

# Gibbs Paradox Revisited from the Fluctuation Theorem with Absolute Irreversibility

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The inclusion of the factor  $\ln(1/N!)$  in the thermodynamic entropy proposed by Gibbs is shown to be equivalent to the validity of the fluctuation theorem with absolute irreversibility for gas mixing.

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The Gibbs paradox (GP) is actually constituted of a set of problems concerning how to define the particle-number dependence of the entropy consistent with thermodynamics and/or statistical mechanics. van Kampen [1] classified it into three distinct issues (see Fig. 1): consistency within thermodynamics (GP-I) [1–3], consistency within classical statistical mechanics (GP-II) [1,4], and consistency between thermodynamics and classical statistical mechanics (GP-III) [1,3,5].

As detailed below, all of them have been settled in the thermodynamic limit [1–5]. However, in view of the growing interest in small thermodynamic systems [6–8], it is worth revisiting the Gibbs paradox in this context. The conventional resolutions to GP-I [1,3] and GP-II [1] apply to small thermodynamic systems as well. However, the one to GP-III cannot be applied to small thermodynamic systems [3].

The issue of GP-III boils down to determining the ambiguity function  $f(N)$ , which gives the difference between the thermodynamic entropy  $S$  and the statistical-mechanical entropy  $S^{\text{stat}}$ ,

$$S(T, V, N) = S^{\text{stat}}(T, V, N) + k_B f(N). \quad (1)$$

In the thermodynamic limit, extensivity of the thermodynamic entropy leads to  $f(N) = -N \ln N + cN$ , where  $c$  is a constant [3,9]. However, extensivity breaks down in small thermodynamic systems. In this Letter, we show that in small thermodynamic systems the fluctuation theorem [7,8,10–17] with absolute irreversibility [18] takes the place of extensivity, leading to  $f(N) = \ln(1/N!) + cN$ .

*A brief history.*—In the 1870s, Gibbs put forth the problem of GP-I [2], pp. 227–229]. Whereas identical-gas mixing at the same temperature and pressure does not produce an extensive amount of entropy, different-gas mixing does. The fact that the latter entropy production stays constant if the difference between two species becomes infinitesimal seems paradoxical. Gibbs ascribed the essence of this problem to the definition of thermodynamic states. This idea was further elaborated by van Kampen [1], Sec. 2–4] who argued that the Clausius equality defines only the difference in entropy of a system where the particle number  $N$  is conserved. Therefore, to determine the  $N$

dependence, we have to introduce a reversible process in which  $N$  is varied. Suppose that two gases at the same temperature and pressure are separated by a partition in a box. For identical gases, opening a channel between the two compartments is reversible. For different gases, this process is irreversible and we have to invoke the familiar reversible procedure with semipermeable walls. Thus, the difference between identical- and different-gas mixings essentially arises from the two different processes used to determine the entropy. Which of the two processes we should use depends on whether we are able or intend to use the semipermeable walls or on how we operationally define the identical thermodynamic states. “Thus, whether such a process is reversible or not depends on how discriminating the observer is. The expression for the entropy [...] depends on whether or not he is able and willing to distinguish between the molecules A and B” ([1], pp. 306–307). As Jaynes put it ([3], Sec. 5), the thermodynamic entropy has “anthropomorphic” nature in that its value depends on “human information.”

About a quarter century later, Gibbs discussed GP-III in his renowned textbook ([5], chapter XV) by introducing two types of phase spaces, “the generic phase” and “the specific phase.” In the generic phase, a set of points in phase space is identified when any point in the set can be obtained by permutation of particles of other points, whereas in the specific phase, they are not. Gibbs preferred the generic phase to the specific phase because the former results in no entropy production for identical-gas mixing ([5], pp. 206–207). Thus, Gibbs introduced the factor

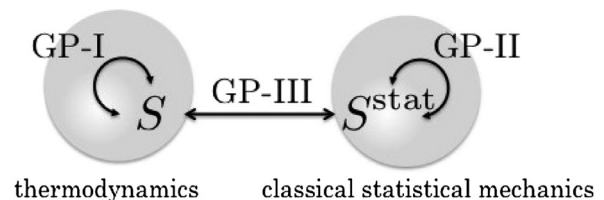


FIG. 1. Three aspects of the Gibbs paradox. GP-I, GP-II, and GP-III concern the consistency within thermodynamics, within classical statistical mechanics, and between thermodynamics and classical statistical mechanics, respectively.

