change in the thermodynamic state of the system upon mixing and, therefore, the corresponding entropy change should be zero. As it stands, Eq. (3) thus leads to some predictions at odds with the theory of thermodynamics. This is this particular inconsistency which is often referred to as *Gibbs' paradox of mixing*. More generally, the Gibbs paradox can also refer to the technical root cause of Gibbs' paradox of mixing; namely the fact that the free energy (and entropy) described by Eq. (3) are not *extensive* quantities contrary to their counterparts in thermodynamics. In fact, the failure of case B is easily seen to be attributable to the fact that, according to Eq. (3), $S_{IG}(N, V, \beta) \neq 2S_{IG}(N/2, V/2, \beta)$. The technical resolution of this problem is surprisingly very simple: one introduces a slightly different partition function $\tilde{Q}(N, V, \beta)$ that reads:

$$\tilde{Q}(N, V, \beta) \equiv \frac{1}{N!}Q(N, V, \beta) \quad (5)$$

and defines equivalently a free energy and entropy, which for an ideal gas give:

$$\begin{aligned}\beta\tilde{A}_{IG}(N, V, \beta) &\equiv -\ln \tilde{Q}_{IG}(N, V, \beta) = -\frac{\tilde{S}_{IG}(N, V, \beta)}{k_B} \\ &= -N \ln \frac{V}{N} - \frac{3}{2}N \ln \frac{2\pi mk_B T}{\xi^2}\end{aligned}\quad (6)$$

The mixing entropy between two gases as in Fig. 1 becomes then:

$$\Delta\tilde{S}_{IG} = Nk_B \ln \frac{\rho_{in}}{\rho_{fin}} \quad (7)$$

where ρ_{in} and ρ_{fin} are respectively the initial and final number densities of the gases undergoing the mixing process. In case A, $\rho_{in} = 2\rho_{fin}$ and Eq. (6) gives back an entropy of mixing of $k_B \ln 2$ per particle. In case B, the number density is unchanged between the final and initial states *i.e.* $\rho_{in} = \rho_{fin}$ and therefore Eq. (6) gives zero mixing entropy. Equivalently, one finds that $\tilde{S}_{IG}(N, V, \beta) = 2\tilde{S}_{IG}(N/2, V/2, \beta)$, illustrating that the Gibbs paradox has been dealt with.

That one must mathematically divide Eq. (1) by $N!$ to retrieve extensive thermodynamic potentials is mostly uncontroversial [30]. It is a different story when it comes to *justifying* why it must be done on *a priori* grounds.

By far, the most widely accepted account consists in interpreting Eq. (5) as the semi-classical limit of a full quantum partition function whereby the $N!$ is a signature of the fermionic or bosonic character of the identical particles comprising the system [1–20]. This rationale is often accompanied by specific claims with regards to the theoretical foundations of *classical* statistical thermodynamics. As a matter of fact, that one must divide Eq. (1) by $N!$ is then considered to be evidence:

- C1 That there is a failure of *classical thermodynamics* which must be supplemented by quantum reasoning to be fully consistent (see *e.g.* Ref. [7]).
- C2 That there is a failure of *classical mechanics*, as a theoretical framework, for which the notion of *indistinguishability* is ultimately foreign (see *e.g.* Refs. [2, 7, 12]).
- C3 That the quantum indistinguishable character of identical particles is necessary to account for the $1/N!$ factor and thus for the extensivity of classical thermodynamics potentials (see *e.g.* Refs. [11, 17–19]).

Again, the author wishes to stress that these claims are made with regards to the foundations of *classical* statistical thermodynamics and not *quantum* statistical thermodynamics. It is also worth noting that the necessity of the quantum indistinguishability to justify the $1/N!$ factor in Eq. (6) implies that:

- C4 In a system where no two particles are the same, one has no reason to divide Eq. (1) by $N!$ and the corresponding thermodynamic potentials cannot be extensive.

Of course C4 is inconsequential for systems of identical particles — and is therefore never stated explicitly — but it will be important for some of the arguments we wish to make in one of the upcoming sections.

There also exist a minority of textbook accounts of the $1/N!$ factor which do not necessitate the quantum indistinguishability argument [21–24, 26, 27] and which, instead, appeal to a classical or an *epistemic* rationale which resonates — intentionally or not — with Gibbs' original work on the topic.

It is the aim of this article to delineate in which sense — if at all — the Gibbs paradox, as explained above, is a problem for the *classical* foundation of *classical* statistical mechanics and if there are not other foundational problems for statistical mechanics which may have deserved more attention and which can be explained away if one adopts an epistemic interpretation of the $1/N!$ factor in Eq. (5).

The structure of the article is as follows: in section II, we will focus on Gibbs' insights on the so-called Gibbs' paradox based on two of its major publications on the thermodynamics and statistical mechanics of mixing,

namely his 1876 article *On the Equilibrium of heterogeneous substances* [31] and his 1902 book on the *Elementary principles in statistical mechanics* [29], and will refute the popular theses C1 and C2 that the classical physics of the time was not equipped with the conceptual tools to address the Gibbs' paradox. We will also stress a particular issue pointed out by Gibbs whose strangeness doesn't disappear with the quantum explanation. Section III will assess the claim C3, of the necessity of quantum indistinguishability to give a rational account of classical statistical mechanics, by looking at ideal continuous mixture systems. We will propose that either C3 is false or it is currently lacking a compelling explanation for the success of a well established branch of classical statistical mechanics; namely the physics of colloids. Section IV will introduce more formally the statistical mechanics of ideal discrete and continuous mixtures to address the problem of the entropy of mixing of two mixtures with different compositions. In so doing, we will find that, in general, the entropy of mixing is proportional to the square of a norm in the space of probability distributions. Section V will focus on the small-size system problem and propose a resolution based on the connection between thermodynamics and information. Finally, we will conclude and discuss the relevance for the foundation of statistical mechanics and teaching of the subject.

II. IN DEFENCE OF GIBBS

A. On the misuse of Gibbs' original canonical ensemble

Stigler's law of eponymy roughly states that *no scientific discovery is named after its original discoverer*. This section aims at determining whether this claim may hold as well in the context of Gibbs' paradox as it is recounted in most textbooks *i.e.* has Gibbs anything to do with the currently taught Gibbs' paradox which did not find any answer before the advent of quantum mechanics? Our answer to this specific question will be negative and for multiple reasons. To begin with, the statement of the paradox relies on the premise that one can apply — and that Gibbs applied carelessly — Eq. (1) in a context of mixing where potentially two identical substances could mix as well. Strangely enough, already in the *Preface* of his seminal book [29] Gibbs explains that he would not dare doing so. Instead he states that he dedicated Chapter 15 to *modifying* the canonical results of the prior chapters (including a priori Eq. (1) which appeared in Ch. 4), to account for the possibility of multiple species comprising identical particles:

Finally, in Chapter XV, we consider the modification of the preceding results which is necessary when we consider systems composed of a number of entirely similar particles of several kinds, all of which kind being entirely

similar to each other, and when one of the numbers of variations to be considered is that of the numbers of the particles of the various kinds which are contained in the system.

So we see unambiguously that, from the outset, Gibbs separates the statistical mechanics of systems with a non-varying amount of matter and that with protocols permitting a variation of the amount of matter. There are few reasons one can think of regarding why he would do so. Firstly, he explains in the remainder of the preface that he could have done differently but preferred separating the

purely thermodynamic laws from those special modifications which belong to the theory of the properties of matter

This passage can refer at least to two things: a) that the laws of thermodynamics were principally considered as those derived by Clausius, in which case changes in the amount of matter was not considered (see for example a discussion by Jaynes of this interpretation [32]) or b) that identifying the various kinds of matter comprising a substance requires chemical knowledge about the substance and in principle incredibly many experiments to assert with confidence that all the different species have been identified, which seems to go beyond purely thermodynamic considerations indeed.

Secondly, there is a reasonable technical reason why varying the number of particles should not necessarily be considered on the same footing as varying, say, the total energy in the system or the accessible volume. In fact, the mechanical foundation of thermodynamics sought out by Gibbs relies on Hamiltonian dynamics and Liouville's theorem. On the one hand, varying the volume accessible to the particles or the total energy simply affect the *location* and the *size* of the total phase space to be explored by the system while, on another hand, varying the number of particles changes the *dimension* of phase space and thus, should be treated with additional care.

So far, we have just shown that Gibbs was well aware of the distinction and extra care one must take when considering systems with varying number of particles and that he would not, a priori, carelessly apply Eq. (1) from his Chap. 4 of Ref. [29] to tackle such a problem. However, it could still be that the further modifications to be added in Chap. 15 of Ref. [29] are still insufficient and amount exactly to what we have derived in the introduction. We wish to claim otherwise in what follows.

