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Unified representation of homogeneous and quasi-homogenous systems in geometrothermodynamics

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ABSTRACT

We analyze homogeneous and quasi-homogeneous thermodynamic systems within the formalism of geometrothermodynamics (GTD). A generalized Euler identity is used to obtain the explicit form of the three Legendre invariant metrics that are known in GTD for the equilibrium space. In so doing, we fix all the arbitrary parameters that enter the GTD metrics in terms of the quasi-homogeneous coefficients. We obtain quite general results that relate the curvature singularities of the equilibrium space with the thermodynamic stability conditions and the phase transition structure of the system. This result allows us to avoid the appearance of non-physical singularities at the level of the equilibrium space.

1. Introduction

Riemannian geometry has been used for a long time in thermodynamics. It was first introduced in thermodynamics and statistical physics by Rao [1], in 1945, by means of a metric whose components in local coordinates coincide with Fisher's information matrix [2]. The Fisher-Rao metric determines the Riemannian structure of the equilibrium space, for which local coordinates are usually taken as corresponding to the extensive variables that are needed to describe the corresponding thermodynamic system. Rao's original work has been and extended and applied by a large number of authors (for a review see, e.g., [3]).

Another approach was used by Weinhold [4] in 1975 and Ruppeiner [5,6] in 1979, who defined Riemannian metrics for the equilibrium space as the Hessian of the internal energy and (minus) the entropy, respectively. The study and applications of Hessian metrics is known nowadays as thermodynamic geometry that is currently a field of activ research [7,8]. Recently, in order to solve some inconsistencies of thermodynamic geometry, in [9,10] a new thermodynamic geometry was proposed, in which the potential of the Hessian metric is changed in such a way that there is a one-to-one correspondence between the divergences of curvature scalars and heat capacities. A similar approach was applied in [11] and [12] to postulate a metric in which the Hessian potential and a conformal factor is chosen such that the phase transition structure of black holes is reproduced.

The formalism of geometrothermodynamics (GTD), proposed in 2007 in [13], is different because it is based upon the physical invariance of classical thermodynamics with respect to Legendre transformations, i.e., with respect to the choice of thermodynamic potential. In this case, the geometric background is different because the equilibrium space is a subspace of the phase space, where Legendre transformations are represented as coordinate transformations and Legendre invariant metrics can be determined. This implies that the Riemannian structure of the equilibrium space cannot be chosen arbitrarily but it is determined by the geometric properties of the phase space. In fact, it was found that in GTD there are three metrics that satisfy the condition of Legendre invariance.

The application of the GTD metrics in some thermodynamic systems has shown that certain curvature singularities appear that cannot be interpreted from a thermodynamic point of view [14]. In particular, it has been found that in certain cases the explicit form of the GTD metrics depend on whether the system is homogeneous or quasi-homogeneous. In this work, we present a solution to these problems. Indeed, we will use the arbitrariness of the coefficients that enter the GTD metrics to obtain general results that are valid independently of the homogeneity properties of the system. In addition, we find that the singularities of the three GTD metrics are directly related to the physical properties of the system under consideration, namely, its stability properties and phase transition structure.

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This work is organized as follows. In Sec. 2, we review the main aspects of quasi-homogeneous and homogeneous thermodynamic systems and introduce notations that are used throughout this work. In Sec. 3, we introduce the formalism of GTD and apply Euler's identity to reduce the explicit form of the GTD metrics. In Sec. 4, we illustrate the application of the GTD metrics in the case of a system with two degrees of freedom. We show that the singularities of the GTD metrics contain information about the stability properties and the phase transition structure of the system under consideration. Finally, in Sec. 5, we summarize and comment our results.

2. Homogeneous and quasi-homogeneous thermodynamics

Consider a thermodynamic system described by the fundamental equation $\Phi = \Phi(E^a)$, where Φ is the thermodynamic potential, usually taken as the entropy or the internal energy, and E^a, $a = 1, 2, \ldots n$ are the n extensive variables that are necessary to describe the system. The fundamental equation is assumed to satisfy the laws of thermodynamics; in particular, the first law of thermodynamics can be written as (summation over repeated indices)

$$d\Phi = I_a dE^a , \quad I_a = \frac{\partial \Phi}{\partial E^a} , \tag{1}$$

where I_a are the corresponding intensive variables dual to E^a.