$\ln(1/N!)$  in classical statistical mechanics to ensure the consistency with thermodynamic observation. van Kampen ([1]) argued that this prescription is guaranteed by convention [namely, by assuming  $f(N) = 0$  in Eq. (1) for the classical statistical-mechanical entropy in the generic phase]. However, Jaynes ([3], Sec. IX) showed that  $f(N)$  can be determined from the extensivity of the thermodynamic entropy as we see later.

In the 1910s and 1920s, the inclusion of the factor  $\ln(1/N!)$  was discussed in the context of statistical mechanics (GP-II). Ehrenfest and Trkal considered the association and dissociation of molecules from a viewpoint of atomic phase space [4], and concluded that the factor  $\ln(1/N!)$  is needed in calculating the chemical potential to guarantee the consistency within classical statistical mechanics. van Kampen ([1], Sec. VII) derived the same factor based on combinatorics by considering a system in contact with an infinitely large particle reservoir.

Since Planck connected the Gibbs paradox with quantum distinguishability (e.g., see Ref. [19]), the view that quantum theory resolves the Gibbs paradox has prevailed in textbooks (for example, see Refs. [20–25]). However, as van Kampen [1] and Jaynes [3] pointed out, the quantum resolution is irrelevant to the Gibbs paradox. First of all, it cannot apply to classical mesoscopic systems such as colloidal particles that are not quantum-mechanically identical due to their distinguishable internal degrees of freedom, yet the factor  $\ln(1/N!)$  is needed to explain experimental results (e.g., see Refs. [26,27]). More importantly, quantum statistical mechanics faces the same problem as classical mechanics because the quantum statistical-mechanical entropy  $S^{q\text{-stat}}$  is related to the thermodynamic entropy  $S$  only up to the ambiguity function  $f^q(N)$  as  $S = S^{q\text{-stat}} + f^q(N)$ . As van Kampen ([1], p. 311) aptly put it, “the Gibbs paradox is no different in quantum mechanics, it is only less manifest”.

*Conventional resolution to GP-III.*—GP-III concerns the relation between the thermodynamic entropy  $S$  and the classical statistical-mechanical entropy  $S^{\text{stat}}$ . While the latter is defined as the Gibbs entropy, namely, the Shannon entropy of the canonical state, the former is defined through the Clausius equality as  $\Delta S = \int_{q,s} \delta Q/T$ , where  $\delta Q$  is the heat transferred from the heat reservoir at temperature  $T$  to the system and the integration is taken along a quasistatic process. We note that the particle number  $N$  cannot be varied in this process; if we start with open systems, the Clausius definition should be modified ([3], Sec. IX). See the discussions section for detail. Therefore, the thermodynamic entropy defined by the Clausius equality has ambiguity about  $N$ , and hence the relation between the thermodynamic entropy and statistical-mechanical entropy should involve some ambiguity function  $f(N)$  as in Eq. (1) [1], Eq. (14); [3], Eq. (16)]. The problem of GP-III is to demonstrate  $f(N) = \ln(1/N!)$  (up to a constant per particle) for the classical statistical-mechanical entropy in the specific phase

[or equivalently  $f(N) = 0$  for the one in the generic phase]. Since “exactly the same argument will apply in quantum statistical mechanics” ([3], Sec. IX), GP-III is the issue not of classical statistical mechanics in particular but of statistical mechanics in general.

Jaynes ([3], Sec. IX) resolved this issue for free particles by analogy with the way by which Pauli phenomenologically determined the  $N$  dependence of the thermodynamic entropy ([9], pp. 38–39). By requiring that the thermodynamic entropy satisfy extensivity,

$$S(T, qV, qN) = qS(T, V, N), \quad \forall q > 0, \quad (2)$$

and by invoking the formula of the statistical-mechanical entropy for an ideal gas  $S^{\text{stat}}(T, V, N) = Nk_B[(3/2) \ln T + \ln V + \text{const}]$ , one can show

$$f(N) = Nf(1) - N \ln N. \quad (3)$$

Here, the first term on the right-hand side of Eq. (3) represents an intrinsic entropy per particle, while the second term amounts to the factor  $\ln(1/N!)$  in the large- $N$  limit. Thus, the requirement of extensivity leads to the desired factor in the thermodynamic limit ( $N \rightarrow \infty$ ).

However, extensivity, in general, breaks down in small thermodynamic systems, and therefore the Pauli-Jaynes resolution cannot apply to them. Jaynes ([3], Sec. IX) expressed his concern about this point by stating that “The Pauli correction [...] ignores the small deviations from extensivity that are essential for treatment of some effects [...]. A truly general and quantitatively accurate definition of entropy must appeal to a deeper principle which is hardly recognized in the current literature [...]”. Moreover, it is unclear how to generalize this approach in the presence of interparticle interactions.

