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The zeroth law in quasi-homogeneous thermodynamics and black holes

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ABSTRACT

Motivated by black holes thermodynamics, we consider the zeroth law of thermodynamics for systems whose entropy is a quasi-homogeneous function of the extensive variables. We show that the generalized Gibbs–Duhem identity and the Maxwell construction for phase coexistence based on the standard zeroth law are incompatible in this case. We argue that the generalized Gibbs–Duhem identity suggests a revision of the zeroth law which in turns permits to reconsider Maxwell's construction in analogy with the standard case. The physical feasibility of our proposal is considered in the particular case of black holes.

1. Introduction

The thermodynamics of black holes contains several peculiarities in contrast to standard thermodynamics. One example is the different scaling behaviour when rescaling the thermodynamic variables. This can be directly verified noting that the entropy of a black hole is – in general – a quasi-homogeneous function of the extensive thermodynamic quantities describing the system [1], and its scaling behavior is dictated by the Smarr relation. Such systems are generically called *quasi-homogeneous*. As a consequence, it is usually recognized that using the formalism of homogeneous thermodynamics in the case of black holes is not fully justified and that a modification of the thermodynamic laws for systems with quasi-homogeneous entropy is called for [1].

It has been established that in systems where entropy and energy are not additive the standard way to define equilibrium has to be adjusted and, in such case, the thermodynamic temperature may not be the correct parameter to be equated at equilibrium [2–9]. In spite of this, it has been repeatedly argued in favor of the existence of first order phase transitions – i.e., coexistence processes – within the framework of black hole thermodynamics. Such arguments are based on the analogy with the van der Waals (vdW) phase diagram and use the Maxwell equal area law to find the coexistence curve *as if* the system was homogeneous (see e.g. [1,10–19] and the references therein).

In this work we consider systems whose entropy is a quasi-homogeneous function of the extensive variables and show that Maxwell's equal area law – based on the definition of thermodynamic equilibrium for homogeneous systems (cf. [20] and the discussion in Section 4.3 in [21]) – is inconsistent with the generalized Gibbs–Duhem (GGD) identity that must hold in such cases [22,23]. We show that this situation can be remedied introducing a new set of the variables defining equilibrium. Based on these generalized variables, we propose a definition of thermodynamic equilibrium originating from the GGD identity and we demonstrate that such revision is essential in Maxwell's construction for phase coexistence. It is worth mentioning that our *generalized zeroth law* reduces to the standard definition for homogeneous systems of degree one.

To illustrate our proposal we discuss two relevant cases: on the one hand, we show that for the Schwarzschild black hole the *new* temperature characterizing equilibrium is constant, i.e. it does not depend on its mass M. This coincides (up to a constant factor) with the result in [24], where such parameter is obtained using a gener-

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alized zeroth law for non-extensive statistical mechanics developed in [6]. This proves that, at least in the Schwarzschild case, there is a consistency between different approaches. On the other hand, we consider the first order phase transition in the Kerr–Anti de Sitter (Kerr–AdS) family of black holes and show that the Maxwell construction as applied in the literature leads to a violation of the GGD. Using the new generalized intensive parameters and according to our definition of thermodynamic equilibrium, such transition seems to disappear. Given the importance of this example in the context of the AdS/CFT correspondence, we believe that this can be relevant for future investigations.

This paper is structured as follows. In Section 2 we review the thermodynamics of quasi-homogeneous systems as developed in [22,23]. In Section 3 we point out the aforementioned mathematical inconsistency between Maxwell's construction based on the standard zeroth law of thermodynamics and the Gibbs–Duhem relation in the case of quasi-homogeneous entropy, and continue by proposing a generalized form of the zeroth law, which is consistent with the corresponding GGD relation. To illustrate the new form of the zeroth law, we consider the examples of Schwarzschild and Kerr–AdS black holes in Section 4, before we conclude in Section 5. Throughout this work we use Planck units, in which $c = G = \hbar = k_\mathrm{B} = 1$.

2. Quasi-homogeneous thermodynamics

In this section we briefly review some results of the thermodynamics of quasi-homogeneous systems obtained in [22,23]. Let us start by recalling some definitions. Unless otherwise stated, we will not use Einstein's sum convention.

Definition 2.1 *(Quasi-homogeneous function).* Let $r, \lambda \in \mathbb{R}$, $\lambda \neq 0$ and $\beta = (\beta_1, \dots, \beta_n) \in \mathbb{R}^n$. A function w of a set of variables $\{q^i\}_{i=1}^n$ is said to be *quasi-homogeneous of degree r and type β* if

$$w(\lambda^{\beta_1} q^1, \dots, \lambda^{\beta_n} q^n) = \lambda^r w(q^1, \dots, q^n)\,. \tag{1}$$

The particular case where $\beta_i = 1$ for every value of i yields the standard scaling relation of homogeneous functions of degree r, i.e.

$$w(\lambda q^1, \dots, \lambda q^n) = \lambda^r w(q^1, \dots, q^n)\,. \tag{2}$$

In the following we will use S instead of w, because the function of interest in thermodynamics is the entropy. The variables $\{q^i\}_{i=1}^n$ are the extensive variables of the system, such as internal energy U, volume V or number of particles N. In standard thermodynamics of extensive systems the entropy is a homogeneous function of degree one of the extensive variables, i.e.,

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)\,, \tag{3}$$

while in black holes thermodynamics the entropy is a quasi-homogeneous function as in Definition 2.1.