B. Gibbs' concepts of Generic and Specific phases

Left with the doubts of the previous paragraph that Gibbs' Ch. 15 modifications to the canonical ensembles could be of a different *nature* than the nowadays commonly accepted resolution, it turns out that we need to

go no further than the second paragraph of Ch. 15 to see that he is on the right track, for he asks:

If two phases differ only in that certain entirely similar particles have changed places with one another, are they to be regarded as identical or different phases?

Here Gibbs queries whether microstates should *a priori* be considered the same or different, from a statistical perspective, when their corresponding phase-space points differ only in that two identical particles have swapped places. He then proposes that:

If the particles are regarded as indistinguishable, it seems in accordance with the spirit of the statistical method to regard the phases as identical.

We believe this reply by Gibbs to be important for multiple reasons. First, retrospectively it hints to the fact that the hyper-extensive behaviour of Eq. (4) arises from overcounting states by considering as different those states which only differ by the spatial permutation of identical particles and, second, Gibbs makes explicit use of the concept of *indistinguishability* of identical particles and how this ought to have an impact on state counting in a statistical reasoning. To the author, this is enough to undermine — and even invalidate — the claim C2 in the sense that, not only indistinguishability was known as a concept of classical statistical mechanics, but it was also used on a priori grounds to make sense of systems with varying number of particles. By no means do we imply that *quantum indistinguishability*, in the sense we think of it today in term of bosons and fermions, was known or even fathomed but the concept of indistinguishability necessary to give a consistent statistical account of systems with varying numbers of particles was, indeed, already present.

Gibbs goes even further and introduces accordingly two categories of microstates (*phases* in his text):

Our present purpose will often require us to use terms *phase*, *density in phase*, *statistical equilibrium* and other connected terms on the supposition that the phases are *not* altered by the exchange of places between similar particles... we shall call them ... generic phases. But we shall be obliged to discuss phases ... such that exchange of positions between similar particles is regarded as changing the phase ... which will be called ... specific phases.

That one may require to discuss specific phases in spite of wanting to focus on generic phases is justified on technical grounds by Gibbs for ‘the analytical description of a specific phase is more simple than that of a generic phase’.

Here Gibbs’ intention appears pretty clear: he aims at considering as relevant states what he calls generic phases

while conceding that for practical reasons he must also use specific phases. Later in the chapter, Gibbs will derive a general result which, applied to the case of a single component system (and translating in our notations) gives:

$$\ln Q_{generic}(N, V, \beta) = \ln Q_{specific}(N, V, \beta) - \ln N! \quad (8)$$

which is nothing but the logarithm of Eq.(5) since $Q_{specific}(N, V, \beta)$ is nothing but $Q(N, V, \beta)$ of Eq. (1).

Finally, in the last page of his book, Gibbs does mention the problem of mixing he is now famous for but not so much as an unsolvable puzzle. Rather he wishes to point out the absurdity that would have resulted had one wanted to work with specific phases instead of generic phases.

From this part we thus conclude that claim C2 — that classical mechanics (comprising statistical mechanics) was not equipped to address the problem of mixing of identical substances — is hardly tenable in light of Gibbs’ work as it is found in his seminal book [29]. One may debate whether his treatment is satisfactory *enough* but that is an entirely different matter.

C. Meaning of a zero entropy of mixing according to Gibbs

In modern texts on statistical mechanics the author is aware of, the concepts of generic and specific phases have not survived. The closest to those would be the distinction between distinguishable and indistinguishable identical particles; that is particles that are identical but *can* be distinguished (*e.g* because they are allegedly localised in space) or cannot be distinguished, *even in principle*. A notable difference between the modern concepts of distinguishable and indistinguishable on the one hand and specific and generic on the other hand is that they do not refer to the same thing. The former is a property of particles imagined individually while the latter is a property of states as they are understood in a statistical description of a substance. That point was already made, in a different fashion, in his 1876 paper where he discusses the classical thermodynamics (no statistical mechanics involved at all) of substances in great details [31]. First, among many other things, he derives on purely thermodynamic grounds that the entropy of a monoatomic substance, recast in this paper’s notation, reads (cf. Eq. (278) in Ref. [31]):

$$S = Nk_B \ln \frac{V}{N} + \frac{3}{2}Nk_B \ln T + NK \quad (9)$$

where K is a constant. From Eq. (9), Gibbs retrieves that for the mixing by diffusion of two different gases the entropy change is $k_B \ln 2$ per particle while for similar gases it is zero. In passing, this indicates that claim C1 — that classical thermodynamics would be in need

of quantum correction — is in fact unsubstantiated for at least Gibbs did not get any inconsistency from using “only” 19th century thermodynamics to the theory of the mixing of gases. Further, Gibbs reflects on what a zero entropy variation means in the case of identical substances [31]:

when we say that two gas-masses of the same kind are mixed under similar circumstances there is no change of energy or entropy, we do not mean that the gases that have been mixed can be separated without change to external bodies. On the contrary, the separation of the gases is entirely impossible ... because we do not recognise any difference in the substance of the two masses.

This passage outlines what we have called above the *epistemic* view. It means that, as far as entropy and its variations are concerned, in a statistical sense, what matters is whether the substances are the same or not and not necessarily whether the particles comprising the substances could be distinguished or not if one were to use, say, a sufficiently good magnifying glass. This is emphasised further in the fact that Gibbs refers to acting on ‘external bodies’ to trigger separation; which bears similarities with interpretations of thermodynamics as a *control theory* [33]. If such an action results in changing an ex-

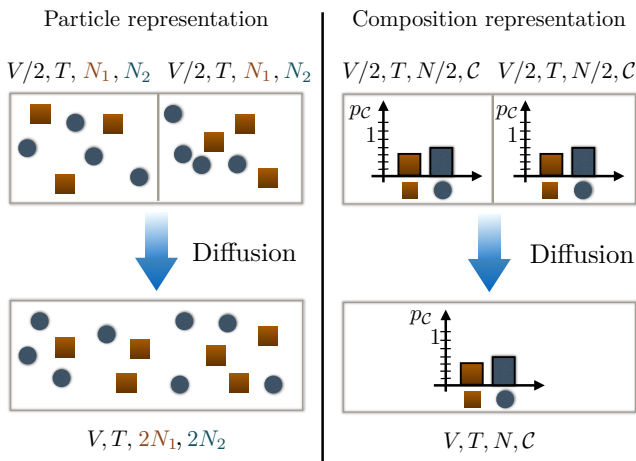


Figure 2. *Mixing of two identical binary mixtures.* Schematic representation of the mixing of two identical binary mixtures. Left panel: particle representation with 3 particles of type 1 and 4 particles of type 2 in each compartment. Right panel: composition representation with molecular fraction of $3/7$ for type 1 and $4/7$ for type 2. We note that the composition is unchanged upon mixing illustrating the fact that two substances can be identical while comprising multiple types of particles.

ternal potential influencing the particles comprising the substances and if the two substances react in the same way with regards to any such external influence (they are identical in their ‘qualities’), then there is no way to separate them indeed and nor is there any way to tell apart

— via such means — the initial state from the final one. The left panel of Fig. 2 illustrates this point by looking at the mixing of two identical binary mixtures. Of course, once the wall is removed there is no way to tell apart the initial from the final state; giving rise then to a zero entropy change.

D. Actual puzzles in Gibbs’ work

We have seen that Gibbs pondered carefully how Eq. (1) should *a priori* be modified in cases with varying numbers of particles and that the mixing problem with the anomaly resulting from using Eq. (1) was solely introduced as a *gedanken* experiment at the end of his book [29] to further convince the not-already-convinced reader of his Ch. 15. This is not to say that Gibbs was not puzzled by some aspects of the thermodynamics of substances. For example, in Ref. [29] he concedes that the rules of statistical mechanics he has laid out are not able to explain the isochoric molar specific heat capacity of polyatomic ideal gases (*e.g.* $5/2R$ instead of $3R$ for diatomic gases). As far as the author is aware, the most compelling explanation to this puzzle does come from quantum mechanics whose quantization of energy levels gives rise to a band gap between rotational and vibrational degrees of freedom whereby the latter are usually not thermally “activated” at room temperature.

Another curiosity, not explicitly presented as a puzzle *per se* — but that Gibbs felt worth mentioning in his article on heterogeneous substances — is the following property of the mixing entropy [31]:

the fact is not less significant that the increase of entropy due to the mixture of gases of different kinds ... is independent of the nature of the gases ... and of the degree of similarity between them.

In this passage, Gibbs points out that the mixing entropy will amount to $k_B \ln 2$ per particle however minute the difference between the substances may be and that it will be zero only when the substances are *exactly* identical.