*Method.*—We use the fluctuation theorem [8,10–17] as the guiding principle for small thermodynamic systems. The Jarzynski equality  $\langle e^{-\beta(W-\Delta F)} \rangle = 1$  [12] determines the equilibrium free-energy difference  $\Delta F$  between two configurations from statistics of work  $W$  in a nonequilibrium process, where the angle brackets denote the statistical average over the work distribution. Unfortunately, the Jarzynski equality cannot apply to gas mixing because the initial state is not a global canonical equilibrium state of the entire box, which does not satisfy the prerequisite for the equality.

We overcome this difficulty by applying the fluctuation theorem in the presence of absolute irreversibility  $\langle e^{-\beta(W-\Delta F)} \rangle = 1 - \lambda$  [18], which allows an initial canonical state with spatial constraints. Here, the term  $\lambda$  is the absolutely irreversible probability that is mathematically defined as the integral of the singular part of the time-reversed probability measure with respect to the forward probability measure [18]. For this singular part, the Crooks fluctuation theorem [13] is ill defined because the dissipative work is divergent with singularly strong

irreversibility, and hence the Jarzynski equality [12] breaks down. We can calculate  $\lambda$  as the sum of the probabilities of the time-reversed events that have no counterparts in the forward process.

To demonstrate the existence of absolute irreversibility in gas mixing, we consider the time-reversed process of gas mixing, namely, wall insertion as illustrated in Fig. 2. The events indicated by blue arrows are absolutely irreversible because they have no counterparts in the forward process. The absolutely irreversible probability  $\lambda$  is given by the sum of the probabilities of these events. Thus, absolute irreversibility of gas mixing originates from fluctuations in the number of particles in each box after wall insertion and may be interpreted as an inevitable loss of information on the particle number in each box before gas mixing [28]. Obviously, such an effect becomes more important as the system gets smaller.

*Main result.*—We now show that the validity of the fluctuation theorem with absolute irreversibility

$$\langle e^{-\beta(W-\Delta F)} \rangle = 1 - \lambda \quad (4)$$

for gas mixing in the isothermal environment is equivalent to the following choice of the ambiguity function:

$$f(N) = Nf(1) - \ln N!. \quad (5)$$

In particular, if the free-energy difference is calculated from Eq. (4), the thermodynamic entropy is defined and  $f(N)$  is given by Eq. (5). Recall that, in the thermodynamic limit, the validity of extensivity (2) is equivalent to Eq. (3). Thus, the fluctuation theorem with absolute irreversibility (4) in small thermodynamic systems takes the place of extensivity (2) in the thermodynamic limit. Note that Eq. (5) differs from Eq. (3) at the subleading order, namely, in the mesoscopic regime.

*Proof.*—First, we assume Eq. (4) to derive Eq. (5). We consider mixing of identical gases and that of different gases

as illustrated in Fig. 2, and assume that gases are initially in thermal equilibrium with inverse temperature  $\beta$ . We assume that gas particles have the same mass and that the interaction potential between two different particles is the same as that between two identical particles. Therefore, the Hamiltonians for the two cases are identical. We also assume that the interactions do not break additivity. By the term additivity, we mean that the thermodynamic entropy of a system consisting of independent subsystems is equal to the sum of the entropies of the individual subsystems. The left (right) box is initially filled with an  $M(N)$ -particle gas with volume  $Mv(Nv)$ , and then the wall is removed. For identical and different gases, Eq. (4) gives  $\langle e^{-\beta(W_{\text{id}}-\Delta F_{\text{id}})} \rangle_{\text{id}} = 1 - \lambda_{\text{id}}$  and  $\langle e^{-\beta(W_{\text{dif}}-\Delta F_{\text{dif}})} \rangle_{\text{dif}} = 1 - \lambda_{\text{dif}}$ , respectively. Because no work is performed upon gas mixing,  $\langle e^{-\beta W_{\text{id}}} \rangle_{\text{id}} = \langle e^{-\beta W_{\text{dif}}} \rangle_{\text{dif}} = 1$  holds. Therefore, we obtain  $\Delta F_{\text{id}} - \Delta F_{\text{dif}} = k_B T \ln[(1 - \lambda_{\text{id}})/(1 - \lambda_{\text{dif}})]$ . Now, we evaluate the left-hand side of this equality. Since  $\Delta F = \Delta U - T\Delta S$  and  $\Delta U_{\text{id}} = \Delta U_{\text{dif}}$  by the assumption of the same interaction potential, we obtain  $\Delta F_{\text{id}} - \Delta F_{\text{dif}} = -T(\Delta S_{\text{id}} - \Delta S_{\text{dif}})$ . Moreover, since the partition functions for the two processes calculated by statistical mechanics based on the specific phase are equal, we have  $\Delta S_{\text{id}}^{\text{stat}} = \Delta S_{\text{dif}}^{\text{stat}}$ . It follows then from Eq. (1) that the difference between the thermodynamic entropy productions can be evaluated only in terms of  $f(N)$  as  $\Delta S_{\text{id}} - \Delta S_{\text{dif}} = k_B(\Delta f_{\text{id}} - \Delta f_{\text{dif}})$ . For identical-gas mixing, the ambiguity function of the initial state is given by  $f_{\text{id}}^{\text{ini}} = f(M) + f(N)$  due to the assumption of additivity, whereas that of the final state is  $f_{\text{id}}^{\text{fin}} = f(M + N)$ , resulting in  $\Delta f_{\text{id}} = f(M + N) - f(M) - f(N)$ . In contrast, for different-gas mixing, we can quasistatically connect the initial and final states by using a semipermeable membrane. As a result, the entropy difference is uniquely determined by the Clausius equality, and therefore the ambiguity function remains unchanged; hence  $\Delta f_{\text{dif}} = 0$ . As a consequence, we obtain