Proposition 2.1. *Let $S = S(q^1, \dots, q^n)$ be a quasi-homogeneous function of degree r and type β. Then, the conjugate variables to the q^i, defined by*

$$p_i\left(q^j\right) \equiv \frac{\partial}{\partial q^i} S\left(q^j\right)\,, \tag{4}$$

are quasi-homogeneous functions of degree $r - \beta_i$ for every value of i.

Proof.

$$\begin{aligned} p_i\left(\lambda^{\beta_j} q^j\right) &= \frac{\partial}{\partial(\lambda^{\beta_i} q^i)} S\left(\lambda^{\beta_j} q^j\right) = \frac{1}{\lambda^{\beta_i}} \frac{\partial}{\partial q^i}\left[\lambda^r S\left(q^j\right)\right] \\ &= \lambda^{r-\beta_i} \frac{\partial}{\partial q^i} S(q^j)\,. \end{aligned} \tag{5}$$

Therefore

$$p_i\left(\lambda^{\beta_j} q^j\right) = \lambda^{r-\beta_i} p_i(q^j)\,. \quad \square \tag{6}$$

Note that if S is homogeneous of degree $r = 1$ [cf. equation (3) above], then the conjugate variables p_i are homogeneous functions of degree 0, i.e. $p_i(\lambda q^j) = p_i(q^j)$, i.e., they do not change when the system is re-scaled. Only in this case, the conjugate variables are *intensive* and we recover the usual thermodynamic quantities, e.g. $1/T$, p/T, μ/T. In all other cases we shall refer to the conjugate variables p_i as the *would-be intensive* quantities, as in [22,23].

Proposition 2.2 *(Euler's Theorem). Let $S = S(q^1, \dots, q^n)$ be a quasi-homogeneous function of degree r and type β. Then*

$$rS(q^j) = \sum_{i=1}^n \beta_i \left[q^i p_i(q^j)\right]. \tag{7}$$

Proof. Consider the derivative of $S(\lambda^{\beta_j} q^j)$ with respect to the scaling parameter λ. On the one hand, since S is a quasi-homogeneous function of degree r and type β, we have

$$\frac{\partial}{\partial \lambda} S(\lambda^{\beta_j} q^j) = \frac{\partial}{\partial \lambda}\left[\lambda^r S(q^j)\right] = r\lambda^{r-1} S(q^j)\,. \tag{8}$$

On the other hand, a direct calculation yields

$$\begin{aligned} \frac{\partial}{\partial \lambda} S(\lambda^{\beta_j} q^j) &= \sum_{i=1}^n \frac{\partial S(\lambda^{\beta_j} q^j)}{\partial(\lambda^{\beta_i} q^i)} \frac{\partial(\lambda^{\beta_i} q^i)}{\partial \lambda} \\ &= \sum_{i=1}^n \frac{\partial S(\lambda^{\beta_j} q^j)}{\partial(\lambda^{\beta_i} q^i)} \left(\beta_i \lambda^{\beta_i - 1} q^i\right) \\ &= \sum_{i=1}^n \left(\beta_i \lambda^{r-1} q^i\right) p_i(q^j), \end{aligned} \tag{9}$$

where the last equality follows from Definition (4) and Eqs. (5) and (6). Thus, combining the results of (8) and (9), Eq. (7) is obtained. □

In standard thermodynamics the above result reduces to the well-known identity for the entropy,

$$S = \frac{1}{T} U - \frac{p}{T} V + \frac{\mu}{T} N\,. \tag{10}$$

With Proposition 2.2, we can write a GGD relation for the case of quasi-homogeneous thermodynamic systems.

Proposition 2.3 *(Generalized Gibbs–Duhem identity). Let $S(q^1, \dots, q^n)$ be a quasi-homogeneous function of degree r and type β and let $\{p_i\}_{i=1}^n$ be the set of conjugate variables [cf. equation (4)]. Then,*

$$\sum_{i=1}^n \left[\,(\beta_i - r)\, p_i(q^j) \mathrm{d}q^i + \beta_i q^i \mathrm{d}p_i(q^j)\right] = 0\,. \tag{11}$$

Proof. Since S satisfies the hypothesis of Proposition 2.2, let us consider the differential of (7), namely

$$r\mathrm{d}S(q^j)=\sum_{i=1}^{n}\beta_i \mathrm{d}\big[q^i p_i(q^j)\big]\,. \tag{12}$$

The left hand side is simply

$$r\mathrm{d}S=r\sum_{i=1}^{n}\frac{\partial}{\partial q^i}S(q^j)\mathrm{d}q^i=r\sum_{i=1}^{n}p_i(q^j)\mathrm{d}q^i\,, \tag{13}$$

whereas the right hand side yields

$$\sum_{i=1}^{n}\beta_i \mathrm{d}\big[q^i p_i(q^j)\big]=\sum_{i=1}^{n}\beta_i\big[q^i\mathrm{d}p_i(q^j)+p_i(q^j)\mathrm{d}q^i\big]\,. \tag{14}$$

