

Comment on “The Gibbs paradox and the distinguishability of identical particles,” by M. A. M. Versteegh and D. Dieks [Am. J. Phys. 79, 741–746 (2011)]

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We revisit recent discussions concerning the Gibbs paradox—the apparent discrepancy between the entropy change upon mixing identical gases as evaluated from the statistical mechanics of classical distinguishable particles and macroscopic thermodynamics. Contrary to what is often stated, we show that thermodynamics does not require this entropy of mixing to be zero. A zero value follows from the implicit assumption that the identical gas particles are indistinguishable. If the identical particles are explicitly assumed to be distinguishable, thermodynamics yields the same entropy of mixing as classical statistical mechanics.

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I. INTRODUCTION

Recently, Versteegh and Dieks¹ wrote an interesting article on the statistical mechanics of identical but distinguishable particles. They argue that classical mechanics requires that particles be considered as distinguishable from one another even if they are identical, that is, have the same intrinsic properties such as charge and mass.² Classical particles follow continuous and non-intersecting trajectories in phase space and their positions and momenta can be precisely determined in principle. These particles can be labeled or distinguished by observing their different histories. Consequently, interchanging the labels on any two particles has a physical consequence and creates a new microstate of the system. The relabeling of the particles leads to a different physical realization of the system because it corresponds to a discontinuous change in the trajectory of either particle, the result of which cannot be generated by a given physical process prior to the interchange. As is well known, explicitly enforcing the distinguishability of the particles leads to the prediction in classical statistical mechanics that the mixing of two identical ideal gases leads to a nonzero change in the entropy of the combined system.

At first glance such a result is puzzling. Macroscopic thermodynamics supposedly requires that the entropy change upon mixing two identical ideal gases be equal to zero. If two containers of, say oxygen, are separated by a partition, the removal of the partition should not lead to an increase in the entropy of the system because there are no discernible changes. We can easily return the partition, without requiring work to be done, to bring the system back to its original state. Because there is no net change in the entropy for this apparently cyclic process, and the entropy could not have decreased when the partition was returned—because no work was performed—we conclude that the removal of the partition cannot have resulted in an increase in the entropy.

If the separate containers instead held different gases, say oxygen and nitrogen, the removal of the partition would lead to an obvious change in the properties of the system. Further-

more, we cannot easily return the system to its original separated state simply by replacing the partition. Work is required to unmix the gases, and so the entropy change upon mixing the different gases must be positive. Because thermodynamics makes no explicit reference to the molecular constituency of matter, the thermodynamic analysis appears to require as input only that the particles are identical or not. Information on whether or not the particles are distinguishable or indistinguishable seems not to be needed.

Because we expect the thermodynamic and statistical mechanical entropies to be consistent, the discrepancy between the zero value of the thermodynamic entropy of mixing identical gases and the nonzero value that follows directly from the classical statistical mechanics of distinguishable particles has been labeled as the Gibbs paradox. To bring the prediction of classical statistical mechanics in line with that of thermodynamics, the total number of microstates is divided by $N!$ (where N is the total number of identical particles) to compensate for the apparent over counting of classical microstates. Despite the previous argument for the distinguishability of classical particles, we still have to treat the particles as being indistinguishable to maintain consistency between classical statistical mechanics and thermodynamics. The justification for treating particles as indistinguishable is usually drawn from quantum mechanics, because this property follows from conditions on the wave function of identical particles.

Although we may be satisfied in invoking quantum mechanics to resolve this discrepancy—and why not, isn't the world governed by quantum mechanics?—Versteegh and Dieks¹ argue that this use does not resolve the problem.³ For one, there are cases in which identical quantum particles behave as being distinguishable, so indistinguishability is not a universal property.² In addition, thermodynamics is a macroscopic approach and does not make explicit reference to the molecular make-up of matter. Why then should thermodynamics not be able to describe properly the thermal properties of classical gases? Furthermore, because the thermodynamic entropy of mixing of identical gases is apparently required to be zero, we have the interesting result that a macroscopic

description of matter, whose foundations were laid when only classical mechanics was known, anticipated a quantum mechanical prediction of molecules.

