

Clausius versus Sackur-Tetrode entropies

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(Dated: February 21, 2013)

Based on the property of extensivity (mathematically, homogeneity of first degree), we derive in a mathematically consistent manner the explicit expressions of the chemical potential μ and the Clausius entropy S for the case of monoatomic ideal gases in open systems within phenomenological thermodynamics. Neither information theoretic nor quantum mechanical statistical concepts are invoked in this derivation. Considering a specific expression of the constant term of S , the derived entropy coincides with the Sackur-Tetrode entropy in the thermodynamic limit. We demonstrate however, that the former limit is not contained in the classical thermodynamic relations, implying that the usual resolutions of Gibbs paradox do not succeed in bridging the gap between the thermodynamics and statistical mechanics. We finally consider the volume of the phase space as an entropic measure, albeit, without invoking the thermodynamic limit to investigate its relation to the thermodynamic equation of state and observables.

Keywords: Clausius (thermodynamical)/statistical entropy; Gibbs paradox; extensivity; thermodynamic limit

I. INTRODUCTION

Gibbs paradox emerges when the same gas occupies two chambers of identical volume V separated by a partition [1]. In addition, both chambers contain equal number of particles N and possess the same total energy U , temperature T , and pressure P . Then, the partition is suddenly removed so that the gases in different chambers are allowed to mix. This is the famous Gibbs scenario. The question is then what the change in entropy would be having removed the partition?

The statistical entropy expressions found in the textbooks are shown to yield the entropy change $2k_B N \ln 2$ (k_B denotes the Boltzmann constant) in the thermodynamic limit [2] when applied to the mixing of the gases upon removal of the partition. What is so particular about the value i.e., $2k_B N \ln 2$, that one can now dub the case in hand as a paradox? The answer lies not in statistical mechanics *per se*, but its relation to thermodynamics: the Gibbs scenario represents a reversible process so that one beforehand knows that the entropy change must be equal to zero according to the second law of thermodynamics, and $2k_B N \ln 2$ is simply not equal to zero. This, *prima facie*, implies that the same process is reversible for thermodynamics whereas it is irreversible when viewed in terms of statistical mechanics. Since this cannot be true, one considers it as paradox, and for historical reasons, dubs it as Gibbs paradox [3].

However, note that thermodynamics is based on the Clausius definition of entropy (this is why it is usually called the thermodynamic entropy) and one assumes that the statistical definitions of entropy are equivalent to the Clausius one so that they must yield the same answer as the thermodynamic entropy [3]. After all, a main aim of statistical mechanics is that one can derive the phenomenological macroscopic relations of thermodynamics from a microscopic view. On the other hand, classical thermodynamics is based on the assumption of extensivity, and therefore the statistical entropy expressions too must preserve this assumption. The textbook resolution of the Gibbs paradox explicitly emphasizes this point so that all one has to do is to make statistical entropy definitions somehow extensive [3]. The usual way to do this is by dividing the number of microstates, phase space volume or phase space surface by $N!$ as a result of the (quantum-mechanical) indistinguishability of the particles, so that using the Stirling approximation, one can now write down extensive statistical entropies and therefore Gibbs paradox is resolved. This final extensive

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entropy expression is called the Sackur-Tetrode (ST) entropy

$$\begin{aligned} S_{\text{ST}}(U, V, N) &= \lim_{N \rightarrow \infty} k_{\text{B}} \ln \left(\frac{\Phi}{h^{3N} N!} \right) = \lim_{N \rightarrow \infty} k_{\text{B}} \ln \left(\frac{\Omega}{h^{3N} N!} \right) \\ &= k_{\text{B}} N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} \ln \left(\frac{3h^2}{4\pi m} \right) \right], \end{aligned} \quad (1)$$

where h is the Planck constant and m denotes the mass of the particle [1]. The Sackur-Tetrode entropy has historically been derived using quantum statistical mechanics for an ideal gas. We also note that an information theoretical derivation of the ST-entropy has been also demonstrated by A. Ben-Naim [4], where the former function is the result of the combination of the following four terms: positional uncertainty, momenta uncertainty, quantum mechanical uncertainty principle and the indistinguishability of the particles. In the same book one may also find an alternative derivation of the factor $N!$, with the Schrödinger equation being the point of departure. S_{ST} is then expressed in terms of the de Broglie wavelength.