Subtracting (13) from (14) and collecting the β_i produces the desired result. □

In the case where S is homogeneous of degree r, equation (11) reduces to

$$(1-r)\sum_{i=1}^{n}p_i(q^j)\mathrm{d}q^i+\sum_{i=1}^{n}q^i\mathrm{d}p_i(q^j)=0\,. \tag{15}$$

From this result it follows that in standard thermodynamics (with $r=1$), using the appropriate identifications of the variables, one obtains the Gibbs–Duhem relation

$$U\mathrm{d}\left(\frac{1}{T}\right)-V\mathrm{d}\left(\frac{p}{T}\right)+N\mathrm{d}\left(\frac{\mu}{T}\right)=0\,, \tag{16}$$

which is a mathematical identity stating that the intensive quantities are not all independent in equilibrium [20].

3. A mathematical inconsistency and its possible resolution

In this section we prove the mathematical inconsistency between the usual zeroth law of thermodynamics, the standard Maxwell construction for coexistence between different phases and the GGD identity, and provide a possible resolution through a redefinition of the equilibrium parameters.

We start from the crucial fact that in ordinary thermodynamics the Gibbs-Duhem identity (16) is mathematically consistent with Maxwell's law for phase coexistence. Here, one considers a single system splitting into two different phases remaining at equilibrium, i.e. sharing the same values of their intensive quantities, while the entropy and volume of the system change, causing a discontinuity in the extensive quantities and thus giving rise to a *first order phase transition*. Clearly in this case the definition of equilibrium between the phases in terms of equal values of the conjugate (intensive) quantities is consistent with (16).

From the above discussion on the role of the intensive variables in Maxwell's construction and its consistency with the Gibbs–Duhem relation (16), it is evident why such consistency is lost in the case of quasi-homogeneous systems, where equation (11) holds. Indeed for the two phases to be at equilibrium, the zeroth law would predict that no change in any of the would-be intensive variables p_i would happen, i.e., $\mathrm{d}p_i=0$ for all i. This implies that the second term in (11) vanishes identically. However, in general the first term in (11) is different from zero, thus leading to an inconsistency. For instance, in the case of a homogeneous entropy of degree r, it follows from the first law $\mathrm{d}S=\sum_{i=1}^{n}p_i\mathrm{d}q^i$ that the first term of (15) is proportional to the change in the entropy during the transition, and hence to the latent heat, which cannot be zero in a first order phase transition.

This inconsistency leads to the two following possibilities: either one gives up the standard formulation of phase coexistence expressed by the Maxwell construction (at least in its usual form), or one has to re-define the conditions for equilibrium, i.e., the zeroth law. Due to the many indications arising from different perspectives pointing to the fact that the zeroth law needs to be revisited for systems with non-additive entropy and energy relations (see e.g. [2–9]), we opt for the latter route.

From the analysis of the homogeneity of the first derivatives of S – see (6) – let us propose the following

Definition 3.1 *(Generalized intensive variables).* Let $S(q^1,\dots,q^n)$ be a quasi-homogeneous function of degree r and type β and let $\{p_i\}_1^n$ be the set of conjugate variables. Assume that $\beta_i\neq 0$ for every i. The quantities

$$\tilde p_i(q^j)\equiv\left[\left(q^i\right)^{\beta_i-r}\right]^{1/\beta_i}p_i(q^j) \tag{17}$$

are called the *generalized intensive variables*.

Indeed, these variables reduce to (4) when S is homogeneous of degree 1. Moreover, one can easily prove the following

Proposition 3.1. *The generalized intensive variables* (17) *are quasi-homogeneous functions of degree 0.*

Proof.

$$\begin{aligned}\tilde p_i(\lambda^{\beta_j}q^j)&=\left[\left(\lambda^{\beta_i}q^i\right)^{\beta_i-r}\right]^{1/\beta_i}p_i(\lambda^{\beta_j}q^j)\\&=\lambda^{\beta_i-r}\left[\left(q^i\right)^{\beta_i-r}\right]^{1/\beta_i}\left[\lambda^{r-\beta_i}p_i(q^j)\right]\\&=\left[\left(q^i\right)^{\beta_i-r}\right]^{1/\beta_i}p_i(q^j)=\tilde p_i(q^j)\,.\quad\square\end{aligned} \tag{18}$$

This is a desirable property for quantities defining a notion of equilibrium as they remain invariant under a scaling of the system. Note that these generalized variables could have been inferred from Eq. (75) in [22]. However, in that work they were not singled out nor were advocated as the correct ones to describe equilibrium.

