

Is Equilibrium Always an Entropy Maximum?¹

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A systematic development is given of the view that in the case of systems with long-range forces and which are therefore nonextensive (in some sense) some thermodynamic results do not hold. Among these is the relation $U - TS + pv = \mu N$ and the Gibbs–Duhem equation. If a search for an equilibrium state is made by maximization of the entropy one may obtain misleading results because superadditivity may be violated. The considerations are worked out for a simple gas model, but they are relevant to black hole thermodynamics. Rather general conclusions can be drawn which transcend special systems.

KEY WORDS: Concavity; non-extensivity; superadditivity; thermodynamic functions.

1. INTRODUCTION

The failure of some thermodynamic results, normally taken to be standard for black hole and other nonextensive systems has recently been discussed.⁽¹⁻³⁾ A unified presentation which incorporates new points is given here.

Consider two thermodynamic systems with similar thermodynamic equations of state. One may think of two ideal gasses, two van der Waals gases, two black holes which are perhaps *both* nonrotating and uncharged, or which are *both* charged and rotating. When such systems are allowed to merge some of their variables are subject to additive conservation laws. For a gas these variables are energy U , volume v , and the number of identical

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particles N . Thus, after merging systems A and B into one system, this system has in an obvious notation values of these variables which are given by

$$\mathbf{X}_{A+B} = \mathbf{X}_A + \mathbf{X}_B, \quad \mathbf{X} \equiv (U, v, N) \quad (1.1)$$

Such variables may be called *extensities*.⁽¹⁾ For black hole systems there are also three extensities, namely, the mass M , the angular momentum J , and the charge Q . Thus

$$\mathbf{X} = (M, J, Q) \quad (1.2)$$

The gas and the black hole system differ in an important respect.

The entropy of a Kerr–Newman black hole is given by

$$S_b = \frac{\pi k}{\hbar c} \left\{ 2GM^2 - Q^2 - 2[G^2M^4 - c^2J^2 - GM^2Q^2]^{1/2} \right\} \quad (1.3)$$

where G is Newton's gravitational constant, k is Boltzmann's constant, c is the velocity of light, and \hbar is Planck's constant divided by 2π . For an ideal gas

$$S_g = bkN \ln(aUv^g/N^h) \quad (h = g + 1) \quad (1.4)$$

where a , b , and g are constants. It is readily seen that if two identical gases are merged, the entropy of the merged system is twice the entropy of one of the original systems. Alternatively expressed, if the two gases were originally in the same equilibrium state, but separated by a partition, the entropy of the two part-systems is unaltered by withdrawal of the partition: the entropy is an extensive variable. For the present purpose⁴ a variable $f(\mathbf{X})$ is extensive if it satisfies for all (positive) a

$$f(a\mathbf{X}) = af(\mathbf{X}) \quad (\mathbf{H}) \quad (1.5)$$

If f represents the entropy and $a = 2$, the left-hand side gives the entropy of the merged system, the right-hand side gives the entropy of the two part-systems.

If two identical black holes are merged, the presence of long-range forces in the form of gravity leads to a more complicated situation, and the entropy is not extensive:

$$S_g(2\mathbf{X}) = 2S_g(\mathbf{X}) \quad (1.6)$$

$$S_b(2\mathbf{X}) \neq 2S_b(\mathbf{X}) \quad (1.7)$$

where an obvious notation has been used. In the *merged* black hole system one has to use $2M$, $2J$, $2Q$ and the relation between $S_b(2\mathbf{X})$ and $S_b(\mathbf{X})$ has

⁴ For a comparison of various definitions see Ref. 4.

to be investigated. It can in fact be shown that

$$S_b(\mathbf{X}_A + \mathbf{X}_B) > S_b(\mathbf{X}_A) + S_b(\mathbf{X}_B) \quad (1.8)$$

This means that the entropy is “*strictly* superadditive,” and this is consistent with (1.7) if one takes $\mathbf{X}_A = \mathbf{X}_B = \mathbf{X}$.