The current discussions on Gibbs paradox generally revolves around whether the factor $N!$ is justified due to the indistinguishability of the particles (and therefore the resolution of the paradox being quantum mechanical) [5], or if it can be obtained classically [6–8]. A possible third way out is to argue that the very existence of the paradox points out to the difference between the statistical and thermodynamical second laws [3].

It is essential to understand that the inclusion of the factor $N!$ has the effect of making the statistical entropy expressions extensive in the thermodynamic limit. Therefore, we aim to derive the thermodynamical i.e., Clausius entropy for monoatomic ideal gas for open systems by focusing on the property of extensivity, albeit without invoking the thermodynamic limit. Then, we argue the implications of this derivation for the ST-entropy and Gibbs paradox. However, it is important to stress that the extensivity property is not only important for the resolution of the Gibbs paradox, but a general requirement for the homogeneous systems (see pp. 971-972 in Ref. [9]).

One might question the motivation for the derivation of the thermodynamic entropy for monoatomic ideal gas, since many textbooks treat it as trivial. However, one usually calculates it by using $dU = TdS - PdV$ for a reversible process without taking the term μdN fully into account. Hence, one obtains, using also the equation of state and explicit expression for the energy, $S(U, V) = Nk_{\text{B}} \left[\frac{3}{2} \ln \left(\frac{U}{N} \right) + \ln(V) \right]$ apart from some irrelevant constant terms. The thermodynamic entropy obtained in this manner is not a function of the number of particles despite the appearance of N . Moreover, it is not extensive and therefore not free of Gibbs paradox! Since we know that it has to be extensive, the textbook account argues, we can divide the volume V by N , which is the thermodynamic *ad hoc* equivalent of dividing the number of microstates by $N!$ in statistical mechanics (see p. 42 in [10] for an explicit statement of this fact). Before proceeding further, it is noted that the scope of the present paper is limited to homogeneous systems and ideal gases with no surface effects. The systems with surface effects, by their very nature, can be non-extensive and must be treated as such.

The paper is organized as follows. Section II reviews the basic relations characterizing the homogenous functions of first degree i.e., the extensivity. Having outlined the formalism of the former functions, in Section III, we apply it to thermodynamic functions to derive the chemical potential and the entropy expression for monoatomic ideal gases in open systems. Section 4 considers the possible implications of the entropy expression derived in the previous section for the ST-entropy and Gibbs paradox. Conclusions are presented in Section V.

II. THERMODYNAMIC EXTENSIVITY

A function $f : \mathbb{R}_+^q \rightarrow \mathbb{R}$ of class $C^{n \geq 2}$ is said to be homogeneous of τ th degree (τd) generally, when it satisfies the following relation

$$f(\alpha \mathbf{x}) = \alpha^\tau f(\mathbf{x}), \quad (2)$$

where $\alpha \in \mathbb{R}_+$ and $\mathbf{x} \in \mathbb{R}_+^q$. Then, homogeneity of degree one (1d) is characterized by Eq. (2) for $\tau = 1$ i.e.,

$$f(\alpha \mathbf{x}) = \alpha f(\mathbf{x}), \quad (3)$$

which is also called extensivity [11]. The differentiation of Eq. (3) with respect to α yields

$$\sum_{i=1}^q x_i \frac{\partial f(\alpha \mathbf{x})}{\partial (\alpha x_i)} = f(\mathbf{x}). \quad (4)$$