Using the generalized intensive variables (17), we can re-write the GGD identity (11) as in [22]:

Proposition 3.2. *Let $S(q^1,\dots,q^n)$ be a quasi-homogeneous function of degree r and type β and let $\{\tilde p_i\}_{i=1}^n$ be the set of generalized intensive variables. Then,*

$$\sum_{i=1}^{n}\beta_i\left(q^i\right)^{r/\beta_i}\mathrm{d}\tilde p_i(q^j)=0\,. \tag{19}$$

Proof. From Eq. (17) we have

$$p_i(q^j)=\tilde p_i(q^j)\left(q^i\right)^{r/\beta_i-1}\,, \tag{20}$$

and we can thus rewrite the identity (11) in terms of the $\tilde p_i(q^j)$ as

$$\sum_{i=1}^{n}\beta_i\left[\left(1-\frac{r}{\beta_i}\right)\tilde p_i\left(q^i\right)^{r/\beta_i-1}\mathrm{d}q^i+q^i\mathrm{d}\left(\tilde p_i\left(q^i\right)^{r/\beta_i-1}\right)\right]=0\,. \tag{21}$$

By explicit calculation of the second term, we can rewrite the above identity as

$$0=\sum_{i=1}^{n}\beta_i\Bigg[\left(1-\frac{r}{\beta_i}\right)\tilde{p}_i\left(q^i\right)^{r/\beta_i-1}\mathrm{d}q^i + q^i\Bigg[\left(q^i\right)^{r/\beta_i-1}\mathrm{d}\tilde{p}_i+\left(\frac{r}{\beta_i}-1\right)\left(q^i\right)^{r/\beta_i-2}\tilde{p}_i\,\mathrm{d}q^i\Bigg]\Bigg] = \sum_{i=1}^{n}\beta_i\left(q^i\right)^{r/\beta_i}\mathrm{d}\tilde{p}_i\,. \quad \square \tag{22}$$

Note that the GGD identity (11) only establishes the existence of a relation between the would-be intensive and the would-be extensive variables, without fixing the values of the generalized intensive variables uniquely. In this sense our choice of the generalized intensive variables (17) is not the only one possible. However, it is motivated by the following considerations. Firstly, (17) reduce to (4) when the entropy is homogeneous of degree 1. Moreover, these quantities are quasi-homogeneous functions of degree 0, thus being true intensive variables (under the appropriate rescalings of the extensive ones). Finally, as stated in Proposition 3.2, using these variables the GGD identity takes the same form as the standard one (cf. [22]). Indeed, Propositions 3.1 and 3.2 suggest the following modification of the notion of thermodynamic equilibrium:

Definition 3.2 *(Thermodynamic equilibrium).* Two systems whose entropy is a quasi-homogeneous function of the same degree and type are in thermodynamic equilibrium with each other if and only if they have the same values of the $\tilde{p}_i(q^j)$.

This is the *generalized zeroth law of thermodynamics* that we propose for any quasi-homogeneous system. Note that Definition 3.2 is mathematically consistent with the identity (11) – cf. (19) – even when considering processes of coexistence as in the case of the usual Maxwell equal area law.

Let us remark that with our prescription one can consider the example of a process of coexistence among different phases at equilibrium without any incongruence, as long as the definition of equilibrium is given by equating the quantities in (17). Note also that our simple redefinition gives a general prediction about the quantities that have to be constant at equilibrium.

In the next section we consider examples from black holes thermodynamics and show that for the Schwarzschild black hole our redefinition of the equilibrium condition yields a constant generalized temperature. This result coincides with a different instance of the generalized zeroth law of thermodynamics resulting from non-extensive statistical mechanics [24]. As a more relevant consequence we will also show that for the Kerr–AdS black hole our construction suggests that a reconsideration of the first order phase transition might be in order.

4. Quasi-homogeneous black hole thermodynamics

In this section we investigate some examples for the above ideas in the context of black hole thermodynamics. In principle, our generalization of the zeroth law can be applied to any black hole system, given that one can easily determine the degrees of homogeneity from the Smarr relation,

$$(D-3)M=(D-2)TS+(D-2)\Omega J-2PV+(D-3)\Phi Q \tag{23}$$

where D is the number of spacetime dimensions, M is the mass of the black hole, T is the Hawking temperature, S is the entropy and the other terms are work terms depending on the black hole family in question [1]. Here, we consider two in particular, namely the Schwarzschild and the Kerr–AdS black holes, to compare our results with previous proposals and to illustrate new features.

4.1. Schwarzschild

The Schwarzschild black hole is the most straightforward example, since its thermodynamics is described by only one extensive variable, i.e., its mass M. The entropy as a function of M is

$$S(M)=4\pi M^2\,, \tag{24}$$

which is a homogeneous function of degree $r=2$. From this the standard temperature is derived as

$$\frac{1}{T}=\frac{\partial S}{\partial M}=8\pi M\,. \tag{25}$$

It is immediate to see that this a homogeneous function of degree 1 with respect to M, and therefore not a real intensive quantity. With (25) and using (17), we can obtain the generalized temperature as