We have arrived at two types of functions: extensive ones in the sense of (1.5) and nonextensive, but strictly superadditive, ones in the sense of (1.8). It is desirable to bridge the gap between these by allowing equality in (1.8). The resulting function will be called “superadditive”:

$$f(X_A + X_B) \geq f(X_A) + f(X_B) \quad (\mathbf{S}) \quad (1.9)$$

This includes the possibilities (1.6) and (1.8). One would expect that an entropy function should be superadditive when two systems are merged.

The functional relations (1.5) and (1.9) have been given the symbols **H** (for homogeneity of order 1) and **S** (for superadditivity). Logical relations involving them and concavity

$$f(\lambda \mathbf{X}_A + [1 - \lambda] \mathbf{X}_B) \geq \lambda f(\mathbf{X}_A) + (1 - \lambda) f(\mathbf{X}_B) \quad (\mathbf{C}) \quad (1.10)$$

will be discussed in Section 6.

2. THE FOURTH LAW OF THERMODYNAMICS

The circumstance that the main variables of thermodynamics in the absence of long-range forces are intensive or extensive, cannot be deduced from the so-called “laws” of thermodynamics. Nonetheless it is a very important characteristic of “normal” thermodynamic systems, and that is why it was recognized as such long ago, before the advent of black holes.^(5,6) It was labeled the fourth law of thermodynamics, though few people have commented on this suggestion, P. G. Wright⁽⁷⁾ and Kestin⁽⁸⁾ being exceptions. Thus black holes lead one to consider the implications of the failure of the fourth law in these systems. In any case, any treatment of “normal” thermodynamics should rule out long-range forces early on in the discussion. Anyone who wants to check carefully which parts of thermodynamics may, or may not, be used when long-range forces play a part will find little in the archival literature. This paper seeks to alleviate this situation by giving the following example.

Assuming (1.5),

$$S^{(a)} \equiv S(aU, av, AN) = aS^{(1)} \quad (2.1)$$

Differentiating with respect to a , using $d(aU)/da = U$, etc., and also

$$\left[\partial S^{(a)} / \partial (aU) \right]_{v,N} = \left[\partial S^{(1)} / \partial U \right]_{v,N} = 1/T, \quad \text{etc.} \quad (2.2)$$

one finds, if μ is the chemical potential,

$$\frac{U}{T} + \frac{pv}{T} - \frac{\mu N}{T} = S^{(1)} \equiv S \quad (2.3)$$

Also

$$T dS = dU + p dv - \mu dN \quad (2.4)$$

Let the Gibbs free energy be defined by

$$G \equiv U + pv - TS \quad (2.5)$$

Then the fourth law in the form (2.1) has enabled us to deduce in (2.3)

$$G = \mu N \quad (2.6)$$

Also by differentiating (2.3), and combining with (2.4), one obtains the Gibbs–Duhem equation,

$$S dT - v dp + N d\mu = 0 \quad (2.7)$$

Neither (2.6) nor (2.7) can be expected to hold once the fourth law has been jettisoned, as it must be for thermodynamic discussions of black holes.

This leads to the need for a simple model system, or theoretical laboratory, to investigate this matter. In order not to be side-tracked by black hole peculiarities let us construct an analogous gas which departs from the ideal gas just enough to violate the fourth law.

3. A GENERALIZED GAS

If b and g are constants let us use from ideal gas theory

$$U = bNkT, \quad pv = gbNkT = gU \quad (3.1)$$

Then

$$\left(\frac{\partial S}{\partial U} \right)_{v,N} = \frac{1}{T} = \frac{bNk}{U} \rightarrow S = bkN \ln U + f_1(v, N) \quad (3.2)$$

$$\left(\frac{\partial S}{\partial v} \right)_{U,N} = \frac{p}{T} = \frac{gbNk}{v} \rightarrow S = gbkN \ln v + f_2(U, N) \quad (3.3)$$

where f_1, f_2 represent constants of integration. One arrives at

$$S = bkN \ln Uv^g + f_3(N)$$

Choose $f_3(N) = -bkN \ln N^h$, where h is a constant. Hence the “theoretical laboratory” will be based on systems with

$$S(\mathbf{X}) = bkN \ln \frac{aUv^g}{N^h} \quad (3.4)$$

Three cases arise⁽²⁾:

$$h < g + 1 \quad (3.5)$$

$$h = g + 1 \quad (3.6)$$

$$h > g + 1 \quad (3.7)$$

The ideal gas corresponds to (3.6) when (1.5) holds and the fourth law is satisfied.