$$f(M + N) - f(M) - f(N) = \ln \frac{1 - \lambda_{\text{dif}}}{1 - \lambda_{\text{id}}}. \quad (6)$$

This result implies that the ambiguity in the thermodynamic entropy represented by  $f(N)$  is directly related to and hence can be removed by the degree of absolute irreversibility in the gas mixing process.

To find  $\lambda$ , let us consider the time-reversed process of gas mixing, i.e., wall insertion as illustrated in Fig. 2. After the insertion, the state may or may not return to the original one. The events in which the state does not return to the original one are absolutely irreversible because they have no counterparts in the forward process. Therefore,  $1 - \lambda$  is equal to the probability that the original state is restored after the wall insertion. Although this probability cannot be calculated explicitly in the presence of interactions, we can compare the probabilities for the two cases. The number of

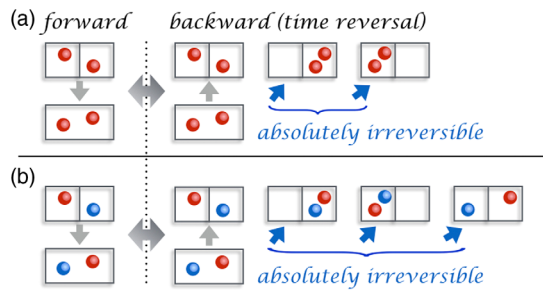


FIG. 2. Gas mixing and its time reversal for (a) identical and (b) different gases. The time-reversed process of gas mixing is the wall insertion for a global thermal equilibrium state. (a) In the time-reversed process, the rightmost two events in which the state does not return to the original one have no counterparts in the forward process. Therefore, they are absolutely irreversible. (b) The probability of absolutely irreversible events is larger due to the presence of the rightmost event that is absent in (a).



combinations for the  $M + N$  particles in which the left box contains  $M$  particles after the wall insertion is equal to the binomial coefficient  ${}_{M+N}C_M := (M + N)!/(M!N!)$ . These partitions can be realized with equal probability due to the assumption of identical interactions. For identical gases, all of them are identified with the original state, whereas there is only one such state for different gases. Therefore, we obtain  $1 - \lambda_{\text{id}} = {}_{M+N}C_M(1 - \lambda_{\text{dif}})$ . Then, equality (6) reduces to  $f(M + N) - f(M) - f(N) = -\ln {}_{M+N}C_M$ . The solution of this functional equation is given by Eq. (5).

Next, we assume Eq. (5) to show Eq. (4). We first consider identical-gas mixing. Let  $Z(N)$  denote the partition function of the gas with the particle number  $N$  and the volume  $Nv$ , calculated by statistical mechanics based on the specific phase. Then, from Eq. (1), the thermodynamic free energy is rewritten as  $F(N) = -\beta^{-1} \ln Z(N) - \beta^{-1} f(N)$ . By substituting Eq. (5) into this formula, we obtain  $F(N) = -\beta^{-1} \ln[Z(N)(f(1))^N/N!]$ . Consequently, the left-hand side of Eq. (4) for identical-gas mixing reduces to  $\langle e^{-\beta(W_{\text{id}} - \Delta F_{\text{id}})} \rangle_{\text{id}} = e^{\beta \Delta F_{\text{id}}} = {}_{M+N}C_M Z(M)Z(N)/Z(M + N)$ . The right-hand side gives the probability to restore by the wall insertion the original state in which the number of particles in the left (right) partition is  $M(N)$ . This is by definition equal to  $1 - \lambda_{\text{id}}$ . Hence, Eq. (4) for identical-gas mixing is shown. A similar procedure vindicates Eq. (4) for different-gas mixing. Thus the equivalence between Eqs. (4) and (5) in gas mixing has been proven.