Fig. 3 illustrates this sudden drop in mixing entropy as the “measure of difference” between two substances is decreased down to zero. That there is such an independence in the mixing entropy on the degree of similarity between the mixed substances in spite of similarities in their qualities is what some authors refer to as being the *actual* Gibbs’ paradox [24, 25]. We note that this discontinuity in the entropy of mixing as a function of the dissimilarity between substances is not affected at all by the quantum indistinguishability approach to the problem of mixing, in fact as we will see in the next section it is rather the opposite.

In this section we have shown that the claims C1 and C2 often accompanying discussions of Gibbs’ paradox and its standard resolution are not supported by the original material available in Refs. [29, 31]. We also showed

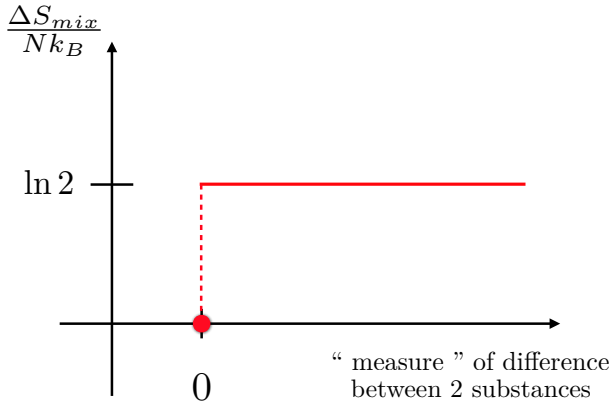


Figure 3. *Another Gibbs' paradox.* Graph illustrating the absence of dependence of the entropy of mixing in the nature and similarity of the two mixed substances except when the latter are exactly identical.

that Gibbs was not guilty of the logical mistake often attributed to him — even by its defenders [32] — of applying an equation where it was not valid. He also did not present the mixing of identical gases as a puzzle or a paradox but merely as a paradigmatic example to justify *a posteriori* some of his reflexions in the latest chapter of Ref. [29]. Finally, we have seen that, as long as the mixing entropy is concerned, Gibbs pointed out the strange feature that its value is independent of the degree of similarity between the substances. As far as the author is aware, this “curiosity”, considered paradoxical by some, has nevertheless failed to attract interest in the statistical mechanics community up to this day. We shall try to discuss some interpretation of it in the fourth section.

III. LIMITS OF THE QUANTUM INDISTINGUISHABILITY ARGUMENT

In the introduction we have briefly recalled that the most popular explanation for the $1/N!$ factor in Eq. (5) was that it was a relic of the quantum indistinguishability character of microscopic particles that can be classified as either fermions or bosons. As a matter of fact, the *Symmetrisation postulate* of quantum mechanics [34, 35] enables one to construct a *single relevant* quantum state from the linear combination of otherwise $N!$ different multiparticle quantum states for identical particles. In this respect, the factor $1/N!$ appears naturally indeed [28]. We also have briefly mentioned the epistemic approach in the introduction which we have delineated a bit more in the previous section focusing on some of Gibbs' writings. The point of this section is to discuss the claim C3 that quantum indistinguishability is *necessary* to rationally account for the $1/N!$ factor of Eq. (5) and thus, ruling out any possibility of a classical rationale.

A. Narrowing down the epistemic view

If we consider one of the (identical) binary mixtures of the left panel of Fig. 2 we see that it can be represented as a gas with fixed thermodynamic variables $(V/2, T, N_1, N_2)$ such that $N_1 + N_2 = N/2$ and with N_1 and N_2 the numbers of particles of species 1 and 2 respectively. Now, there is an alternative equivalent view to represent this thermodynamic state. One can introduce the ratios $p_1 \equiv 2N_1/N$ and $p_2 \equiv 2N_2/N$, such that $p_1 + p_2 = 1$ and characterise the *composition* \mathcal{C} of the substance by the pair of probabilities (p_1, p_2) . This enables us to express the state of the substance in terms of its total amount of matter and composition: $(V/2, T, N_1, N_2) \equiv (V/2, T, N/2, \mathcal{C})$. If we have in mind a mixing scenario *a la Gibbs* where densities and temperatures are kept fixed, then the *identity* of a substance to be mixed is fully characterised by its composition. The left panel of Fig. 2 can thus be reassessed as the mixing between binary substances with the same composition as depicted in the right panel of Fig. 2. Following Gibbs, the entropy of mixing of two identical substances (thus with same composition) is zero.

Let us now try to generalise these concepts a bit more. Consider a discrete attribute X of the constituents of a substance such that particles with different values of this attribute can be separated (more on this in the last section) by the external means at our disposal. A *mixture* with composition \mathcal{C} will be characterised by a probability distribution of values of X , $p_{\mathcal{C}}(X = x) = p_{\mathcal{C}}(x)$ (cf. left panel of Fig. 5). Akin to the binary mixture scenario, if one mixes two substances with the same composition, as characterised by their probability distribution $p_{\mathcal{C}}(x)$, in otherwise identical conditions, then following Gibbs' insight compels us to expect a zero mixing entropy for any discrete mixture. In more general terms, the epistemic view posits that the thermodynamic potentials of a mixture ought to be extensive if there is a well defined composition \mathcal{C} for the substance under consideration *i.e.* the concept of varying the amount of matter of a substance, all other things being equal, is well defined as long as there is a well defined notion of composition for the said substance.

B. Compatibility between the quantum and epistemic arguments

In the spirit of a re-reading of the Bohr-Einstein debate by Jaynes [36], we wish to argue that the quantum indistinguishability and the epistemic arguments need not be seen as either contradictory or even incompatible, for they do not talk about the same things. Since the epistemic view focuses first and foremost on the actual possibility of separating two substances via external means it is not prescriptive on how should one comprehend the microscopic details with regards to the specific identities of their constituents. Based on claim C4 and on the discus-

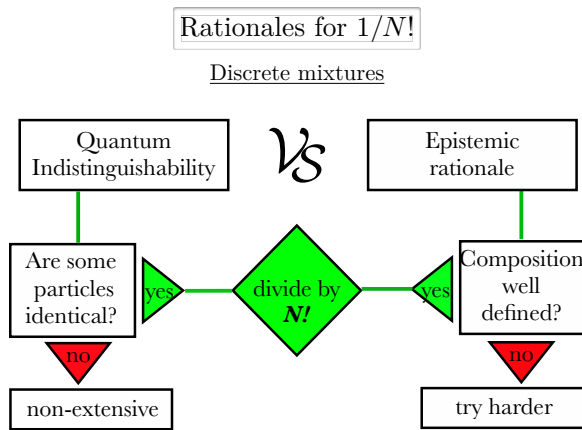


Figure 4. $N!$ rationales chart flow for discrete mixtures. Chart flow representation of the two viewpoints often opposed to justify the use of $1/N!$ in Eq. (5), namely the quantum indistinguishability viewpoint and the epistemic viewpoint. Propositions highlighted in green are “ True ” within the followed viewpoint and are propagated to further elements, if there are any. “ Truth ” propagation is represented by a green line in the diagram. Likewise, propositions highlighted in red are “ False ” within the followed viewpoint and do not propagate to further elements. We notice that in the case of discrete mixtures both viewpoints consider as “ True ” the proposition that one must divide Eq. (1) by $N!$.

sion of the previous paragraph, Fig. 4 gives a “ chart flow ” representation of how these two different arguments can be graphically viewed in their simplest versions. We see that the reasonings associated with each argument do not cross each other (and thus do not conflict) except possibly at the conclusion that one should divide Eq. (1) by $N!$. For single component and discrete mixture systems, Fig. 4 claims that the quantum and epistemic viewpoints are perfectly compatible with each other.

Incompatibility may arise, however, when an exclusivity claim is made, making then Fig. 4 invalid. For example the often made stronger claim C3 that the quantum rationale is the *only* viable justification on which to ground classical statistical mechanics seems to rely on a predefined notion of rationality which either imposes quantum mechanics from the outset or posits — via claims C1 or C2 — the inadequacy of classical mechanics (including statistical mechanics) to address the issue at hand. Based on the previous section, we argue that C1 and C2 are incorrect — or at least strongly arguable — assumptions to begin with and since we do not see on which ground should quantum mechanics be imposed as more rational than classical statistical arguments we will keep the view depicted by Fig. 4 which supports compatibility of the the quantum and epistemic arguments at the expense of undermining the exclusivity claim of C3. We will see in what follows that C3 may have more problems than its exclusivity claim being challenged.

C. Pushing the quantum and epistemic view to their limits

We now consider a mixture whose composition is characterised by an attribute X of the constituents that takes on real values.