One can verify at once that the chemical potential does not always satisfy (2.6). Using Eqs. (3.1)–(3.4) one finds

$$\left(\frac{\partial S}{\partial N} \right)_{U,v} = - \frac{\mu}{T} = \frac{S}{N} - hbk \quad (3.8)$$

whence

$$\mu N = G + (h - g - 1)U \quad (3.9)$$

Thus (2.6) holds only in the case (3.6). Many other ideal gas relations remain valid. For example, the heat capacities at constant pressure and volume are

$$C_p = (g + 1)U/T, \quad C_v = U/T, \quad C_p/C_v = g + 1 \quad (3.10)$$

Among the amendments needed one finds, starting with (3.9) instead of (2.6), an amended Gibbs–Duhem relation

$$S dT - v dp + N d\mu = (h - g - 1)bk d(NT) \quad (3.11)$$

Thus

$$\left(\frac{\partial \mu}{\partial N} \right)_{T,p} = (h - g - 1)(bkT/N) \quad (3.12)$$

whereas the left-hand side vanishes in normal thermodynamics.

4. ENTROPY MAXIMIZATION: AN UNPHYSICAL RESULT

Consider two generalized gases *A* and *B* separated by a partition. The total entropy is

$$\begin{aligned} S &\equiv S(\mathbf{X}_A) + S(\mathbf{X}_B) \\ &= kbN_A \ln \frac{aU_A v_A^g}{N_A^h} + kb(N - N_A) \ln \frac{a(U - U_A)(v - v_A)^g}{(N - N_A)^h} \end{aligned} \quad (4.1)$$

For an extremum,

$$\left(\frac{\partial S}{\partial U_A} \right)_{v_A, N_A} = \left(\frac{\partial S}{\partial v_A} \right)_{U_A, N_A} = \left(\frac{\partial S}{\partial N_A} \right)_{U_A, v_A} = 0 \quad (4.2)$$

These conditions imply equality of intensive variables. Using (3.2), (3.3) and (3.8),

$$T_A = T_B \rightarrow U_A/bN_A k = U_B/bN_B k \quad (4.3)$$

$$p_A = p_B \rightarrow gU_A/v_A = gU_B/v_B \quad (4.4)$$

$$\mu_A = \mu_B \rightarrow S_A/N_A = S_B/N_B \quad (4.5)$$

One finds from (4.3) and (4.4) the normal and sensible conditions

$$\frac{U_B}{U_A} = \frac{v_B}{v_A} = \frac{N_B}{N_A} \quad (\equiv \lambda) \quad (4.6)$$

Inserting this into (4.5) a new and unexpected condition is found:

$$\mu_A - \mu_B = bkT_A(g + 1 - h)\ln \lambda \quad (4.7)$$

In the nonextensive cases (3.5), (3.7) an extremum requires a specific value of λ , namely, $\lambda = 1$, so that for an extremum to be possible for the function (4.1) with respect to X_A , one needs $X_A = X_B$. In other cases the conditions for an extremum are not satisfied.