$$\tilde{T}=TM=\frac{1}{8\pi}\,, \tag{26}$$

i.e., a constant. Note that, a constant is – trivially – a real intensive quantity, as it does not change with any scaling of M. Note also that by (19) the generalized intensive quantities cannot be independent. This means that in this case, since there is only one such generalized intensive quantity, it must be a constant. This fact outlines that the Schwarzschild black hole is not a proper thermodynamic system. However, it is interesting to see that even in this case our formalism coincides with previous approaches. Indeed, a similar result, i.e., a constant generalized temperature, has been obtained previously for the Schwarzschild black hole [24] by using the generalized zeroth law derived from non-extensive statistical mechanics proposed in [6]. In this work, the most general conditions for thermal equilibrium of systems with non-additive energy and entropy are established by using a method based on the definition of the so-called formal logarithms of these quantities. However, the same method was also applied in [25] in the analysis of the Kerr black hole, resulting in a constant generalized temperature, regardless of the angular momentum, identical to the Schwarzschild case – an indication that the result may be unphysical, as the authors point out themselves. Moreover, from our formalism a dependence of the generalized temperature on the angular momentum is to be expected. Finally, in [26,27] the Rényi entropy was used as the formal logarithm of the Bekenstein–Hawking entropy. In this case the temperature for the Schwarzschild case depends on the mass M and is not intensive. The connection of our proposal to these approaches and the general question of the underlying behaviour of the energy and entropy is thus not quite clear and might be addressed in future works.

4.2. Kerr–AdS

Kerr black holes in asymptotically Anti–de Sitter space are thermodynamically determined by three extensive variables, namely their mass M, angular momentum J and pressure P, which is defined via the cosmological constant Λ of the spacetime as

$$P=-\frac{\Lambda}{8\pi}\,. \tag{27}$$

The cosmological constant is usually included as a pressure into the thermodynamic description of black holes [28,10,1], and thus it turns out that the internal energy of the black hole is

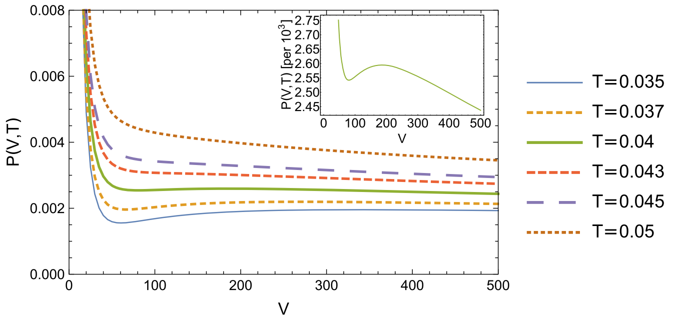

Fig. 1. Equation of state $P(V,T)$ for different values of T and with $J=1$. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

$$U = M - PV\,, \tag{28}$$

and therefore the mass of the black hole is identified with the enthalpy

$$M \equiv H = U + PV\,. \tag{29}$$

For the Kerr–AdS black hole one obtains [10]

$$H(S,P,J) = \frac{1}{2}\sqrt{\frac{4\pi^2 J^2\left(\frac{8PS}{3}+1\right)+\left(\frac{8PS^2}{3}+S\right)^2}{\pi S}}\,, \tag{30}$$

and from this, provided $J \neq 0$, it is possible to calculate the expression for the internal energy as

$$U(S,V,J) = \left(\frac{\pi}{S}\right)^3\left[\left(\frac{3V}{4\pi}\right)\left\{\frac{S^2}{2\pi^2}+J^2\right\} - J^2\left\{\left(\frac{3V}{4\pi}\right)^2-\left(\frac{S}{\pi}\right)^3\right\}^{1/2}\right]. \tag{31}$$

For simplicity and without loss of generality, we will limit further analyses to positive angular momenta, i.e., $J>0$. The temperature and pressure can be easily obtained as

$$T = \frac{1}{8S^4}\left[\frac{6\pi^{3/2}J^2\left(9\pi V^2-8S^3\right)}{\sqrt{9\pi V^2-16S^3}} - 18\pi^2 J^2 V - 3S^2 V\right], \tag{32}$$

and

$$P = \frac{3}{8S^3}\left[2\pi^2 J\left(J - \frac{3\sqrt{\pi}\,JV}{\sqrt{9\pi V^2-16S^3}}\right)+S^2\right], \tag{33}$$

respectively.

The case of Kerr–AdS is particularly interesting for our purposes because its equation of state, i.e., the relation $P(V,T)$ at fixed J, qualitatively shows the same oscillatory behaviour as a vdW fluid, which is generally taken as an indication of the presence of a first order phase transition, sometimes referred to as the CCK phase transition [14,29,30]. To see this let us fix $J=1$ from now on and first look at Fig. 1, where we plot $P(V,T)$ as a function of V for various choices of T, with the inlet zooming in on one of the curves to show the characteristic vdW bump. The region of the bump is the area where one would apply the Maxwell equal area law in analogy to ordinary thermodynamics [10]. A different (equivalent) way to look at such transition is by considering the graph of the Gibbs free energy,

$$G(T,P,J) = U - TS + PV\,. \tag{34}$$

To illustrate the multi-valued behavior of the Gibbs free energy we plot in Figs. 2 and 3 the cuts along the lines of constant T and P, respectively, featuring the characteristic swallowtails.