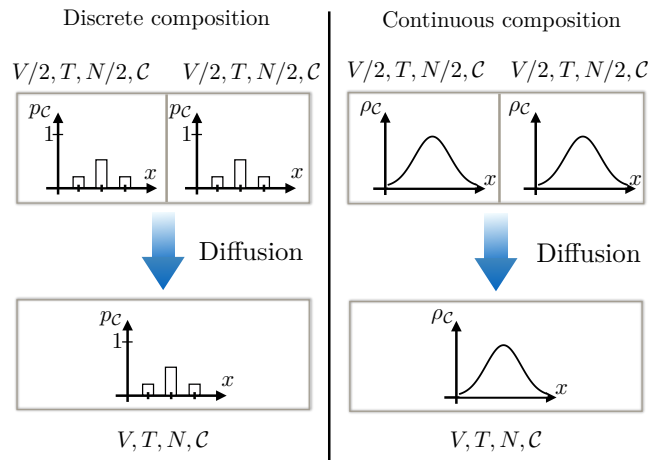


Figure 5. *Composition representation*. Schematic representation of the characterisation of a composition by the probability distribution of an attribute X of its constituents modelled as a random variable. Left panel: discrete mixture with a discrete probability distribution. Right panel: continuous mixture with a continuous probability distribution. Both panels illustrate that upon mixing two mixtures with the same composition, all other things being equal, the composition of the final mixture is unchanged.

Extending the considerations of the previous paragraphs to the continuous case, the composition of such a polydisperse system will then be represented by a probability density $\rho_C(x)$ as illustrated in the right panel of Fig. 5. The question is then to determine what happens to the entropy if one is to mix two polydisperse substances characterised by the same probability density $\rho_C(x)$. Here we make the “ leap of faith ” that, even in this case, if the substances are identical in composition, then there is no way to separate them — via any external means acting on the substances without altering their composition — and the mixing entropy should be zero; thus entailing that a factor $1/N!$ of some sort must be used in Eq. (1) to compensate the otherwise super-extensive growth of the phase space volume. On the contrary, the quantum indistinguishability argument reaches a different conclusion. As a matter of fact, continuous mixtures have the property that no two particles have *exactly* the same attribute value x , *even in the thermodynamic limit* [37], so they cannot be indistinguishable in the quantum sense.

Thus, following claim C4, the quantum indistinguishability argument can justify neither the extensivity of a continuous mixture nor the technical use of a $1/N!$ correction factor in the partition function. The situation for polydisperse substances is then summarised in Fig.

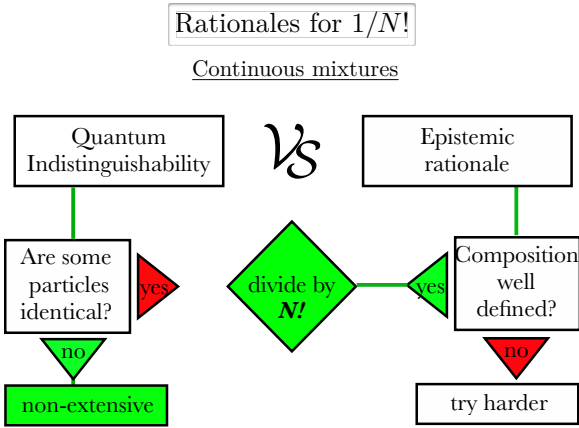


Figure 6. $N!$ rationales chart flow for continuous mixtures. Chart flow representation of the two viewpoints often opposed to justify the use of $1/N!$ in Eq. (5), namely the quantum indistinguishability viewpoint and the epistemic viewpoint. Propositions highlighted in green are “True” within the followed viewpoint and are propagated to further elements, if there are any. “Truth” propagation is represented by a green line in the diagram. Likewise, propositions highlighted in red are “False” within the followed viewpoint and do not propagate to further elements. We notice that the quantum and epistemic viewpoints disagree on the “Truth” character of the proposition that one must divide Eq. (1) by $N!$.

6 where we see that the quantum and epistemic views reach opposite conclusions with regards to the extensivity of the thermodynamic potentials of such substances. Of course, the next question is to know *which view is supported by evidence*.

To answer this question we shall appeal to the statistical mechanics of colloids which has been a very successful branch of statistical mechanics for about a century, predicting and verifying for example the existence of entropy driven ordering in systems with hard core repulsion [38, 39]. Colloidal particles are mesoscopic objects whose state of motion is sensitive to thermal fluctuations and the thermodynamics of simple colloidal substances appears well understood within the framework of a classical statistical mechanics derived from Eq. (5). Yet colloidal particles are polydisperse in many of their features *e.g.* mass and size to name two obvious such features. As a result, the success of a statistical mechanics of colloids based on Eq. (5) appears as a challenge to the quantum indistinguishability viewpoint. On the contrary, recent studies have pointed out that the foundations of the physics of polydisperse systems in general and colloids in particular was unproblematic if one adopts the epistemic viewpoint [40–42]. Finally, a recent experimental study on colloids further supports the epistemic view as underpinning the success of classical statistical mechanics at the expense of the quantum view [43]. We believe this is enough evidence to either reject or strongly undermine

claim C3, in that, as it currently stands, the quantum argument on which it relies cannot explain the success of the physics of colloids and would need to be amended to do so. Note that even if an amended version of the quantum argument were to be made, it would probably not undermine the epistemic view and we would be back to a peaceful coexistence between the quantum and epistemic arguments as depicted in Fig. 4.

In this section we have reduced the epistemic view to knowing whether two substances were characterised by the same composition probability distributions. We have argued that the quantum indistinguishability and epistemic arguments were perfectly compatible for discrete mixtures. They only seem to disagree if an exclusivity claim is made from either side (like claim C3 in favour of the quantum argument) or in the case of polydisperse systems. Since C3 is the current dominant view, we have emphasised that its exclusivity claim for discrete mixtures is unwarranted and that, even when presupposing quantum mechanics as more rational, C3 should either be rejected or seriously amended based on the success of the statistical mechanics of colloids.

IV. A POSSIBLE ANSWER TO THE “REAL” GIBBS’ PARADOX

In section II we have pointed out the curiosity that the entropy of mixing of two different substances was independent of how close in their ‘qualities’ they appeared to be (cf. Fig. 3). In this section we wish to interpret the mixing of two substances, in otherwise equal circumstances, in the broadest possible sense *i.e.* as being the mixing of two *a priori* polydisperse substances 1 and 2 with respective compositions \mathcal{C}_1 and \mathcal{C}_2 (cf. Fig. 7).

Like Gibbs’ discussion in Ref. [31], we shall focus on the change in entropy due to the mixing by diffusion of two polydisperse (ideal) gases. To derive it we shall first look at the entropy of an ideal discrete mixture — for which the quantum and epistemic views agree — which we will use as a basis to derive a more general result for continuous mixtures.

A. Entropy of an ideal discrete mixture

For ideal gases, Eq. (5) can readily be generalised to discrete mixtures comprising n different species each with N_i identical particles of mass m_i :

$$Q_{generic}(N, V, T, \mathcal{C}) = \prod_{i=1}^n \frac{1}{N_i!} \left(\frac{V}{(\xi/\sqrt{2\pi m_i k_B T})^3} \right)^{N_i} \quad (10)$$

where we have kept Gibbs’ terminology of generic phase to specify how states are to be interpreted in this equation. In the thermodynamic limit, the corresponding en-

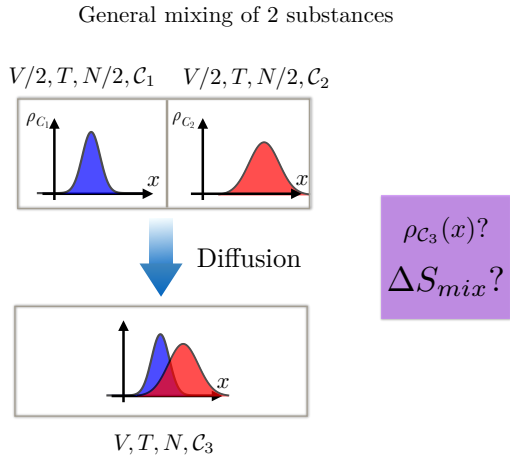


Figure 7. *Mixing of two polydisperse gases.* Composition representation of the mixing of two continuous mixtures 1 and 2 of composition \mathcal{C}_1 and \mathcal{C}_2 respectively. At this stage, one may want to determine the entropy of mixing of such substances as well as the final composition. This may shed some light on the initial paradox of similarity independence of the entropy of mixing pointed out by Gibbs in Ref. [31].

entropy reads in the :

$$\begin{aligned}
 S_{generic}(N, V, T, \mathcal{C}) \simeq & Nk_B \left(\ln V + \frac{3}{2} \ln T + \tilde{K} \right) \\
 & + k_B \sum_{i=1}^n N_i \ln m_i^{3/2} \\
 & - k_B \sum_{i=1}^n (N_i \ln N_i - N_i) \quad (11)
 \end{aligned}$$