Our discussion seems to lead to an inescapable conclusion as argued by Versteegh and Dieks.¹ The statistical mechanical, or Boltzmann, entropy, and the thermodynamic, or Clausius, entropy, are not the same entity and have different meanings. To avoid any problems, we need to realize that entropy is defined differently in statistical mechanics and thermodynamics. Others have argued that agreement can be preserved by the introduction of a reduced Boltzmann entropy for classical particles, whereby the division by $N!$ is automatically included.⁴

Although the previous arguments and discussion are compelling, what appears to not have been appreciated fully is that thermodynamics does not require that the entropy of mixing of identical gases be zero. The thermodynamic analysis rests on an implicit assumption that the identical particles are indistinguishable. If the identical particles are explicitly assumed to be distinguishable, the thermodynamic entropy of mixing matches precisely the classical statistical mechanical prediction. The specification of whether or not the particles are distinguishable or indistinguishable is up to the experimenter. Because the results of known experiments, or at least the types of experiments that can be performed at present, appear to be consistent with identical particles being indistinguishable, nearly all the thermodynamic analyses of the mixing of identical gases implicitly assume the indistinguishability of the particles.

Such an assumption, however, need not always be invoked in thermodynamics, which we demonstrate in Sec. II. There we show that the classical statistical mechanical results for both distinguishable and indistinguishable particles can be directly obtained within thermodynamics. Hence, there is no Gibbs paradox after all. Thermodynamics and classical statistical mechanics are consistent with one another, and describe the same entropy concept.

An excellent discussion that overlaps with some of what we present here and includes an historical overview of aspects of the Gibbs paradox which appear in Gibbs' writings, appears in the work of Jaynes.⁵ Gibbs was aware that thermodynamics does not require the mixing of identical gases to be zero. Supplemental information about the distinguishability of the particles had to be provided by the experimenter. He did not reiterate this point in his later writings on statistical mechanics, which might explain why the Gibbs paradox has persisted. An acknowledgment that the zero entropy of mixing in identical gases is not a fundamental fact of thermodynamics, and a proper thermodynamic analysis of the mixing of distinguishable particles should be consistent with classical statistical mechanics, can also be found in the work of Dieks,² van Kampen³ and Nagle.⁶ An alternate viewpoint for the resolution of the Gibbs paradox has been presented by Swendsen.⁷ Here, the entropy of mixing of identical particles, either distinguishable or indistinguishable, is always taken to be zero, while a different counting scheme for enumerating the number of microstates of classical distinguishable particles is proposed that naturally gives rise to the required division by $N!$.

II. ENTROPY OF MIXING OF IDEAL GASES

We first consider the thermodynamic derivation of the entropy of mixing of two different ideal gases, A and B.⁸ In a

container of total volume V at fixed temperature T , a partition separates the two gases such that the initial pressures of each are identical and equal to P . Thus, the number of particles and initial occupied volumes of each gas are related as follows

$$\frac{N_A}{V_A} = \frac{N_B}{V_B}, \quad (1)$$

where N_i and V_i are the number of particles and initial volume of species i , and $V = V_A + V_B$. The partition is now split into two movable membranes, one that is permeable to A but impermeable to B, and the other is permeable to B but impermeable to A. The latter membrane is now moved to one side, such that A undergoes a reversible, isothermal expansion to occupy the entire container. A portion of A now overlaps with B, but because ideal gas particles at the same temperature are (in effect) noninteracting and the membrane is permeable to B, the expansion occurs as if B were not present. Starting from the combined first and second laws, the differential change in the entropy of A is given by

$$dS_A = \frac{1}{T}dU_A + \frac{P_A}{T}dV_A, \quad (2)$$

where S_A , U_A , and $P_A = N_A k T / V_A$ are the entropy, internal energy, and the pressure of gas A, respectively, with k being the Boltzmann's constant. Because the process is isothermal (and at constant mass), the internal energy of the ideal gas is constant, so Eq. (2) evaluated over the reversible expansion, from the initial volume V_A to the final volume V yields

$$\Delta S_A = N_A k \ln \frac{V}{V_A} = -N_A k \ln y_A, \quad (3)$$

where y_A is the mole fraction of A in the final mixture, and we have used Eq. (1). The other membrane is now reversibly and isothermally expanded so that B is allowed to occupy the total volume V as well. Similar calculations yield

$$\Delta S_B = N_B k \ln \frac{V}{V_B} = -N_B k \ln y_B. \quad (4)$$

The sum of these two entropy changes leads to the total entropy of mixing for this process

$$\Delta S_{\text{mix}} = -N_A k \ln y_A - N_B k \ln y_B. \quad (5)$$

If the number of particles of type A and B are the same, we have that $\Delta S_{\text{mix}} = Nk \ln 2$, where $N = N_A + N_B$.