Eq. (4) is valid for any $\alpha \in \mathbb{R}_+$, thus we can choose $\alpha = 1$ without loss of generality. We then obtain

$$f(\mathbf{x}) = \sum_{i=1}^q x_i A_i(\mathbf{x}), \quad (5)$$

where $A_i(\mathbf{x}) := \partial f(\mathbf{x})/\partial x_i$. The above equation is referred to as *Euler's 1d-homogeneous function theorem*, stating that a 1dH-function $f(\mathbf{x})$ can always be expressed in the form of Eq. (5). It can easily be shown that the relation between Eq. (3) and Eq. (5) is bijective. From the latter equation we see that the functions $A_i(\mathbf{x})$ are 0d-homogeneous (0dH) or equivalently intensive, i.e., $A_i(\alpha \mathbf{x}) = A_i(\mathbf{x})$. Computing the partial derivative of $f(\mathbf{x})$ in Eq. (5) with respect to x_j , we obtain

$$\frac{\partial f(\mathbf{x})}{\partial x_j} = A_j(\mathbf{x}) + \sum_{i=1}^q x_i \frac{\partial A_i(\mathbf{x})}{\partial x_j}, \quad (6)$$

implying

$$\sum_{i=1}^q x_i \frac{\partial A_i(\mathbf{x})}{\partial x_j} = 0. \quad (7)$$

As can be seen, Eq. (7) is satisfied by any 1dH-function and thus it presents another characteristic relation of the former class of functions. In fact, Eq. (7) presents a set of q conditions, since $j = 1, \dots, q$.

Now, we want to prove the reverse, namely if Eq. (7) is true, then $f(\mathbf{x})$ is 1dH. Eq. (7) is valid for any translation $\tilde{f}(\mathbf{x})$ of $f(\mathbf{x})$, i.e., $\tilde{f}(\mathbf{x}) = f(\mathbf{x}) + c$, where c is a constant, so that $\tilde{A}_i(\mathbf{x}) := \partial \tilde{f}(\mathbf{x})/\partial x_i = \partial f(\mathbf{x})/\partial x_i = A_i(\mathbf{x})$. Multiplying Eq. (7) by dx_j and then summing over all j 's in the aforementioned equation yields

$$\sum_{j=1}^q \sum_{i=1}^q x_i \frac{\partial \tilde{A}_i(\mathbf{x})}{\partial x_j} dx_j = \sum_{i=1}^q \sum_{j=1}^q x_i \frac{\partial \tilde{A}_i(\mathbf{x})}{\partial x_j} dx_j = \sum_{i=1}^q x_i d\tilde{A}_i(\mathbf{x}) = 0. \quad (8)$$

The change in the order of the summation in Eq. (8) can be performed, since $\sum_{j=1}^q (\sum_{i=1}^q x_i [\partial \tilde{A}_i(\mathbf{x})/\partial x_j]) dx_j = 0 < \infty < \infty$. Adding the term $\sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i$ in Eq. (8), we obtain

$$\begin{aligned} \sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i &= \sum_{i=1}^q \tilde{A}_i(\mathbf{x}) dx_i + \sum_{i=1}^q x_i d\tilde{A}_i(\mathbf{x}) \Rightarrow \\ d\tilde{f}(\mathbf{x}) &= d\left(\sum_{i=1}^q x_i \tilde{A}_i(\mathbf{x})\right) \Rightarrow \tilde{f}(\mathbf{x}) = \sum_{i=1}^q x_i \tilde{A}_i(\mathbf{x}) + a \Rightarrow \\ f(\mathbf{x}) &= \sum_{i=1}^q x_i A_i(\mathbf{x}) + (a - c), \end{aligned} \quad (9)$$

where a is an integration constant. We can always choose $c = a$, so that Eq. (9) is identified with Eq. (5). Herewith, we have proven that the conditions in Eq. (7) are necessary and sufficient conditions for having 1d-homogeneity. Thus, they can be considered as an alternative definition of 1dH-functions. An important consequence of Eq. (7) (or equivalently Eq. (8)) is that the differential of the function $f(\mathbf{x})$ is exact

$$df(\mathbf{x}) = \sum_{i=1}^q A_i(\mathbf{x}) dx_i + \sum_{i=1}^q x_i dA_i(\mathbf{x}) \stackrel{(8)}{=} \sum_{i=1}^q A_i(\mathbf{x}) dx_i = \sum_{i=1}^q \frac{\partial f(\mathbf{x})}{\partial x_i} dx_i, \quad (10)$$

implying simply, that there are indeed functions satisfying Eq. (3).