Where \tilde{K} is a constant. Eq. (11) contains explicitly the total number of particles in the substance N but also the number of particle of each species N_i . In line with the discussion of section III, we shall recast it solely in term of N and the composition \mathcal{C} . To this end, we introduce the probability distribution $p_{\mathcal{C}(i)}$ such that a) $N_i \equiv N p_{\mathcal{C}(i)}$ and b) the now defined composition ensures that varying the system size can be done in well controlled manner. Eq. (11) reads then:

$$\begin{aligned}
 S_{generic}(N, V, T, \mathcal{C}) \simeq & Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \tilde{K} + 1 \right) \\
 & + k_B N \langle \ln m_i^{3/2} \rangle_{\mathcal{C}} \\
 & + N s(\mathcal{C}) \quad (12)
 \end{aligned}$$

where $\langle \ln m_i^{3/2} \rangle_{\mathcal{C}} \equiv \sum_{i=1}^n p_{\mathcal{C}(i)} \ln m_i^{3/2}$ and where we have introduced the *composition entropy* [44]:

$$s(\mathcal{C}) \equiv -k_B \sum_{i=1}^n p_{\mathcal{C}(i)} \ln p_{\mathcal{C}(i)} \quad (13)$$

Note that Eq. (13) is often referred to as the *mixing entropy*. However, to avoid ambiguous terminology we

refrain from referring to it in this way, for we consider that a mixing entropy ought to be the *variation* of entropy of a system as two or multiple substances initially separated have mixed by diffusion.

Eq. (12) is insightful in many regards. First it separates contributions to the generic entropy owing to composition from those related to the substance as a whole. Second, related to the first remark, it appears that as long as the composition is kept fixed the terms on the second and third lines of Eq. (12) are constant too and can be absorbed in \tilde{K} such that one may define $K = k_B(\tilde{K} + 1 + \langle \ln m_i^{3/2} \rangle_{\mathcal{C}}) + s(\mathcal{C})$ such that, *at fixed composition*, Eq. (12) reduces to Eq. (9) obtained by Gibbs in Ref. [31]. So, provided its composition remains unchanged, the thermodynamic behaviour of a mixture of ideal gases is equivalent to that of a single component ideal gas. With regards to the discussion on the $1/N!$ factor in Eq. (5), this implies that its justification need not rely on an exact identity relation amongst the particles comprising the system. It seems that it is *enough* [44] that the composition be well defined, as the epistemic view suggests in Fig. 4 for example. That a mixture can be conceptualised as a single component system is not really surprising. After all, one of the first practice questions a first year undergraduate student might be asked in a thermodynamics course would be to determine the number of moles of *air* given volume, temperature and pressure conditions; as if air was a single species. Of course, this was already emphasised by Gibbs in his 1876 paper, for example p. 214 [31]:

[Eq. (9)] applies to all gases of *constant composition* for which the matter is entirely determined by a single variable $[N]$.

We shall now try to see how this translates for continuous mixtures.

B. Entropy of an ideal continuous mixture

Continuous mixtures are characterised by an attribute X of the particles that is a continuous random variable. As such, the corresponding probabilities suffer from the same difficulties as those of continuous probability theory and must be “fixed” in the same way:

- The probability to have a particle with $X = x$ is exactly zero.
- One must lump a range of values together in an interval $[x, x + \Delta x]$ so as to define:

$$p_{\mathcal{C}}(X \in [x, x + \Delta x]) = \rho_{\mathcal{C}}^{\Delta}(x) \Delta x \quad (14)$$

where Δx can be interpreted as setting the “grain-ing” of the domain of integration of X and $\rho_{\mathcal{C}}^{\Delta}$ is the corresponding *coarse grained* probability density [45].

- One may define an *effective species*, associated to the equivalence class $z \sim y$ iff ($z \in [x, x + \Delta x]$ and $y \in [x, x + \Delta x]$), with population number:

$$N_x^\Delta \equiv N \rho_C^\Delta(x) \Delta x \quad (15)$$

inducing an *effective discrete composition* \mathcal{C}^Δ for a covering set of finite Δx .

From Eq. (15), the same reasoning as that of the previous section can be carried out to give an entropy $S_{generic}(N, V, T, \mathcal{C}^\Delta)$. One may then define [41] the entropy of the system as being the limit [46]:

$$S_{generic}(N, V, T, \mathcal{C}) = \lim_{\Delta x \rightarrow 0} S(N, V, T, \mathcal{C}^\Delta) \quad (16)$$

which gives:

$$\begin{aligned} S_{generic}(N, VT, \mathcal{C}) &\simeq N k_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \tilde{K} + 1 \right) \\ &\quad + k_B N \langle \ln m(x)^{3/2} \rangle_{\mathcal{C}} \\ &\quad + N s_\Lambda(\mathcal{C}) \end{aligned} \quad (17)$$

where $\langle \ln m(x)^{3/2} \rangle_{\mathcal{C}} \equiv \int dx \rho_{\mathcal{C}}(x) \ln m(x)^{3/2}$ and where we have introduced the *continuous composition entropy*:

$$s_\Lambda(\mathcal{C}) \equiv -k_B \int dx \rho_{\mathcal{C}}(x) \ln(\Lambda(x) \rho_{\mathcal{C}}(x)) \quad (18)$$

which is nothing but the continuous *Shannon entropy* associated to the probability density $\rho_{\mathcal{C}}(x)$ where $\Lambda(x)$ is a function appearing when taking the limit of Δx towards zero.

Two remarks are now in order.

First, as before, at fixed composition (and graining function) Eq. (18) can reduce to Eq. (9) provided one introduces $K = k_B(\tilde{K} + 1 + \langle \ln m(x)^{3/2} \rangle_{\mathcal{C}}) + s_\Lambda(\mathcal{C})$. This means that, provided the conclusions we may draw from the mathematical treatment we have presented are to be trusted, even a polydisperse gas can be interpreted as a single component gas which, when extrapolated to the more general Eq. (5) supports the idea that an exact detailed knowledge of the identity of the particles is unnecessary to justify the factor $1/N!$. It seems sufficient to *know* that the composition is kept constant to justify this factor regardless of what that composition may be. Since such a knowledge is a prerequisite to talk about a substance at all (one may not know how to talk about a substance whose composition changes all the time) this further brings a mathematical foundation to the epistemic view from the more well defined statistical mechanics of discrete mixtures.

Second, the use of the continuous Shannon entropy $s_\Lambda(\mathcal{C})$ in Eq. (17) is not without technical and conceptual issues. As a matter of fact, contrary to the standard Shannon entropy, it is easy to see that the continuous Shannon entropy is not positive definite and its form is not invariant under a change of variable. Furthermore, it is not clear what should the function $\Lambda(x)$ be *a priori* and how

it should be interpreted. This is sometimes referred to as the *measure problem* [47]. In spite of these issues, we have just seen in the previous paragraph that, as long as the composition is fixed, the value of $s_\Lambda(\mathcal{C})$ is inconsequential for the thermodynamics of the system as it can be absorbed into a constant term in the ideal part of the entropy (and as a corollary that of the chemical potential too) of the substance. So, issues may not arise for the thermodynamic properties of substances at fixed composition. However, in a mixing scenario the composition does change and it is worth seeing what is the role played by the composition entropies.

In the last two parts we have derived conclusions based on Eq. (5) which corroborate a general remark made by Gibbs that Eq. (6) applies to all gases of constant composition for which in actuality the matter is entirely determined by the single variable N .