For later use, we note that the entropy of the final state, or that of the mixture of A and B, can be written as

$$S_{\text{final}} = \Delta S_{\text{mix}} + S_{\text{init}}^A + S_{\text{init}}^B, \quad (6)$$

where S_{init}^i is the initial entropy of species i before the mixing process occurs, and all quantities are evaluated at the same temperature and pressure. By using Eqs. (5) and (6), we can show that the partial molar entropy of species i in the ideal gas mixture, \bar{S}_i , is given by⁹

$$\bar{S}_i = s_i - k \ln y_i, \quad (7)$$

where s_i is the entropy per particle of species i at the same temperature and pressure of the mixture and \bar{S}_i is also a per particle quantity.

In the derivation of Eq. (5), we needed only to know that a molecule of type A can be distinguished from a molecule of type B. We did not require information about the distinguishability or indistinguishability of A or B particles among themselves.

We now consider how to proceed if we have identical gases on either side of the partition at the start of the process. As noted, it is typically argued that the removal of the partition should not cause any property of the entire system to change. We begin with two identical gases at the same T and P , and finish with the same gas at the same T and P , with no change in the volume of the composite system. The final entropy should just be the sum of the two entropies of the initial identical gases, which in this case implies no change in the entropy for this process. How can the entropy of mixing identical gases be anything other than zero? A nonzero value implies that, in principle, work can be extracted from this process. In other words, simply by opening a door, and allowing the air on either side to mix, we can create a process to generate work. Because no one is aware of any way to implement this process, the entropy change upon mixing identical gases must be zero.

Nevertheless, is this conclusion warranted? We have implicitly assumed that the particles comprising the identical gases are indistinguishable. Because there is no known way of tracking the identical particles on either side of the partition before it is removed, we should not be able to devise a process to extract work from the mixing of identical gases. We don't yet have the means, or more specifically a membrane, to identify or prohibit the motion of some subset of a collection of identical particles. Hence, the conclusion that the mixing of identical gases should not lead to an increase in entropy follows from our experience, or what is our inability to carry out a particular process, rather than what is strictly required from thermodynamics.

To see more clearly why a zero value of the entropy of mixing identical gases is not required by thermodynamics, we repeat the previous thermodynamic analysis while making the explicit assumption that the identical gases on either side of the partition are distinguishable. Because we can track and keep separate the identities of each particle, we are now able to employ membranes that are permeable only to a given subset of the identical particles. Thus, as before, we split the initial partition into two membranes, one that is permeable to just those particles initially on the right and the other that is permeable to just those particles initially on the left. The situation is now equivalent to the earlier analysis of the mixing of the two pure gases A and B. If the number of particles of each identical gas is the same, we therefore find that $\Delta S_{\text{mix}} = Nk \ln 2$ for the mixing of two identical and distinguishable gases, matching what is obtained from classical statistical mechanics.¹

In this thought experiment the practicality of devising such a membrane to separate identical but distinguishable particles should not confuse the fundamental issue.⁶ In principle, classical particles can be traced indefinitely, and so in principle, there should be some way to separate particles based on their past trajectories and origins.² Furthermore, if we are interested only in the changes of a given state function such as the entropy, the actual manner in which a process is carried out is irrelevant in thermodynamics. Thermodynamics makes frequent use of impractical reversible pathways, processes that are essential to determining changes in the entropy of a system. As an example, we often consider in thermodynamics the reversible addition or dele-

tion of particles from a system. How this process is carried out is almost never specified. In statistical mechanics, some details of the process are specified, though the pathway is by no means practical. Because the chemical potential of a particle is related to the reversible work required to insert or delete a particle, expressions for the chemical potential are obtained by considering various unphysical pathways in which a particle is either "slowly turned on or off" via some interparticle potential coupling parameter,¹⁰ or "scaled up or down in size."¹¹