It is also worth remarking that Eq. (7) can be rewritten as $\sum_{i=1}^q x_i [\partial A_j(\mathbf{x})/\partial x_i] = 0$, because of the equality $\partial A_i(\mathbf{x})/\partial x_j = \partial A_j(\mathbf{x})/\partial x_i$ which holds true for any $C^{n \geq 2}$ -function. One can easily verify that the former equation is the respective result of Eq. (5) for 0dH functions. It becomes obvious then that Eq. (7) fully characterizes both the 1dH-function $f(\mathbf{x})$ and the 0dH-functions $A_i(\mathbf{x})$ simultaneously.

III. CLAUSIUS ENTROPY FOR OPEN SYSTEMS

We now make use of the results presented in the previous section on 1dH- and 0dH-functions to model thermodynamic quantities, considering three independent variables, i.e. U , V and N . Further, we assume a 1dH-function $S = S(U, V, N)$ as the thermodynamic entropy. Then, according to Eq. (5), S can be expressed as follows

$$S(U, V, N) = \frac{1}{T(U, V, N)}U + \frac{P(U, V, N)}{T(U, V, N)}V - \frac{\mu(U, V, N)}{T(U, V, N)}N, \quad (11)$$

where

$$\begin{aligned} \frac{1}{T(U, V, N)} &:= \frac{\partial S(U, V, N)}{\partial U}, & \frac{P(U, V, N)}{T(U, V, N)} &:= \frac{\partial S(U, V, N)}{\partial V}, \\ \frac{\mu(U, V, N)}{T(U, V, N)} &:= -\frac{\partial S(U, V, N)}{\partial N}. \end{aligned} \quad (12)$$

In thermodynamics, Eq. (11) is referred to as the *Euler equation* [12]. The left hand side of the definitions in Eq. (12) are thermodynamic observables, where μ denotes the chemical potential. All thermodynamic observables must be 0dH-functions (intensive), since otherwise the assumption of S being 1dH (extensive) cannot hold true. As shown in the previous section, S has to satisfy the conditions in Eq. (7). In the thermodynamic notation the former conditions take the form

$$U \frac{\partial}{\partial U} \frac{1}{T} + V \frac{\partial}{\partial U} \frac{P}{T} - N \frac{\partial}{\partial U} \frac{\mu}{T} = 0, \quad (13a)$$

$$U \frac{\partial}{\partial V} \frac{1}{T} + V \frac{\partial}{\partial V} \frac{P}{T} - N \frac{\partial}{\partial V} \frac{\mu}{T} = 0, \quad (13b)$$

$$U \frac{\partial}{\partial N} \frac{1}{T} + V \frac{\partial}{\partial N} \frac{P}{T} - N \frac{\partial}{\partial N} \frac{\mu}{T} = 0. \quad (13c)$$

If the 0dH-functions P, T and μ satisfy Eq. (13), then the differential of S is exact yielding the well-known first law of thermodynamics

$$T dS = dU + P dV - \mu dN, \quad (14)$$

which is also the conservation of energy [13].

Considering the relations in Eq. (13) simultaneously, they can be written as

$$U d\left(\frac{1}{T}\right) + V d\left(\frac{P}{T}\right) - N d\left(\frac{\mu}{T}\right) = 0. \quad (15)$$

We identify Eq. (15) with the well known *Gibbs-Duhem relation* [14].

Let us now explore the conditions in Eq. (13) for the case of an ideal monoatomic gas in an open system, $dN \neq 0$. The expressions of pressure and temperature are given by

$$P(U, V, N) = P(U, V) = \frac{2U}{3V}, \quad T(U, V, N) = T(U, N) = \frac{2U}{3k_B N}. \quad (16)$$