C. Mixing between two polydisperse gases

We now consider the mixing of two polydisperse gases 1 and 2 both with a polydispersity in the property X of the particles. The gases are initially separated and with the same pressure and temperature. The initial state of the system has the entropy $S_i = S_{generic}(N/2, V/2, T, \mathcal{C}_1) + S_{generic}(N/2, V/2, T, \mathcal{C}_2)$. In order to apply Eq. (17) to the final state once the gases are mixed, we need to determine the new composition \mathcal{C}_3 of the mixture resulting from the diffusion of gases 1 and 2 in all the accessible volume. In absence of chemical reaction, conservation of the number of particles in each species x gives $\rho_{\mathcal{C}_3}(x) = (\rho_{\mathcal{C}_1}(x) + \rho_{\mathcal{C}_2}(x))/2$. The entropy of the final state then reads $S_f = S_{generic}(N, V, T, \mathcal{C}_3)$. The mixing entropy $\Delta S_{mix} \equiv S_f - S_i$ is found to depend solely on N and the composition entropies and takes on a very simple form [44]:

$$\begin{aligned} \Delta S_{mix} &= \frac{N}{2} (2s_\Lambda(\mathcal{C}_3) - s_\Lambda(\mathcal{C}_1) - s_\Lambda(\mathcal{C}_2)) \\ &= N k_B D_{JS}(\mathcal{C}_1 || \mathcal{C}_2) \end{aligned} \quad (19)$$

Where $D_{JS}(\mathcal{C}_1 || \mathcal{C}_2)$ is the *Jensen-Shannon (JS) divergence* defined by:

$$D_{JS}(\mathcal{C}_1 || \mathcal{C}_2) \equiv \frac{1}{2} \int dx \left(\rho_{\mathcal{C}_1} \ln \frac{2\rho_{\mathcal{C}_1}}{\rho_{\mathcal{C}_1} + \rho_{\mathcal{C}_2}} + \rho_{\mathcal{C}_2} \ln \frac{2\rho_{\mathcal{C}_2}}{\rho_{\mathcal{C}_1} + \rho_{\mathcal{C}_2}} \right) \quad (20)$$

At this stage, multiple comments are in order:

- In spite of the dependence of the composition entropies $s_\Lambda(\mathcal{C}_1)$, $s_\Lambda(\mathcal{C}_2)$ and $s_\Lambda(\mathcal{C}_3)$ in the graining function $\Lambda(x)$, the final result for the mixing entropy in Eq. (19) is *independent* of it.
- The JS divergence expressed in Eq. (20) has a form invariant under a change of variable. This is easily seen since the argument of the logarithm is the ratio between two probability densities, so the Jacobians

corresponding to a change of variable would cancel out.

- The JS divergence is *positive definite, symmetric* under the exchange of the probability densities and its square root satisfies the *triangular inequality*; it is the square of a *norm in probability space* [48].
- As the square of a norm it has the unusual feature of being bounded from above by $\ln 2$.

It is now possible to interpret Eq. (19): the entropy of mixing per particle between any two substances is equal (up to a factor k_B) to the square distance between the probability densities characterising the substances' composition and it saturates at the value $\ln 2$ when the substances are very dissimilar, thus retrieving Eq. (4). Furthermore, Eq. (19) supports Gibbs' original insight discussed in section II that when mixing two substances what matters is whether the substances (and not the particles comprising the substances) are identical or not. However, the picture emerging from eq. (19) *adds* to Gibbs' account in that the mixing entropy is now quantitatively expressible in term of a distance squared between the substances.

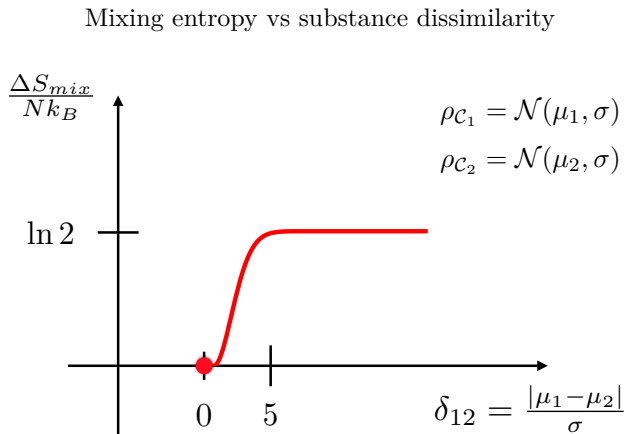


Figure 8. *A solution to the “real” Gibbs’ paradox.* Plot of the dimensionless mixing entropy per particle as a function of the dissimilarity δ_{12} between two polydisperse substances with compositions \mathcal{C}_1 and \mathcal{C}_2 both normally distributed with the same standard deviation but with different means μ_1 and μ_2 respectively. Contrary to Fig. 3 illustrating an expected sharp drop from $\ln 2$ to zero as two substances become strictly identical, we observe here that $\Delta S_{mix}/Nk_B$ goes continuously to zero as the substances become more and more similar *i.e.* as the overlap between their probability distributions increases.

In particular, the mixing entropy has plenty of room to assume any value between zero and $\ln 2$ as the substances become more and more similar. In Fig. 8 we illustrate this point by looking at two compositions \mathcal{C}_1 and \mathcal{C}_2 characterised by the densities $\rho_{\mathcal{C}_1} = \mathcal{N}(\mu_1, \sigma)$ and $\rho_{\mathcal{C}_2} = \mathcal{N}(\mu_2, \sigma)$ respectively and where $\mathcal{N}(\mu, \sigma)$ is

a normal distribution of mean μ and standard deviation σ . Since the two distributions have the same standard deviation, the quantity $\delta_{12} = |\mu_1 - \mu_2|/\sigma$ can serve as an intuitive measure of the distance between \mathcal{C}_1 and \mathcal{C}_2 with the advantage that it goes to infinity thus corresponding to a situation analogous to the schematic plot of Fig. 3. From Fig. 8 we see that for large values of δ_{12} and for $\delta_{12} = 0$ the quantity $\Delta S_{mix}/Nk_B$ agrees with Gibbs. However, the value of $\Delta S_{mix}/Nk_B$ obtained from Eq. (19) varies continuously to zero as δ_{12} is approaching zero too, thus removing the “curiosity” pointed out by Gibbs in his 1876 paper. As a side comment, we note that $D_{JS}(\mathcal{C}_1||\mathcal{C}_2)$ also informs on how two probability densities can be told apart and that is when the value of the JS divergence gets very close to $\ln 2$. In the particular case of Fig. 8 we see that it happens when $|\mu_1 - \mu_2|$ is around the now quite popular 5σ value.

In this section, we have derived statistical mechanics results based on a straightforward generalisation of Eq. (5) to discrete mixtures. We have shown that, as long as the composition is kept constant, an ideal gas mixture — be it discrete or continuous — will be equivalent to a single component ideal gas, as pointed out by Gibbs in his work on heterogeneous substances [31]. Extrapolated to non-ideal substances this result means that the combinatorial term of any mixture can be replaced by a $1/N!$ for all practical purposes, as long as the composition is unchanged. Of course, interacting systems may undergo phase transitions *in composition* in which case the composition-dependent term played by the composition entropy will play a crucial role [44, 49]. Another case whereby composition is expected to change is upon the mixing of two mixtures. We have shown that in the most general case the mixing entropy was proportional to a squared distance in the space of probability distributions. Finally, upon interpreting the mixing of substances *a la Gibbs* as the mixing of two polydisperse systems, we find that the strange fact that the mixing entropy did not seem to depend on the degree of similarity between the substances — the “real” Gibbs’ paradox — readily disappears and instead varies continuously for $\ln 2$ to zero as the degree of dissimilarity goes to zero.

V. SMALL SYSTEMS AND LINK WITH THE LANDAUER BOUND

A possible objection that can be raised against the epistemic approach presented so far is that it appears to rely on the assumption that each realisation of a composition will be a faithful representation of the underlying distribution it is sampled from. Although this assumption might hold true in the thermodynamic limit [49], for finite size systems the actual composition may be quite different from the underlying distribution; thus impacting the entropy of mixing. For example, one may argue that upon considering the mixing of two polydisperse systems with one particle each, surely in many occasions the

entropy of mixing will be different from zero even if the polydispersities are the same! In fact, it is not clear that it should be so. In the spirit of Gibbs' insight from Ref. [31], it would indeed depend on the external means being used to separate the substances back to their original state. If these means are the same for very small samples and large ones, then some similarities between the two mixing entropies may be observed. This section is aimed at investigating these similarities and differences between very very small and large systems, as it were, provided the external means being used to separate the substances are assumed to be the same; otherwise we may comparing apples and oranges.

A. Demixing of a single particle system

As far as equilibrium states are concerned, the entropy change upon mixing two substances is equal to the opposite of the entropy change upon demixing them. Because the protocol that may be used to separate the substances back to their original state plays an important role in the epistemic view, we shall here look at the demixing entropy of a single particle system. One may — rightly — wonder how is demixing envisioned at all when only a single particle is involved. We argue that this extreme system does make sense in the context of an infinite number of trials.

To see this we consider a separation protocol \mathcal{P} (e.g. dragging a filter across the system or turning on an external field) which has the following random outcomes when applied on any particle with feature X and sampled from composition \mathcal{C}_3 (given by $\rho_{\mathcal{C}_3}(x) = (\rho_{\mathcal{C}_1} + \rho_{\mathcal{C}_2})/2$):

$$\rho(x|left) = \rho_{\mathcal{C}_1} \quad (21)$$

$$\rho(x|right) = \rho_{\mathcal{C}_2} \quad (22)$$

where $\rho(x|left)$ and $\rho(x|right)$ are the conditional probability densities for finding a particle with feature $X \in [x, x + dx]$ knowing that it is on the left and right of the box respectively. Now, the composition — as characterised by a probability density — associated to the left hand side or the right hand side of the box becomes a *feature* of the *separation protocol*. Again, this is a formal way to express Gibbs' emphasis on the external means used to separate two substances discussed in section II. Now, considering a particle with attribute $X \in [x, x + dx]$ freely moving in a box, the rate of success for the separation protocol to bring it, say, to the left hand side of the box [50] reads:

$$r(x) = \frac{\rho_{\mathcal{C}_1}}{\rho_{\mathcal{C}_1} + \rho_{\mathcal{C}_2}} \quad (23)$$

Of course, it follows from Eq. (23) that the rate of failure for bringing the particle to the left hand side of the box, or equivalently the rate of success for bringing it to the right hand side, is $1 - r(x)$.