The membranes we have discussed are clearly not the standard passive membranes used for separating non-identical particles, but instead require some level of information processing through the use of submicroscopic computers located within the membranes or Maxwell's demon.² The gathering of the needed information, say by detecting light photons scattered by the particles, leads to another increase in the entropy of the universe, which cannot be overlooked in some processes.¹²⁻¹⁴ We argue that this entropy increase occurs separately from the entropy increase due to the mixing of distinguishable particles. We can employ similar active membranes to aid in the mixing of the different gases A and B. The entropy change that should be assigned to these membranes or Maxwell's demon would appear in addition to the entropy change due to mixing the different gases, and reflects our choice of having followed a more difficult route to the same final state. Passive membranes presumably carry out the separation based on size differences and not on molecular histories. Thus, no entropy penalty is incurred by or assigned to these membranes. Active membranes must gather information about which particle is approaching some molecular-sized trap door, information that is needed when selecting between ideal gas particles. As noted, this data collection gives rise to another contribution to the entropy increase of the universe.¹² Switching from passive to active membranes does not alter the fact that there is a separate entropy increase due to the mixing of distinguishable particles, or even different gases A and B. Nevertheless, we note that the thermodynamics of Maxwell's demon is an important topic that might require further investigation. As discussions of Maxwell's demon illustrate,^{13,14} there is an intimate relation between entropy and accessible information, which is also one of the conclusions of the present work.

The entropy of mixing identical distinguishable particles can be obtained in a related way using Eq. (7). For example, we can express the entropy of a mixture comprised of two species A and B in terms of the sum of the product of the partial molar entropy of species i and the number of particles of i

$$S_{\text{mixture}} = N_A \bar{S}_A + N_B \bar{S}_B. \quad (8)$$

For identical but distinguishable particles we must treat the gas as a mixture comprised of separate species. Note that A and B are treated as different components because we have some way of distinguishing their identities. If there were a way to distinguish the identities of particles of a single kind, we should then treat the identical particles as comprising a mixture with N total species.⁶ So, if we begin with a gas of N_R identical but distinguishable particles on the right side, with each of the N_R components having a mole fraction of $1/N_R$, and N_L identical but distinguishable particles on the left, each with a mole fraction of $1/N_L$, the total entropy of this initial state is

$$\begin{aligned}
S_{\text{initial}} &= \sum_{N_R} \bar{S}_R + \sum_{N_L} \bar{S}_L \\
&= N_R s + N_R k \ln N_R + N_L s + N_L k \ln N_L,
\end{aligned} \tag{9}$$

where, for example, \bar{S}_R is the partial molar entropy of any one of the particles on the right side and s refers to the same entropy per particle of any one of the N identical particles. After mixing with no change in T and P , the entropy of the final state is equal to

$$S_{\text{final}} = \sum_N \bar{S}_f = Ns + Nk \ln N, \tag{10}$$

in which the final mole fraction of each component is $y = 1/N$ and the partial molar entropy of any one of the N particles in this final state is \bar{S}_f . Hence, the entropy of mixing identical but distinguishable ideal gases is given by

$$\Delta S_{\text{mix}} = -N_R k \ln \frac{N_R}{N} - N_L k \ln \frac{N_L}{N}, \tag{11}$$

a result identical to Eq. (5). If the number of particles of each identical gas is the same, we again find that $\Delta S_{\text{mix}} = Nk \ln 2$.

In contrast, if we assume that the identical gases are indistinguishable, that is we cannot keep track of the identities of the particles, we are also assuming that there are no membranes capable of allowing only some subset of particles to pass freely through them. Thus, a given membrane will be permeable to either all or none of the indistinguishable particles. We can now mix the gases by again splitting the partition into two permeable membranes. But because the gases are allowed to pass freely through either membrane, the net force on the membranes will always be zero. No work is therefore required to displace the membranes either to the right or left. Given that the temperature is constant, so that there is also no change in the internal energy, the heat transfer into or out of the system must also be zero. Consequently, the entropy change upon mixing identical and indistinguishable gases is zero. Likewise, we cannot treat the indistinguishable particles as separate components; each identical gas is a pure component system. Hence, the partial molar entropy is equal to the entropy per particle of the pure component gas, which leads us to conclude that $\Delta S_{\text{mix}} = 0$. This result also follows directly from the classical statistical mechanical entropy when the total number of accessible states of the system is divided by $N!$ to account for the indistinguishability of the particles.