This seems a rather unphysical result since one may have pairs of systems with other λ values. The unphysical nature of this result is confirmed below. First evaluate (4.1) using (4.6) with $\lambda = 1$. One finds the entropy at the extremum to be

$$S_i = bkN[(h - g - 1)\ln 2 + \ln aUv^g/N^h]$$

The subscript i stands for "initial" with the separating partition in position. Upon withdrawal of the partition the final entropy is exactly (3.4), U, v, N being the total values of the extensivities in the sense of (1.1). Hence

$$S_f - S_i = -bkN(h - g - 1)\ln 2 \quad (4.8)$$

Thus

$$\left. \begin{array}{l} \text{the entropy rises upon merging only if } h < g + 1, \\ \text{it falls if } h > g + 1 \end{array} \right\} \quad (4.9)$$

To ensure the extremum is a maximum the quantity (4.1) must satisfy three further conditions at the extremum (4.6) with $\lambda = 1^{(1)}$:

$$\left(\frac{\partial^2 S}{\partial U_A^2} \right)_{v_A, N_A} < 0, \quad \left| \begin{array}{cc} \partial^2 S / \partial U_A^2 & \partial^2 S / \partial U_A \partial v_A \\ \partial^2 S / \partial v_A \partial U_A & \partial^2 S / \partial v_A^2 \end{array} \right| > 0 \quad (4.10)$$

$$\left| \begin{array}{ccc} \partial^2 S / \partial U_A^2 & \partial^2 S / \partial U_A \partial v_A & \partial^2 S / \partial U_A \partial N_A \\ \partial^2 S / \partial v_A \partial U_A & \partial^2 S / \partial v_A^2 & \partial^2 S / \partial v_A \partial N_A \\ \partial^2 S / \partial N_A \partial U_A & \partial^2 S / \partial N_A \partial v_A & \partial^2 S / \partial N_A^2 \end{array} \right| < 0 \quad (4.11)$$

There is no problem about the conditions (4.10) which are identically fulfilled for our gas:

$$-2bkN_A/U_A^2 < 0, \quad g(2bkN_A/U_A v_A)^2 > 0 \quad (4.12)$$

(4.12) may be reinterpreted in the more familiar form

$$\frac{1}{C_{A,v} T_A^2} > 0, \quad \frac{1}{T_A} \left(\frac{\partial p_A}{\partial v_A} \right)_{T_A, N_A} > 0 \quad (4.13)$$

which one obtains if one is not committed to a particular equation of state. The third condition, i.e. (4.11), leads to $h > g + 1$ since it requires

$$\frac{8gb^3k^3N_A}{U_A^2 v_A^2} (g + 1 - h) < 0 \quad (4.14)$$

Using (3.12) it may be interpreted to mean

$$(\partial \mu_A / \partial N_A)_{T_A, P_A} > 0 \quad (4.15)$$

There is sufficient repulsion between the particles for the chemical potential at constant temperature and pressure to increase upon addition of a particle.

The condition for an extremum led to (4.9). The condition for a maximum fastens on to the second case, namely, (3.7). Thus on merging of the two identical systems the entropy drops, and this is unphysical. After all, the removal of a constraint is expected to increase the entropy. Against one's expectation the determinantal condition did not pick out the first case (4.9) which would seem more physical.

In the case (3.6) of an extensive entropy no complications arise: λ in (4.6) can be left general, the condition (4.7) is automatically fulfilled and so are the determinantal conditions.

5. ENTROPY SUPERADDITIVITY

The last case (4.9) is ruled out if we adopt the view that superadditivity of the entropy for the whole range of the variables \mathbf{X}_A is a key requirement, overriding, if necessary, entropy maximization. To find the condition for superadditivity consider

$$F(\mathbf{X}_A) \equiv S(\mathbf{X}) - S(\mathbf{X}_A) - S(\mathbf{X} - \mathbf{X}_A) \quad (5.1)$$

for the system (3.4). One requires $F(\mathbf{X}_A) \geq 0$ and finds

$$\exp \left[- \frac{F(\mathbf{X}_A)}{bkN} \right] = \left[\frac{u(\alpha, \gamma)}{u(\gamma, \gamma)} \right]^\gamma \left[\frac{u(\beta, \gamma)}{u(\gamma, \gamma)} \right]^{g\gamma} u(\gamma, \gamma)^{(g+1-h)\gamma} \leq 1 \quad (5.2)$$