Now that we have shown how one could envision the demixing of system with composition \mathcal{C}_3 into two compositions \mathcal{C}_1 and \mathcal{C}_2 by consider solely single particle systems, we shall see in the next section how one may relate it to an apparently very different system, namely the 1-bit of memory.

B. Link with a 1-bit memory system

A 1-bit memory system is a system which can assume two well-defined states. Although it does not necessarily strike one as obvious, a system comprising a single particle in a box is actually one of those systems that can easily be mapped onto a 1-bit memory system. It is known since at least Szilar's recasting of Maxwell's demon problem but, instead of making heat flow from cold to hot without doing work, is meant to extract work from a gas at equilibrium by acquiring information about the position of its constituents [51]. The strategy to perform

Mapping from 1-particle system to 1-bit memory

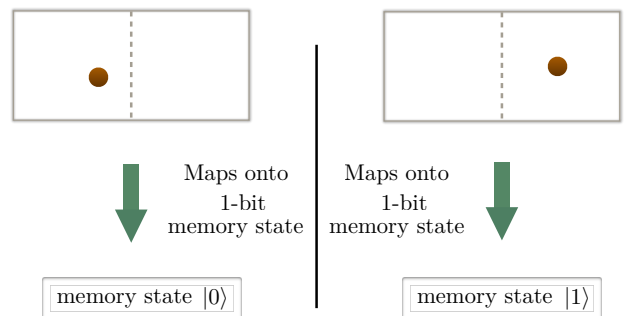


Figure 9. *Mapping a 1-particle system onto a 1-bit memory system.* Schematic representation on how a single particle in a box can be mapped onto a 1-bit memory state depending on where it is located with respect to a virtual dividing surface splitting the box in two equal parts. The bit memory states are denoted $|0\rangle$ and $|1\rangle$ depending on whether the particle in the left hand side of the box or the right hand side respectively.

the mapping is illustrated in Fig. 9 and amounts to splitting the box in two equal parts and define the equivalence class of states where the particle is on the left hand side of the box as the memory state $|0\rangle$ and define the equivalence class of states where the particle is on the right hand side of the box as the memory state $|1\rangle$.

We shall now try to see how this mapping can be of any use in trying to estimate the mixing entropy for such a system.

C. Making use of Landauer's principle

In 1961 R. Landauer proposed a connection between thermodynamics and computation by positing that resetting a 1-bit memory from a thermal state could not be done without dissipating heat and thus without any associated increase of entropy [52]. More specifically he postulated that the minimum amount of energy to be dissipated to reset one bit to state $|0\rangle$ for example, was:

$$E_{diss} = k_B T \ln 2 \quad (24)$$

so as to balance at least the entropy change associated to the state of the bit. Although it can be verified in a wide variety of models in statistical mechanics and can appear to some as somewhat tautological or trivial, Landauer's principle remains a *principle* in that its statement is independent of the specific physical model being used to emulate a 1-bit memory system [53]. A recent experiment testing of Landauer's principle has reported that, in practice, Landauer's principle could be violated by having 1-bit memory systems being reseted by dissipating less than $k_B T \ln 2$ on average [54]. They noted, however, that the violation is only apparent, for the resetting protocol onto a dedicated memory state is not always successful in their experiments. In this view, given a rate of success r for one of the outcomes of the resetting operation they proposed a generalised Landauer bound which reads:

$$E_{diss;r} = k_B T \ln 2 + k_B T (r \ln r + (1-r) \ln(1-r)) \quad (25)$$

where the first term in the right hand side of Eq. (25) is nothing but the standard Landauer bound of eq. (24) and the second (negative) term is proportional to minus the Shannon entropy of the resetting protocol onto a target memory state. It follows that if the protocol is fully certain to succeed *i.e.* $r = 1$ or $r = 0$, then one retrieves Landauer's principle while if it is maximally uncertain to succeed *i.e.* $r = 1/2$, then there is no information difference between the initial state of the bit and the final one and the dissipated energy is zero.

One way to interpret Eq. (25) is to realise that as soon as the resetting onto a specific state of the memory bit (say state $|0\rangle$) is not certain then the bit can be reseted by either finishing in state $|0\rangle$ or in state $|1\rangle$; in either case the prior state of the memory has been lost. So for each instance of a resetting operation one has:

- End state is $|0\rangle$ and $E_{diss}(|0\rangle) = k_B T \ln 2 + k_B T \ln r$, where $k_B T \ln r$ can be interpreted as the dissipated energy being saved by compromising on the degree of certainty of the outcome [19].
- End state is $|1\rangle$ and $E_{diss}(|1\rangle) = k_B T \ln 2 + k_B T \ln(1-r)$, where $k_B T \ln(1-r)$ can likewise be interpreted as the dissipated energy being saved by compromising on the degree of certainty of the outcome [19].

Overall, the expectation of the energy dissipated by the resetting protocol is $rE_{diss}(|0\rangle) + (1-r)E_{diss}(|1\rangle)$ which gives Eq. (25).

Since we have mapped our demixing problem onto a memory resetting problem, we can determine the energy dissipated by applying the separation protocol \mathcal{P} to a single equilibrated particle in a box with attribute $X \in [x, x + dx]$ by applying Eq. (25) and replacing r with $r(x)$.

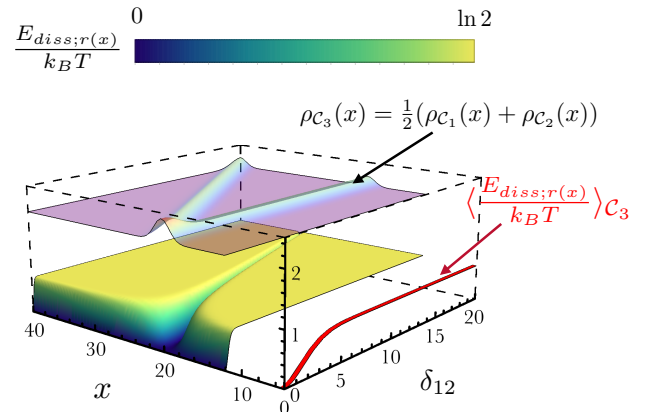


Figure 10. *Dissipated energy conditioned on particle type.* Plot of the dissipated energy surface as a function particle type and a measure of how dissimilar are the compositions \mathcal{C}_1 and \mathcal{C}_2 . The semi-transparent surface above the energy surface represents the distribution $\rho_{\mathcal{C}_3}$ which is used to compute the weighted average of $E_{diss;r(x)}/k_B T$ over the values of x to get the curve of $\langle E_{diss;r(x)}/k_B T \rangle_{\mathcal{C}_3}$ coinciding with that of $\Delta S_{mix}/Nk_B$ in Fig. 7.

In Fig. 10 we plot the dimensionless energy to be dissipated by the protocol \mathcal{P} , $E_{diss;r(x)}/k_B T$ as a function of x and $\delta_{12} = |\mu_1 - \mu_2|/\sigma$ for the distributions $\rho_{\mathcal{C}_1} = \mathcal{N}(\mu_1, \sigma)$ and $\rho_{\mathcal{C}_2} = \mathcal{N}(\mu_2, \sigma)$ as in section III. For a given value of δ_{12} , we see that the dissipated energy depends on the particle type x and is often different from the JS divergence. In particular, there is always a value x^* , at which $\rho_{\mathcal{C}_1}$ and $\rho_{\mathcal{C}_2}$ intersect, for which the energy dissipated is zero. Likewise, there is a large set of values of x in the tails of the distributions giving rise to $E_{diss;r(x)}/k_B T = \ln 2$ corresponding to the expectation that small systems must somehow be more certain to be separated. This intuition is certainly correct but limited by the *resolution* of the separation protocol \mathcal{P} precisely given by δ_{12} . One may argue that, in this case, the resolution can always be sharpened to increase certainty but, we believe, that would be missing the point because the protocol \mathcal{P} is precisely expected to reconstruct compositions \mathcal{C}_1 and \mathcal{C}_2 if we repeat the separation experiment sufficiently many times on particles sampled from a parent composition \mathcal{C}_3 . Were we to use a sharper protocol to discriminate more accurately two values of x , this *reconstruction criterion* — which is the whole point of the present discussion —

would not be met. In fact, the average work per particle to reconstruct the compositions \mathcal{C}_1 and \mathcal{C}_2 on either side of the box (from sampling individual particles from \mathcal{C}_3 and apply \mathcal{P}) corresponds to a weighted average over the variable x of $E_{diss;r(x)}$ with weight $\rho_{\mathcal{C}_3}$ giving then [44]:

$$\langle E_{diss;r(x)} \rangle_{\mathcal{C}_3} = k_B T D_{JS}(\mathcal{C}_1 || \mathcal{C}_2) \quad (26)$$

whose corresponding curve as a function of δ_{12} is illustrated (in red) as projected onto the plane $(E_{diss;r(x)}/k_B T, \delta_{12})$ in Fig. 10. We notice that, provided $\Delta S_{mix}/N$ is interpreted as $\langle E_{diss;r(x)} \rangle_{\mathcal{C}_3}/T$, it is identical to the solution of the “real” Gibbs’ paradox we have proposed at the end of section IV in Fig. 8.