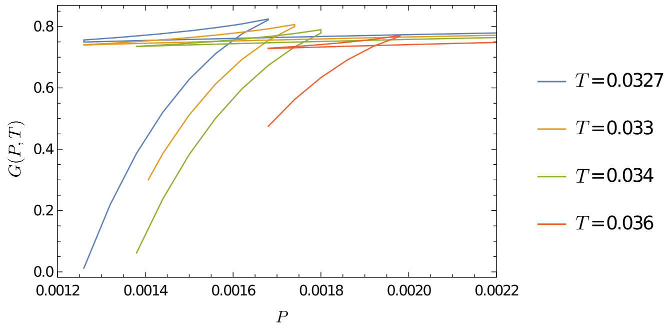

Fig. 2. Cuts of the Gibbs free energy at constant T. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

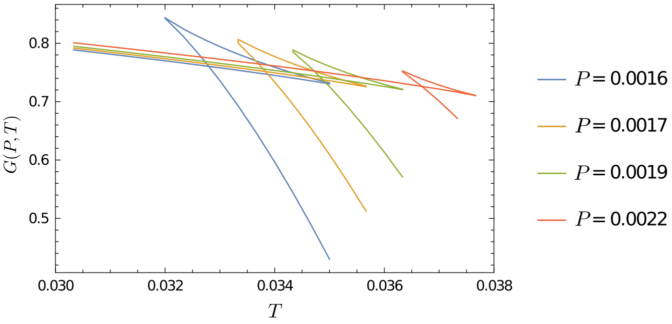

Fig. 3. Cuts of the Gibbs free energy at constant P. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

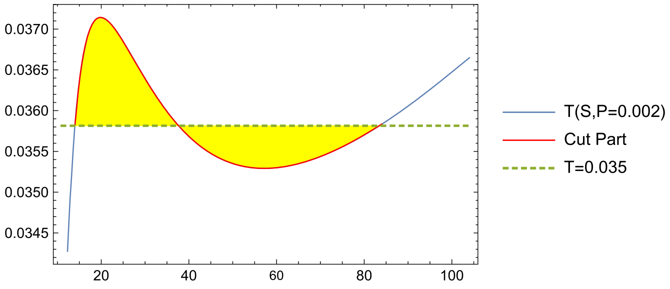

Fig. 4. Equation of state $T(S,P)$ for $J=1$ and $P=0.002$, together with the standard Maxwell construction. The two colored areas are equal. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

Based on the above analogy with the vdW phase diagram, it has been argued that there is a first order phase transition between small and large Kerr–AdS black holes, for appropriate values of the temperature and pressure. Indeed, the standard Maxwell construction can be performed, and the form of the coexistence curve can be calculated [14,29–31]. In the following we use this example – which is considered to be well understood in the literature – to claim that a revision due to the GGD identity is called for.

We start by showing that the standard Maxwell construction in this case is inconsistent with the GGD identity. To do so, it is more convenient to use the equation of state $T(S,P)$, as plotted in Fig. 4. For appropriate values of T and P, this equation of state exhibits an oscillatory behavior, as for the case of $P(T,V)$ above (cf. Fig. 1). The corresponding value for the transition temperature is also calculated using Maxwell's equal area law.

Now we proceed to verify the GGD identity for this case. Using the Smarr relation (23) applied to four spacetime dimensions (and $Q=0$), we have

$$S = \frac{1}{2T}U + \frac{3}{2}\frac{P}{T}V - \frac{\Omega}{T}J\,. \tag{35}$$

Table 1
Values of T_{tr}, $\mathrm{Maxwell}_{\mathrm{Dev}}$ and $\mathrm{GGD}_{\mathrm{Dev}}$ obtained numerically from Maxwell's equal area law for different choices of P_{tr}. More details in the text.

P_{tr}	T_{tr}	$\mathrm{Maxwell}_{\mathrm{Dev}}$	$\mathrm{GGD}_{\mathrm{Dev}}$
1.0×10^{-3}	2.6×10^{-2}	1.8×10^{-2}	6.5×10^{-1}
1.6×10^{-3}	3.2×10^{-2}	2.2×10^{-2}	4.6×10^{-1}
2.0×10^{-3}	3.5×10^{-2}	2.2×10^{-3}	3.6×10^{-1}
2.6×10^{-3}	3.9×10^{-2}	4.5×10^{-3}	2.0×10^{-1}

From this, we can determine the degrees of homogeneity of the variables T, P and Ω as $\beta_T = 1/2$, $\beta_P = 3/2$ and $\beta_\Omega = 1$ (cf. Eq. (7)). The overall degree of homogeneity of the entropy is $r = 1$. Therefore, the GGD (11) in the Kerr–AdS case reads

$$-\frac{1}{2T}\mathrm{d}U + \frac{1}{2}\frac{P}{T}\mathrm{d}V + \frac{1}{2}U\mathrm{d}\left(\frac{1}{T}\right) + \frac{3}{2}V\mathrm{d}\left(\frac{P}{T}\right) + J\mathrm{d}\left(\frac{\Omega}{T}\right) = 0\,. \tag{36}$$