The pressure in Eq. (16) has been derived within the kinetic gas theory. The temperature in Eq. (16), within classical thermodynamics, presents an *ad hoc* definition, being compatible with the equation of state for the ideal gases, i.e., $PV = k_B NT$. Indeed, combining P and T in Eq. (16) one obtains the former equation of state. Apparently, the functions P and T are 0dH. In the mathematically trivial case of constant pressure and temperature, $dP = 0 = dT \Rightarrow U \sim N$ and $V \sim N$, Eq. (13) yields a constant chemical potential μ . In this case, the respective entropy function in Eq. (11) is 1dH and linear with respect to N , i.e., $S(U, V, N) = S(N) \sim N$. For the general case of varying pressure and temperature i.e. $dP \neq 0$ and $dT \neq 0$, from Eq. (13), we read

$$\frac{\partial}{\partial U} \mu(U, V, N) = \frac{1}{U} \mu(U, V, N) - \frac{1}{N}, \quad (17a)$$

$$\frac{\partial}{\partial V} \mu(U, V, N) = -\frac{2U}{3VN}, \quad (17b)$$

$$\frac{\partial}{\partial N} \mu(U, V, N) = -\frac{1}{N} \mu(U, V, N) + \frac{5U}{3N^2}, \quad (17c)$$

respectively. Solving this system of differential equations, we are able to determine the expression of the chemical potential compatible with Eqs. (14) and (16). The aforementioned system can be solved stepwise. We first solve Eq. (17a). The result will depend on an integration constant $Z(V, N)$, with respect to U . Then, plugging the former result into Eq. (17b), $Z(V, N)$ reduces to an integration constant $Z'(N)$. Finally, following the same procedure with Eq. (17c), $Z'(N)$ reduces to a constant, which cannot be further reduced. Thus, for varying pressure and temperature, the monoatomic ideal gas chemical potential is determined apart from a constant ξ as

$$\mu(U, V, N) = \frac{U}{N} \left[\xi + \ln \left(\frac{N}{U} \right) + \frac{2}{3} \ln \left(\frac{N}{V} \right) \right]. \quad (18)$$

As expected, the μ -function is 0dH. The respective entropy function S in Eq. (11) is then 1dH, given as

$$S(U, V, N) = k_B N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} \xi \right]. \quad (19)$$

Studying the validity of S , we observe that the function S in Eq. (19) can be derived by means of the 1d-homogeneity formalism when $P, T, \mu \neq \{0, \text{const.}, \pm\infty\}$, beforehand, and when $dU \neq 0$, $dV \neq 0$ and $dN \neq 0$, simultaneously. If one of the former differentials is equal to zero, implying that the respective variable is a constant, then the 1d-homogeneity formalism is not applicable, since in this case not all of the partial derivatives of S , i.e., $1/T$, P/T or μ/T are 0dH.

Comparing now the Clausius ideal gas entropy S in Eq. (19) with the Sackur-Tetrode entropy S_{ST} in Eq. (1), we observe that they are the same when ξ takes the value $\xi = \ln \left(\frac{3h^2}{4\pi m} \right)$. This specific expression of ξ cannot be obtained by virtue of the 1d-homogeneity analysis but only within quantum statistical mechanics.

Before closing this section, we note that Eq. (19) can also be found in [15] where the thermodynamic extensivity is implicitly assumed, and not focused in detail.

IV. ON GIBBS PARADOX

We now explore the implications of the derived thermodynamic results on the Gibbs paradox. If one compares Eq. (19) with the usual expression found in the textbooks i.e., Eq. (1), one is inclined to consider that the only difference lies in the additive term including the Planck constant. This would still not be a major difference in the sense that this additive term would be washed out when one considers the entropy change, so that it cannot be important for the resolution in Gibbs paradox. In other words, quantum mechanics might be interesting to fully determine the entropy expression, but it is irrelevant considering the entropy changes and hence for the Gibbs paradox.