Table 1. Summary of Properties of Generalized Ideal Gas^a

I	II	III	IV
$\mu N - G, (\partial \mu / \partial N)_{T,p}$ Entropy	$h < g + 1$ Negative Nonextensive	$h = g + 1$ Zero Extensive	$h > g + 1$ Positive Nonextensive
Results of entropy maximization	A strict maximum of S does not exist, since (4.11) fails	A strict maximum exists if $\frac{U_B}{U_A} = \frac{v_B}{v_A} = \frac{N_B}{N_A} (\equiv \lambda)$	As in column III but $\lambda = 1$ is needed
On merging two identical systems	Entropy increases	Entropy stays constant	Entropy falls; see (4.8)
Superadditivity of S	Satisfied for all \mathbf{X}_A with inequality ($\mathbf{X}_A \neq 0, \mathbf{X}$)	Satisfied for all \mathbf{X}_A with equality	Not satisfied for all \mathbf{X}_A
Functional relations	\bar{H}, \bar{C}, S	H, C, S	\bar{H}, C, \bar{S}
Comments	Two systems of this type coalesce. The sign of C_c as a condition for an extremum is irrelevant	Normal gas	Entropy maximization has led to an unphysical result.

^aEntropy, S_c , of two part-systems A and B , given by (4.1), is considered as a function of $\mathbf{X}_A = (U_A, v_A, N_A)$, $\mathbf{X}_A + \mathbf{X}_B = (U, v, N)$ being fixed.

Here

$$\alpha \equiv \frac{U_A}{U}, \quad \beta \equiv \frac{v_A}{v}, \quad \gamma \equiv \frac{N_A}{N}$$

and

$$u(\alpha, \gamma)^\gamma \equiv \alpha^\gamma (1 - \alpha)^{1-\gamma}$$

The function u satisfies⁽²⁾

$$u(\alpha, \gamma) \leq u(\gamma, \gamma)$$

and the function $u(\gamma, \gamma)$ has the value unity at $\gamma = 0, 1$ and a minimum $u(\frac{1}{2}, \frac{1}{2}) = \frac{1}{2}$. Thus, exponents apart, each factor in the central term of (5.2) lies between 0 and 1. Thus (5.2) is satisfied for whole range of \mathbf{X}_A 's values if

$$h \leq g + 1 \tag{5.3}$$

This is the physically more realistic first option in (4.9). For equality in (5.2) one needs $\alpha = \beta = \gamma$ and $h = g + 1$. This is identical to (4.6) with λ unspecified. Thus for an extensive entropy function entropy maximization and the superadditivity condition yield identical results.

Let us now take $h = g = 1$ for simplicity. Such a generalized gas has a *strictly* superadditive entropy; it violates the condition for a maximum in the entropy of two separated systems as a function of \mathbf{X}_A . Two such systems therefore merge with an increase in entropy just as in the black hole case. Maximization of the entropy leads to the unphysical possibility of an equilibrium state between the systems only because superadditivity of the entropy is not ensured in this procedure.

A summary of the properties of the gas is given in Table I. Here $\bar{\mathbf{H}}$ means that the expression for S is *not* homogeneous of first order in \mathbf{X}_A according to (1.5), while \mathbf{H} means that it is. A similar notation is used with respect to (1.9) and (1.10). We repeat our earlier assertion⁽¹⁾ that superadditivity must take the place of concavity (or maximization) when these two conditions cannot both be true.

6. CONCLUSIONS

The generalized gas has now served its purpose and it is desirable to summarize the theoretical situation in general, without reference to it.

We first observe that for continuous function the three principles introduced in Section 1 are related by⁽³⁾

$$\mathbf{C} + \mathbf{S} \rightarrow \mathbf{H} \tag{6.1}$$

The proof notes that by concavity (1.10) with $\lambda = n^{-1}$, $\mathbf{X}_A = \mathbf{Y}$ and $\mathbf{X}_B = 0$

implies

$$S(n^{-1}\mathbf{Y}) \geq n^{-1}S(\mathbf{Y}) \quad (6.2)$$

On the other hand, superadditivity (1.9) with $\mathbf{X}_A = \mathbf{X}_B$ applied repeatedly implies $S(n\mathbf{X}) \geq nS(\mathbf{X})$, i.e., with $n\mathbf{X} = \mathbf{Y}$,