III. CONCLUSIONS

The predictions of the thermodynamic and statistical mechanical entropies, whether for distinguishable or indistinguishable identical particles, are consistent. Hence, there is no such thing as the Gibbs paradox. Thermodynamics, just like statistical mechanics, requires that all the information needed to completely reproduce the system be specified. For nearly all systems of interest for which a thermodynamic analysis is performed, we invoke what is known as the Duhem's theorem: a thermodynamic state is completely characterized by specifying only the number of particles of each species and two other independently variable properties.¹⁵ The need for such a limited amount of information is

based on experience. At present, there appears to be no way to separately label and track the locations of identical particles in a fluid. Hence, the only relevant thermodynamic descriptor of a given species seems to be its total number of particles. In other words, we have assumed from the outset that the particles are indistinguishable. If the particles were distinguishable in some experimentally realizable way, this information would have to be included in the set of variables used to reproduce the thermodynamic state of the system.^{2,5} Consequently, the value of the entropy of mixing gases is not constrained by thermodynamics, but rather by the intrinsic properties of the system. The entropy of mixing depends upon what information is accessible to the experimenter. As van Kampen³ astutely has reminded us, the experimenter sometimes chooses to neglect some potentially accessible information. For example, the thermodynamic analyses of compressors and turbines often use tabulated values of the entropy of steam, which were generated by ignoring the fact that the steam is actually a mixture of normal and heavy water.

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¹M. A. M. Versteegh and D. Dieks, "The Gibbs paradox and the distinguishability of identical particles," *Am. J. Phys.* **79**, 741–746 (2011).

²D. Dieks, "The Gibbs Paradox Revisited," in *Explanation, Prediction, and Confirmation*, edited by D. Dieks, W. J. Gonzales, S. Hartmann, T. Uebel, and M. Weber (Springer, New York, 2011), pp. 367–377.

³Why quantum mechanics is irrelevant to the resolution of the Gibbs paradox is also discussed in detail by N. G. van Kampen, "The Gibbs paradox," in *Essays in Theoretical Physics*, edited by W. E. Parry (Pergamon, New York, 1984), pp. 303–312.

⁴C.-H. Cheng, "Thermodynamics of the system of distinguishable particles," *Entropy* **11**, 326–333 (2009).

⁵E. T. Jaynes, "The Gibbs Paradox" in *Maximum Entropy and Bayesian Methods*, edited by C. R. Smith, G. J. Erickson, and P. O. Neudorfer (Kluwer Academic, Dordrecht, 1992), pp. 1–22.

⁶J. F. Nagle, "Regarding the entropy of distinguishable particles," *J. Stat. Phys.* **117**, 1047–1062 (2004).

⁷R. H. Swendsen, "Statistical mechanics of classical systems of distinguishable particles," *J. Stat. Phys.* **107**, 1143–1166 (2002); "Statistical mechanics of colloids and Boltzmann's definition of the entropy," *Am. J. Phys.* **74**, 187–190 (2006); "How physicists disagree on the meaning of entropy," *Am. J. Phys.* **79**, 342–348 (2011).

⁸Although this derivation appears in various sources, we follow the approach in H. Reiss, *Methods of Thermodynamics* (Dover, Mineola, NY, 1996), pp. 90–93.

⁹J. W. Tester and M. Modell, *Thermodynamics and Its Applications*, 3rd ed. (Prentice Hall PTR, Upper Saddle River, NJ, 1997), p. 343.

¹⁰D. A. McQuarrie, *Statistical Mechanics* (University Science Books, Sausalito, CA, 2000), pp. 263–264.

¹¹M. Heying and D. S. Corti, "Scaled particle theory revisited: New conditions and improved predictions of the properties of the hard sphere fluid," *J. Phys. Chem. B* **108**, 19756–19768 (2004).

¹²L. Brillouin, *Science and Information Theory* (Academic, New York, 1956), Chap. XIII.

¹³H. S. Leff, "Available work from a finite source and sink: How effective is a Maxwell's demon?," *Am. J. Phys.* **55**, 701–705 (1987).

¹⁴H. S. Leff, "Maxwell's demon, power, and time," *Am. J. Phys.* **58**, 135–142 (1990) and references therein.

¹⁵Reference 9, p. 16.