On the other hand, this is not the whole story, since Eq. (19) is derived by assuming a nonconstant temperature (making its direct application to Gibbs paradox untenable, since Gibbs paradox assumes constant temperature) contrary to Eq. (1). As a matter of fact, the thermodynamic formulation of the previous section indicates that for constant (T, P, N) just as required by Gibbs paradox for each compartment, we have $S(U, V, N) = S(N) \sim N$, since one then concludes that $\frac{U}{V}$ and $\frac{U}{N}$ are constant (so is then $\frac{V}{N}$) as can be seen from Eq. (16). Note that this information on the entropy expression is enough to understand that the thermodynamic entropy change is zero for the Gibbs paradox, indicating reversibility of the process [16]. This proportionality i.e., $S(N) \sim N$, is indeed what one concludes also from Eq. (1), considering that it is derived under the assumption of fixed T and N , since one then has $U \sim N$ and $V \sim N$. Therefore, the terms $\frac{U}{N}$ and $\frac{V}{N}$ can be considered as a constant, hence the sole term of importance is proportionality to N , namely, $S_{\text{ST}} \sim k_B N$. It is worth remarking that the rigorous thermodynamic treatment in the previous section is far more general than the usual textbook treatments so that Eq. (19) is more general than Eq. (1) in its scope of applications if one does not consider the quantum-mechanical additive term.

Another important difference is concerning the thermodynamic limit. The present thermodynamic treatment shows no need for the thermodynamic limit, whereas Eq. (1) is derived in the thermodynamic limit as all other resolutions of Gibbs paradox. To shed light on this issue, namely whether phenomenological thermodynamics implicitly contains the thermodynamic limit, or equivalently whether S and S_{ST} are identical, we consider the general solution (gs) of the first law of thermodynamics in Eq. (14), regarding the ideal gas entropy function.

The latter is given as in Eq. (19), with the ξ -term being a function of N , i.e., $\xi \rightarrow \Theta(N)$, namely

$$S_{\text{gs}}(U, V, N) = k_B N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} \Theta(N) \right]. \quad (20)$$

In this general case, the chemical potential, $\mu_{\text{gs}} = -T(\partial S_{\text{gs}}/\partial N)$, may generally not preserve the 0dH property. From Eqs. (1) and (20), we observe that in the case of ST-entropy the Θ -function in finite systems is inhomogeneous and

has the explicit expression

$$\Theta_{\text{ST}}(N) = \xi + \frac{2}{3} \left[1 - \ln(N) + \frac{\ln(N!)}{N} \right], \quad (21)$$

satisfying the $\lim_{N \rightarrow \infty} \Theta_{\text{ST}}(N) = \xi$ limit. Let us then explore the most general expression of $\Theta(N)$ compatible with 1d-homogeneity, $S_{\text{gs}} \rightarrow S_{\text{gs}}^{\text{1dH}}$ (and $\mu_{\text{gs}} \rightarrow \mu_{\text{gs}}^{\text{0dH}}$). Therefore, we compute again the conditions in Eq. (13), in terms of S_{gs} now. From the first two conditions we do not obtain any new information, yet the last one yields

$$N \frac{\partial^2 \Theta(N)}{\partial N^2} + 2 \frac{\partial \Theta(N)}{\partial N} = 0 \quad \Rightarrow \quad \Theta(N) = a_1 - \frac{a_2}{N}, \quad (22)$$

where a_1 and a_2 are integration constants. Plugging the result in Eq. (22) into Eq. (20), we obtain

$$\begin{aligned} S_{\text{gs}}^{\text{1dH}}(U, V, N) &= \frac{1}{T(U, V, N)} U + \frac{P(U, V, N)}{T(U, V, N)} V - \frac{\mu_{\text{gs}}^{\text{0dH}}(U, V, N)}{T(U, V, N)} N + \frac{3}{2} k_{\text{B}} a_2 \\ &= k_{\text{B}} N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{U}{N} \right) + \frac{5}{2} - \frac{3}{2} a_1 \right] + \frac{3}{2} k_{\text{B}} a_2, \end{aligned} \quad (23)$$

where $\mu_{\text{gs}}^{\text{0dH}} = \mu$ in Eq. (18) with $a_1 \equiv \xi$. Comparing Eqs. (19) and (23), it becomes obvious that $S_{\text{gs}}^{\text{1dH}}$ contains an extra additive constant. However, in Eq. (9) we showed that such a constant can always be transformed away. Thus, the $\frac{3}{2} k_{\text{B}} a_2$ -term has neither physical nor mathematical impact on $S_{\text{gs}}^{\text{1dH}}$ so that the former is identified with S in Eq. (19). Eq. (22) then unveils that the thermodynamic limit is *not* included in the phenomenological thermodynamic equations. If it would be included, then the a_2 -term would not appear, $\lim_{N \rightarrow \infty} a_2/N = 0$. Accordingly, the Clausius 1dH entropy function S in Eq. (19), derived by means of purely thermodynamic relations, is distinct from the 1dH ST-entropy, derived within statistical mechanics in Eq. (1).