In this section we have looked at systems made of a single particle in a box and defined a demixing protocol to address the small system size objection. By using a mapping between the demixing protocol and the resetting of a 1-bit memory we have made use of a generalised Landauer’s principle applicable to cases where the resetting protocol on one target memory state is not always successful. Using this generalised principle, we have derived that indeed depending on the specific identity the various particle types x may contribute very differently to the energy to be dissipated to reconstruct compositions \mathcal{C}_1 and \mathcal{C}_2 on either side of the box. This can be a first step to address the possibility of mixing experiments in the case where the starting sample is an unlikely realisation of the parent composition. However, in a context where both the sampling from a parent composition and the separation protocol are repeated greatly many times, then the inferred energy to be dissipated per particle is directly proportional to the JS divergence as found in section IV.

VI. CONCLUSION AND DISCUSSION

In this paper, we have challenged the standard narrative of Gibbs’ paradox which is claimed to undermine a classical foundation to classical statistical mechanics and require a quantum foundation instead.

In section II we showed that the puzzle commonly referred to as Gibbs’ paradox did not originate from Gibbs’ writing [29, 31] since he did not reach the theoretical inconsistency discussed in section I. Instead we found that already then he proposed essentially the same justification for the use of Eq. (5) as is done nowadays in most textbooks [1–20]; the twist being that he uses classical rationales for that; namely classical indistinguishability of particles and statistical reasoning both articulated around what we called the epistemic viewpoint. This has lead us to conclude that the claims C1 and C2, that classical physics was unequipped to derive valid conclusions on the mixing of identical substances, were neither theoretically nor historically accurate in light of the evidence found in Refs. [29, 31].

In section III we argued that the epistemic and quantum

viewpoints on the Gibbs’ paradox were not *a priori* to be opposed to one another since they do not refer to the same thing. By relating the epistemic view point to identification of a substance to its probability distribution with regards to a specific attribute, we advocated for a peaceful compatibility between the two views for discrete mixtures in general and single component systems more specifically. In these cases, the claim C3 of the necessity of quantum indistinguishability to justify the factor $N!$ can only be valid if either C1 and C2 are true, which we rejected in section II, or if quantum mechanical-based arguments are given superiority for rationality from the outset; which then probably needs to be justified on other grounds (*e.g.* methodological or metaphysical). Pushing the quantum and epistemic views to their limits in the case of continuous mixtures we showed that they reach contradictory conclusions on the extensivity of such systems, thus undermining one of the views. We suggested that the conclusion of the epistemic view was fully consistent with the success of the physics of colloids while, on the contrary, the quantum indistinguishability was not. We concluded that either C3 is false or the quantum mechanics-based argument on which it relies needs to be seriously modified to accommodate this new constraint. Even in that case however we stressed that there would not be any reason to consider the quantum view rationally superior to the epistemic view.

To support this conclusion we set out to determine the entropy of mixing of polydisperse gases in section IV. Starting from Eq. (5), where both the quantum and epistemic views agree, we extended the statistical mechanics formalism to continuous mixtures from the mathematics of the probability distributions characterising their composition. For both discrete and continuous mixtures the entropy was fully extensive and was that of a single component gas up to an additional term depending solely on the composition, the composition entropy. This lead us to conclude that any ideal gas with constant composition — be it discrete or continuous — had not only an extensive entropy but could also be considered as a single-component gas. We noted that this constant composition condition could be violated via spontaneous phase transition *in composition* in interacting systems or more generally by mixing processes. We addressed the latter problem by noticing that the change in entropy upon mixing two gases in equal circumstances only depended on the composition entropies of the gases being mixed; ending-up with an expression which can be interpreted as the square of a *metric* in the space of probability distributions. We have shown that, when applied to the mixing of two normally distributed polydisperse systems, this generalised entropy of mixing did go continuously to zero as the similarity between the substances is increased. This result holds in principle for any mixing process between substances characterised by continuous distributions and resolves, in this sense, a curiosity pointed out by Gibbs in Ref. [31]. At least two questions are still remaining: what about finite size systems and what does the contin-

uous probability distribution may mean? In section V, we addressed these two issues by focusing on the idea of separation protocol *i.e.* the external means one is willing to use to separate two substances from a mixed state. We argued that one way to interpret the epistemic view was to relate the probability distributions not so much to single realisations of a composition but rather to the protocol enabling a distinction between two substances in the first place. Thus, considering a protocol that could separate a composition \mathcal{C}_3 into two compositions \mathcal{C}_1 and \mathcal{C}_2 we determined the energy to be dissipated by the said protocol given it was acting on a known species. This was done by making use of a mapping between the demixing of a substance into two substances and the uncertain reset of a 1-bit memory from a thermal state. This explicit analogy with information erasure further strengthens the idea of the entropy of mixing being successfully accounted for by the epistemic viewpoint.

This work has mainly focused on Gibbs' work and a slight extension of his views — as understood by the author — to the statistical mechanics of ideal mixtures. With regards to claim C2 however, it is worth noting that one important premise for it to hold is that there exists a single undebatable view about how classical concepts of classical mechanics should look like and be applied in a statistical context. Nonetheless, the point has been raised however that it was not the case and that at least two concepts of mechanical states could be conceived in mechanics, one owing to Newton and the other to Laplace [55, 56]. We do not wish to pursue this aspect of the discussion further here but, if anything, it only *adds* to the case against C2 we have put forward in section II.

Further research and clarification on the notion of indistinguishability might be required. For instance, although a traditional understanding of indistinguishability still makes sense in the context of discrete mixtures, it seems impossible to apply it *as is* in the case of continuous mix-

tures. One might instead rely on a less particle-based notion but rather on an ensemble-based notion. Thus, in the case of section V, particles may be said to belong to the same equivalence class provided they end-up on the same side of the box under the action of the separation protocol; they become “ indistinguishable ” in this very specific sense. One may argue that statistical mechanics should not be influenced by such external considerations but it is not so clear to the author. The very existence of Gibbs' ensembles illustrates the fact that knowledge about the external constrains on the system does influence the *a priori* probabilities one gives to the microstates. Why should the knowledge about whether the substance under study has a well defined composition or not be treated differently than, say, knowing that the volume or pressure is fixed?

In our summary of section II above, we have omitted purposely the fact that Gibbs did mention the mixing of identical gases and did point out that if one were to use Eq. (1) he would get an inconsistency with basic thermodynamics. There, Gibbs does not seem to refer to this example as a puzzle at all but rather as a *reductio ad absurdum* argument illustrating the rationality of using generic phases over specific phases.

In the end, we have argued that Gibbs' paradox does not constitute a problem for the classical foundation of classical statistical mechanics as they were essentially laid out by Gibbs in his work [29] — and by his predecessors — when quantum mechanics did not exist. The epistemic viewpoint of entropy and that of identity at the substance level (rather than at the particle level) fully account for both the rationality of Eq. (5) and the success of the statistical mechanics of colloids. On the contrary, when continuous mixtures are considered, the “ Gibbs paradox ” could refer to the current inconsistency between the quantum indistinguishability argument for classical extensivity and the success of a classical statistical mechanics based on Eq. (5) to apprehend the physics of — polydisperse — colloids.

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- [46] This limit must be interpreted in a careful way for it does not exist in actuality. One must interpret Δx as comprising two contributions $\Lambda(x)$ and ϵ such that $\Delta x = \Lambda(x)\epsilon$ and interpret the limit when Δx tends to zero as the limit when ϵ tends to zero at fixed $\Lambda(x)$. A diverging term in $-\ln \epsilon$ appears which makes the limit non-existent. To bypass this issue, one may regularise by subtracting $-\ln \epsilon$ from the limit.
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