Note that the last three terms have an analogous form with the standard Gibbs–Duhem relation (16) (although with different coefficients). Now let us use the standard Maxwell equal area law to prove an inconsistency with (36). By the usual argument, the two coexisting phases are in equilibrium and therefore all the last three terms vanish along the coexistence process. Thus we are left with the following expression

$$-\frac{1}{2T_{\mathrm{tr}}}\Delta U + \frac{1}{2}\frac{P_{\mathrm{tr}}}{T_{\mathrm{tr}}}\Delta V = 0\,, \tag{37}$$

where ΔU and ΔV represent the jumps in these quantities along the coexistence line and T_{tr} and P_{tr} are the constant values of the temperature and pressure along the transition. Eq. (37) can be further simplified to

$$\Delta U - P_{\mathrm{tr}}\Delta V = T_{\mathrm{tr}}\Delta S - 2P_{\mathrm{tr}}\Delta V = 0\,, \tag{38}$$

where in the last equality we made use of the first law (with J constant), that is, $\Delta U = T_{\mathrm{tr}}\Delta S - P_{\mathrm{tr}}\Delta V$. Now it is an easy exercise to use the values of T_{tr}, P_{tr}, ΔS and ΔV calculated using the standard Maxwell construction to show that Eq. (38) is not satisfied, i.e., that there is an inconsistency with the GGD identity. Table 1 shows the results of these calculations for different values of the transition pressure P_{tr}. In the first column we report the chosen values for the transition pressure P_{tr}. In the second column we provide the corresponding transition temperature T_{tr}, calculated using the standard Maxwell construction. In the third column we show that the area law is satisfied, by checking that the deviation from zero of the difference between the two areas in yellow in Fig. 4 is negligible. In the last column we demonstrate that the GGD identity (38) is not satisfied, by showing that the deviation from zero is large compared to that of the area law, and thus not negligible.

Since the analysis of the phase transition in terms of the standard definition of thermodynamic equilibrium leads to an inconsistency with the GGD identity, we now reconsider the phase transition in terms of the generalized intensive quantities defined in (17). From Eq. (17) and (35), we can infer the generalized intensive variables responsible for equilibrium as

$$\frac{1}{\tilde{T}} = \frac{1}{TU} \quad \text{and} \quad \frac{\tilde{P}}{\tilde{T}} = \frac{P}{T}V^{1/3}\,. \tag{39}$$

Combining the two expressions, we end up with the generalized thermodynamic equilibrium parameters

$$\tilde{T} = TU \quad \text{and} \quad \tilde{P} = PUV^{1/3}\,. \tag{40}$$

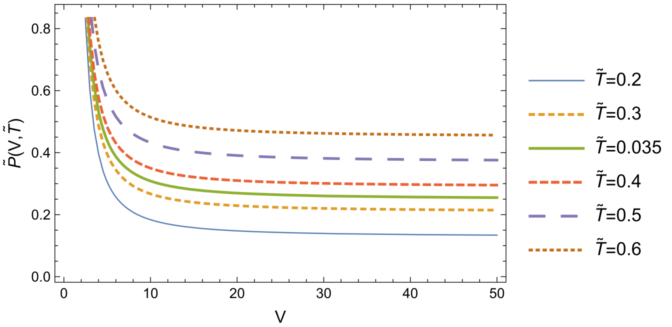

Fig. 5. Equation of state $\tilde{P}(V,\tilde{T})$ at constant $\tilde{T}$. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

By construction, these functions are quasi-homogeneous of degree 0 and type $\beta = (1, 3/2, 1)$ with respect to the correspondingly rescaled extensive variables S, V and J, i.e.,

$$\tilde{T}(\lambda^1 S, \lambda^{3/2} V, \lambda^1 J) = \lambda^0\, \tilde{T}(S, V, J)\,, \tag{41}$$

$$\tilde{P}(\lambda^1 S, \lambda^{3/2} V, \lambda^1 J) = \lambda^0\, \tilde{P}(S, V, J)\,. \tag{42}$$

In terms of S and V (for $J = 1$) these read

$$\begin{aligned}\tilde{T}(S,V) = {} & \frac{3V\pi^{13/2}}{8S^7}\left[-36\left(\frac{S}{\pi}\right)^3 - 10\left(\frac{S}{\pi}\right)^5 + 27\left(\frac{V}{\pi}\right)^2\right.\\ & \left. + 9\left(\frac{S}{\pi}\right)^2\left(\frac{V}{\pi}\right)^2\right] + \frac{3\pi^6}{64S^7}\sqrt{9\pi V^2 - 16S^3}\left[32\left(\frac{S}{\pi}\right)^3\right.\\ & \left. - 72\left(\frac{V}{\pi}\right)^2 - 24\left(\frac{S}{\pi}\right)^2\left(\frac{V}{\pi}\right)^2 - 3\left(\frac{S}{\pi}\right)^4\left(\frac{V}{\pi}\right)^2\right]\end{aligned} \tag{43}$$

and

$$\begin{aligned}\tilde{P}(S,V) = {} & \frac{9\pi^{5/2}V^{4/3}}{32S^6}\sqrt{9\pi V^2 - 16S^3}\left(2\pi^2 + S^2\right)\\ & \times\left(6\pi^2 V + 3S^2 V - 2\pi^{3/2}\sqrt{9\pi V^2 - 16S^3}\right).\end{aligned} \tag{44}$$

Note that in order to show the quasi-homogeneity of these functions by rescaling the extensive variables, it is necessary to recover the terms containing J, including it as an extensive variable. Using these expressions, we can return to the plot of the equation of state, but now in terms of the new variables, plotting $\tilde{P}(V,\tilde{T})$ as a function of V for different choices of $\tilde{T}$. As can be seen in Fig. 5, the curves are monotonously decreasing, therefore the system appears to be stable and there is no necessity for the Maxwell construction. The same effect can be observed using the Gibbs free energy. We can re-express definition (34) in terms of the new intensive variables $\tilde{T}$ and $\tilde{P}$ and calculate the function $G(\tilde{T}, \tilde{P}, J)$, inverting Eqs. (43) and (44) numerically. The result can be seen in figures Figs. 6 and 7, where cuts at constant $\tilde{T}$ and $\tilde{P}$ show that the Gibbs free energy in terms of the generalized intensive variables is a single-valued smooth function.