Although we have discussed the discrepancy related to the thermodynamic limit above only for the case of ST-entropy, the main *morale* can be readily applied to all textbook attempts of resolving Gibbs paradox, since all of them, in bridging the gap between thermodynamics and statistical mechanics, make use of the thermodynamic limit argument. However, it is evident from the discussions so far that thermodynamics does not invoke thermodynamic limit at all, whereas statistical mechanics depends on it to yield the same results obtained in thermodynamics. In this sense, the division by $N!$ in Eq. (1) seems to be *ad hoc* even though it is said to be justified by arguments regarding classical or quantum mechanical statistical mechanics, since the thermodynamics by itself does not invoke any such limit.

Turning our attention to the statistical mechanics now, we can analyze whether a statistical description without thermodynamic limit is possible at all. If possible, this description must be valid independent of the number of degrees of freedom. Therefore, a thermodynamically consistent choice among the statistical definitions of entropy is in order. For this purpose, we consider the entropy in terms of the phase space volume S_{Φ} as an example. The volume of the phase space for the ideal gas reads [1]

$$\Phi(U, V) = C_{3N} \left[\frac{V}{h^3} (2mU)^{3/2} \right]^N, \quad (24)$$

where $C_{3N} = \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}$. The $\Gamma(x)$ in the denominator represents the gamma function with the argument x . In order to obtain the volume entropy, it suffices to take the logarithm of the phase space volume, and multiply it by the Boltzmann constant k_{B} so that

$$S_{\Phi}(U, V) = k_{\text{B}} \ln(A) + N k_{\text{B}} \ln(V) + \frac{3N k_{\text{B}}}{2} \ln(U), \quad (25)$$

where A is a constant depending on h , m and N . The thermodynamics of the system can be calculated by taking partial derivative of the volume entropy with respect to extensive variables i.e., energy U and volume V . The first partial derivative evidently provides the expression for the temperature i.e.,

$$T_{\Phi} = \left(\frac{\partial S_{\Phi}(U, V)}{\partial U} \right)^{-1} = \frac{2U}{3N k_{\text{B}}}. \quad (26)$$

The subscript Φ indicates that the quantities are calculated by using the volume entropy. The partial derivative of the volume entropy with respect to extensive variable V provides the equation of state for the ideal gas

$$\frac{P_{\Phi}}{T_{\Phi}} = \frac{\partial S_{\Phi}(U, V)}{\partial V} = \frac{Nk_{\text{B}}}{V}. \quad (27)$$

It is very important to realize that all the equations above, the equation of state and the temperature for the ideal gas, are obtained in terms of the volume entropy without invoking the thermodynamic limit. Moreover, combining Eqs. (26) and (27), we can also obtain

$$P_{\Phi}(U, V) = \frac{2U}{3V}. \quad (28)$$

The inspection of Eqs. (26) and (28) shows that they are exactly the same as Eq. (16). This shows that, contrary to the widely held view, the statistical treatments do not *only* have to be valid for large number of particles although the same expressions are obtained in phenomenological thermodynamics for macroscopic systems (or through kinetic theory). We also note that the equipartition theorem, $\frac{kT}{2} = \left\langle \frac{p^2}{2m} \right\rangle$, which defines the kinetic temperature in terms of the microcanonical probability density average is also valid independently of the number of degrees of freedom if one uses the volume entropy S_{Φ} [17, 18].