*Discussions.*—We have demonstrated that the validity of Eq. (4) is equivalent to that of Eq. (5). Therefore, mathematically speaking, requiring either of them produces the same results. However, from a physical point of view, thermodynamics should have an operational basis. In this sense, it is noteworthy that Eq. (4) defines the equilibrium free-energy difference from statistics of the work that we can operationally obtain by repeating the same nonequilibrium process. Therefore, we think that requiring Eq. (4) as the starting point is more appropriate for thermodynamics as an operational theory.

As clarified in the context of GP-I [1–3], the thermodynamic entropy depends on the operational capability of an observer. Therefore, to deal with the thermodynamic entropy, we must define what we mean by the same and different states operationally. This is the conventional wisdom to resolve the Gibbs paradox. We do so by introducing different probabilities of absolute irreversibility for the two mixing processes because they are defined as the probability of time-reversed events that do not have the counterparts in the forward process.

As we have discussed above, the fluctuation theorem with absolute irreversibility (4) is closely related to extensivity (2). For simplicity, we consider mixing of identical ideal gases with the same temperature and volume:  $(T, V, N|T, V, N) \rightarrow (T, 2V, 2N)$ . In the thermodynamic limit, we can explicitly show from Eq. (4) that the thermodynamic entropy production upon gas mixing is

subextensive, and such a subextensive correction is thermodynamically ignored, giving  $S(T, V, N|T, V, N) = S(T, 2V, 2N)$ . Therefore, assuming additivity  $S(T, V, N|T, V, N) = S(T, V, N) + S(T, V, N) = 2S(T, V, N)$ , we obtain  $S(T, 2V, 2N) = 2S(T, V, N)$ , which is nothing but extensivity (2) with  $q = 2$ . Thus, Eq. (4) reduces to extensivity (2) in the thermodynamic limit.

We have dealt with interacting gases by assuming that the interaction does not break additivity. In the Pauli-Jaynes method [3,9], only noninteracting gases were discussed. Although it is possible to extend their method to interacting gases such as van der Waals gases, a general discussion seems intractable because we have to invoke the specific form of the statistical-mechanical entropy. In contrast, our method can cope with general interacting gases with additivity. We consider both identical- and different-gas mixing and form the ratio of their entropy productions to cancel out the effects of interactions. We translate the free-energy difference  $\Delta F$ , which is not explicitly computable, into the absolutely irreversible probability  $\lambda$ , which is not either. However,  $\Delta F_{\text{id}} - \Delta F_{\text{dif}}$  is computable because the right-hand side of Eq. (6) can be evaluated by combinatorics alone. Thus, the fluctuation theorem with absolute irreversibility (4) plays a decisive role in removing the ambiguity  $f(N)$  in the presence of interparticle interactions, although the fluctuations of work do not exist in gas mixing.

One may wonder why we do not consider the thermodynamic entropy of an open system from the beginning. We could extend the Clausius definition to an open system as  $\Delta S = \int_{q.s.} (\delta Q + \mu dN)/T$ . However, to define the thermodynamic entropy in this way, we must define the chemical potential  $\mu$  beforehand. The crucial point is that the chemical potential is defined from the very  $N$  dependence of the thermodynamic entropy as  $\mu = T\partial S/\partial N$ . We thus end up with a circular argument.

Finally, we discuss why we consider isothermal systems instead of isolated systems. First of all, Gibbs [2] originally considered an isothermal setup at a constant temperature. Furthermore, in small isolated systems, the relation between thermodynamics and statistical mechanics is not completely understood. On the other hand, in isothermal systems, thermodynamic responses are considered to be reproduced by statistical mechanics as long as the heat bath is infinitely large. Thus, GP-III is more well defined in isothermal systems than in isolated systems.

*Conclusion.*—We have demonstrated that the validity of the fluctuation theorem with absolute irreversibility (4) is equivalent to the particular form (5) of the ambiguity function of the thermodynamic entropy in Eq. (1). However, requiring Eq. (4) is more appropriate than requiring Eq. (5) from an operational point of view.

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