We conclude that for the Kerr–AdS black hole the standard Maxwell equal area law is inconsistent with the GGD identity. Besides, the use of the generalized intensive variables proposed here as the parameters defining thermodynamic equilibrium seems to indicate that there is no first order phase transition between large and small black holes, as previously argued in the literature. However, our results deserve more investigation. Perhaps a comparison with explicit models directly constructed from statistical mechanics could shed more light on the validity of such statements. Alternatively, an analysis involving thermodynamic response functions

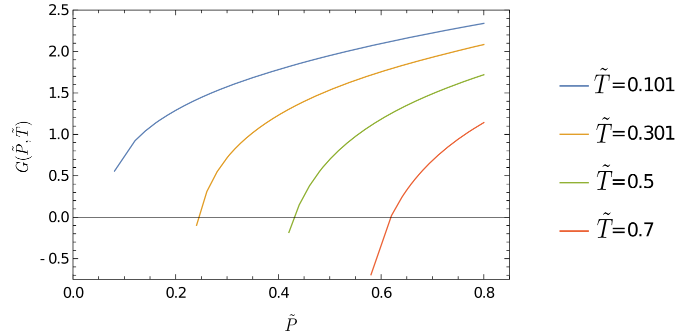

Fig. 6. Cuts of the Gibbs free energy at constant $\tilde{T}$. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

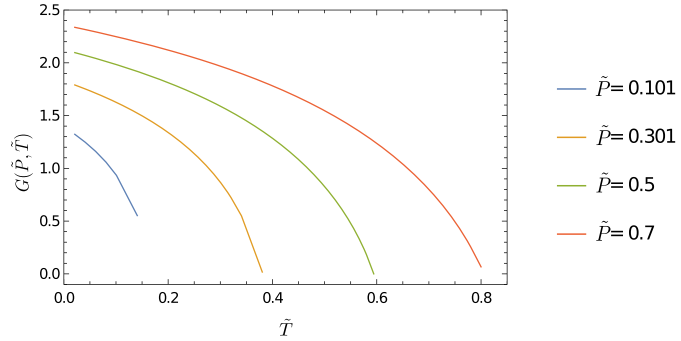

Fig. 7. Cuts of the Gibbs free energy at constant $\tilde{P}$. (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

could be interesting, although the significance of these response functions in the context of a generalized zeroth law should be re-evaluated.

5. Conclusions and future directions

In this work we consider a generalization of the zeroth law of thermodynamics for systems whose thermodynamic entropy is a quasi-homogeneous function of the (would-be) extensive variables (Definition 3.2). Originating from the generalized version of the Gibbs-Duhem identity, we show how to define the generalized intensive variables that can be used to define thermodynamic equilibrium in such general cases (Definition 3.1). Moreover, we prove that this new definition resolves an inconsistency between the use of the standard Maxwell equal area law and the GGD identity that is usually overlooked, especially in the literature regarding the thermodynamics of black holes. Within this context, we consider two examples where the application of our generalized zeroth law should be relevant, namely the Schwarzschild and the Kerr–AdS black holes. The former is important because with our approach we recover a previous result found in [24], derived from a different perspective. The latter example is of interest because in the usual treatment the Kerr–AdS family of black holes shows a behavior which is very similar to that of a van der Waals fluid, including a first order phase transition. However, we argue that the use of the standard Maxwell equal area law in such case is not fully consistent and that using the generalized intensive variables that we have introduced here in order to define thermodynamic equilibrium, such phase transition disappears. This statement however should be further investigated in other contexts in order to corroborate such a conclusion.

Our results are intended to be a step forward towards a deeper formal understanding of the thermodynamic properties of systems with quasi-homogeneous entropy. However, it also calls for more detailed investigations. One can use the arguments given here to understand whether other reported first order phase transitions in black holes are consistent with their respective GGD identities or not (cf. e.g. [11–19]). It would also be interesting to study the implications of the present analysis for the conditions of equilibrium between black holes and heat reservoirs, e.g. a Schwarzschild black hole in a hot flat space. Moreover, we would like to extend the comparison between our approach and the one presented in [6, 24–27] to other cases to see whether the agreement we found for the Schwarzschild black hole holds in more general contexts. Besides, it would be worth using explicit calculations as in [4,5] to check whether our prediction of the new thermodynamic parameters defining equilibrium can be tested by numerical experiments, and to compare our results with the formalism proposed in [32,33] presenting a different instance of a GGD relation for systems with long-range interactions. These directions will be the subject of future work.

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