We emphasize again that all these nice results are obtained without the thermodynamic limit. Therefore, it is natural to ask where the thermodynamic limit is needed if it is needed at all. Despite the results so far, it is easy to see that even the volume entropy falls short of being the thermodynamic Clausius entropy, since it is not extensive as can be seen from Eq. (25). One must instead have a term $\frac{V}{N}$ so that one can also resolve the Gibbs paradox in terms of a statistical entropy expression i.e., the volume entropy in this case. Due to Eq. (24), one sees that dividing the volume V by N is tantamount to dividing the phase space volume Φ by N^N . Therefore, if thermodynamics does not include the thermodynamic limit, the equivalence between the thermodynamic and statistical entropies requires the division of the phase space volume by N^N . However, assuming that the statistical physics is valid for large number of particles only, the term N^N is approximated by the Stirling approximation, namely, $N^N \sim e^N N!$. Then, all the previous thermodynamic equalities such as the definition of temperature and ideal gas state equation remain valid also within Stirling approximation, since they have been valid for any number of particles to begin with. In addition to this, one resolves the Gibbs paradox in the thermodynamic limit by relying on the Stirling approximation.

On the other hand, the thermodynamic entropy is extensive without thermodynamic limit as shown in the previous section, since the definition of extensivity in thermodynamics is rigorously defined as a mathematical property without a limiting procedure. Therefore, a true equivalence can only be constructed by finding a way to divide the phase space volume by N^N as a result of mixing in Gibbs scenario without making use of the thermodynamic limit. Otherwise, one either defines a new reduced statistical entropy, and maintains that it is the same as the thermodynamical one [6] only in the thermodynamic limit, or defends the view that the statistical mechanical second law is different than the thermodynamical one [3].

V. CONCLUSIONS

We have shown that the Clausius i.e. thermodynamic entropy of a monoatomic ideal gas in its most general form (including open systems) can be obtained by taking the property of extensivity as the point of departure. This thermodynamic entropy expression seems not to differ from the statistical ST-entropy apart from an additive quantum-mechanical term, which can be neglected when one considers the change in entropies as required by the second law of thermodynamics. Therefore, we conclude that the quantum mechanical arguments should not play a decisive role in the resolution of Gibbs paradox, since one considers the thermodynamic second law in its resolution, rendering the constant additive terms unimportant. Note that the irrelevance of the quantum mechanics for the Gibbs paradox can also be argued by observing that the narrow wave packets too can follow almost classical trajectories, and hence they can be considered to be distinguishable (see Ref. [3] for more on this issue).

Another important difference between thermodynamics and statistical mechanics concerning the Gibbs paradox is that the former does not invoke the thermodynamic limit whereas the latter does. In other words, even though one can justify the usual division by $N!$ in statistical mechanics (be it quantum or classical arguments), this does not warrant a resolution of Gibbs paradox, if the paradox is accepted to stem from the comparison between the thermodynamic and statistical second laws. The reason is that the thermodynamic entropy conforms to the second law for reversible processes independent of the number of degrees of freedom, whereas the statistical entropy measure succeeds at this

only in the thermodynamic limit (note that even ST-entropy is obtained in statistical mechanics by appeal to the thermodynamic limit). An exact equivalence between the thermodynamics and statistical mechanics concerning the Gibbs paradox can be achieved fully either through dividing the volume V by N , or equivalently, the phase space volume Φ by N^N , not by the term $N!$ which requires the thermodynamic limit.

Finally, we remarked that some important thermodynamical equations such as the definition of temperature and the equation of state for the ideal gas can be derived in statistical mechanics just as in thermodynamics i.e. without invoking the thermodynamic limit by adopting the volume entropy S_Φ . However, even in this case, one is forced to find a justification for dividing the volume V by N (or equivalently, the phase space volume Φ by N^N), or accept that the statistical entropy expression is not the same as the thermodynamic Clausius definition.

Although we have mainly focused on the mathematical structure of the thermodynamics and its relation to the statistical mechanics with an emphasis on the Gibbs paradox in particular, it is worth noting that the thermodynamics is phenomenological and therefore of experimental nature. For this aspect of the thermodynamics and its possible relation to the resolution of the Gibbs paradox, we refer the interested reader to Ref. [19].

Acknowledgments

We thank Sumiyoshi Abe for fruitful discussions and Joshua T. Berryman for corrections in English. T.O. acknowledges partial support by the THALES Project MACOMSYS, funded by the ESPA Program of the Ministry of Education of Hellas.

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