$$S(\mathbf{Y}) \geq nS(n^{-1}\mathbf{Y}) \quad (6.3)$$

From (6.2) and (6.3)

$$S(n\mathbf{X}) = nS(\mathbf{X}) \quad (6.4)$$

whence \mathbf{H} given by (1.5) follows by extending (6.4) first to rational multiples of \mathbf{X} and then to all multiples. Given that the thermodynamic functions to be considered are continuous in their arguments, it follows that if \mathbf{H} fails then \mathbf{C} and \mathbf{S} cannot both be true. The following eight logical possibilities may therefore be enumerated for a thermodynamic system:

$$\begin{array}{cccc} \boxed{(\mathbf{S}, \mathbf{H}, \mathbf{C})} & \underline{(\mathbf{S}, \bar{\mathbf{H}}, \mathbf{C})} & \underline{(\mathbf{S}, \mathbf{H}, \bar{\mathbf{C}})} & \boxed{(\mathbf{S}, \bar{\mathbf{H}}, \bar{\mathbf{C}})} \\ \underline{(\bar{\mathbf{S}}, \mathbf{H}, \mathbf{C})} & \boxed{(\bar{\mathbf{S}}, \bar{\mathbf{H}}, \mathbf{C})} & \underline{(\bar{\mathbf{S}}, \mathbf{H}, \bar{\mathbf{C}})} & \underline{(\bar{\mathbf{S}}, \bar{\mathbf{H}}, \bar{\mathbf{C}})} \end{array} \quad (6.5)$$

The three underlined possibilities are logically inconsistent by virtue of, in turn, (6.1) and

$$\mathbf{S} + \mathbf{H} \rightarrow \mathbf{C} \quad (\text{Refs. 9, 10, 1}) \quad (6.6)$$

and

$$\mathbf{C} + \mathbf{H} \rightarrow \mathbf{S} \quad (\text{Refs. 9, 10, 1})$$

If one shares the view,⁽¹⁾ reiterated here, that the essence of the second law resides in superadditivity particularly under conditions (of which nonextensivity is one) when superadditivity and concavity cannot both be true, then the bottom line (6.5) is also ruled out, not on logical but on physical grounds. The three possibilities illustrated in Table I have been boxed, one of them being unphysical, as was noted in the table. There remain only two cases which are acceptable on logical and physical grounds and they have been illustrated in columns II and III of Table I.

The scheme outlined can be applied in various ways. Here we investigate what negative heat capacity, $C < 0$, implies. Note that \mathbf{C} implies $C > 0$ as in (4.13). Hence, using the validity of \mathbf{S} for thermodynamics systems, invert (6.6), $\mathbf{S} + \mathbf{H} \rightarrow \mathbf{C} \rightarrow (C > 0)$, to find the failure of both \mathbf{H} and \mathbf{C} :

$$(C < 0) \rightarrow \bar{\mathbf{H}} \quad \text{and} \quad (C < 0) \rightarrow \bar{\mathbf{C}} \quad (6.7)$$

This result enables one to establish a link with microscopic investigations. Notable among these are those which, studying gravitating fermions, arrive at their well-known property $C < 0$ (see, for example, Refs. 11 and 12). Again systems of high-density hadronic matter, treated by the statistical bootstrap model, also arrive at $C < 0$ (see, for example, Refs. 13 and 14). It has not been put in these papers quite in this way, but one can say about these models that, assuming superadditivity of the entropy function, they must imply lack of homogeneity and concavity of the entropy. The assumption of superadditivity is vital for this statement. It is clearly desirable that these models be examined in detail to see if they are indeed of the type (S, \bar{H}, \bar{C}) in (6.5). Because amendments to normal thermodynamics are brought about by \bar{H} [see, for example, Eq. (3.9)], it is also of interest to examine arguments concerning gravitational phase transitions (see, for example, Ref. 15 and papers cited therein) from the point of view of the present paper.

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