Homogeneity is an important property of ordinary thermodynamic systems and is related to the extensive character of the variables E^a [15], implying that the fundamental equation is represented by a homogeneous function, i.e.,

$$\Phi(\lambda E^a) = \lambda^{\beta_\Phi} \Phi(E^a) , \tag{2}$$

where λ is a positive constant and β_Φ is the degree of homogeneity of the function Φ. Usually, $\beta_\Phi = 1$ for ordinary systems. However, there exist also systems in which the homogeneity condition is not satisfied [16] such as large-scale inhomogeneous systems [17], black holes [18], and others. To correctly handle this type of systems [19–22], it is necessary to use quasi-homogeneous functions that satisfy the condition

$$\Phi(\lambda^{\beta_a} E^a) = \lambda^{\beta_\Phi} \Phi(E^a) , \tag{3}$$

where β_a are the coefficients of quasi-homogeneity that characterize the system. If $\beta_a = 1 \ \forall a$, we return to the case of homogeneous systems.

It is important to notice that, in general, it is possible to introduce new extensive variables $E^{a'}$ that absorb the coefficients β_a and the function $\Phi(E^{a'})$ becomes homogeneous of degree one. This change of variables is allowed from a mathematical point of view, but it is not convenient from a physical point of view because it could affect the thermodynamic properties of the system [22,23]. Indeed, although the laws of thermodynamics do not depend on the value of the quasi-homogeneous coefficients β_a, the Euler identity and the Gibbs-Duhem relationship contain the constants β_a explicitly, namely, [23]

$$\beta_{ab} I^a E^b = \beta_\Phi \Phi , \quad \text{and} \quad (\beta_{ab} - \beta_\Phi \delta_{ab}) I^a dE^b + \beta_{ab} E^b dI^a = 0 , \tag{4}$$

respectively, with $I_a = \delta_{ab} I^b$ and

$$\delta_{ab} = \mathrm{diag}(1, 1, \ldots, 1) , \quad \beta_{ab} = \mathrm{diag}(\beta_1, \beta_2, \ldots, \beta_n). \tag{5}$$

Therefore, the correct use of these relationships is important in order not to affect the thermodynamic properties of the system and the geometric properties of the equilibrium space [24].

3. Geometrothermodynamics

The main ingredient of the GTD formalism is Legendre invariance, which is handled as diffeomorphism invariance. To this end, it is necessary to introduce the $2n + 1$ dimensional phase space $\mathcal{T}$ with coordinates $Z^A = (\Phi, E^a, I^a)$. Then, a Legendre transformation can be defined on $\mathcal{T}$ as a coordinate transformation of the form $Z^A \rightarrow \tilde{Z}^A = (\tilde{\Phi}, \tilde{E}^a, \tilde{I}^a)$ such that [25]

$$\Phi = \tilde{\Phi} - \delta_{kl} \tilde{E}^k \tilde{I}^l , \quad E^i = -\tilde{I}^i, \quad E^j = \tilde{E}^j, \quad I^i = \tilde{E}^i, \quad I^j = \tilde{I}^j , \tag{6}$$

where $i \cup j$ is any disjoint decomposition of the set of indices $\{1, \ldots, n\}$, and $k, l = 1, \ldots, i$. In particular, for $i = \emptyset$ we obtain the identity transformation, and for $i = \{1, \ldots, n\}$, Eq. (6) defines a total Legendre transformation. Then, it is possible to show that the Legendre invariant metrics $G = G_{AB} dZ^A dZ^B$ on $\mathcal{T}$ can be written as

$$G^{I} = (d\Phi - I_a dE^a)^2 + (\xi_{ab} E^a I^b)(\delta_{cd} dE^c dI^d) , \tag{7}$$

$$G^{II} = (d\Phi - I_a dE^a)^2 + (\xi_{ab} E^a I^b)(\eta_{cd} dE^c dI^d) , \tag{8}$$

$$G^{III} = (d\Phi - I_a dE^a)^2 + \sum_{a=1}^{n} \xi_a (E_a I_a)^{2k+1} dE^a dI^a , \tag{9}$$

where $\eta_{ab} = \mathrm{diag}(-1, 1, \cdots, 1)$, ξ_a are real constants, ξ_{ab} is a diagonal $n \times n$ real matrix, and k is an integer. It turns out that the condition of Legendre invariance does not fix completely the form of the metric components G_{AB} but leaves the coefficients k, ξ_a, and ξ_{ab} arbitrary. In previous works, it was assumed that $\xi_a = 1 \ \forall a$ and $\xi_{ab} = \delta_{ab}$ as the simplest possible case. Now, it is clear that this choice is correct in the case of homogeneous systems, but it could lead to inconsistencies in quasi-homogeneous systems. This is due to the fact that the explicit form of the corresponding metrics of the equilibrium space turn out to depend on the type of system under consideration. To fix this problem, we proceed as follows.

In GTD, the equilibrium space $\mathcal{E}$ is a subspace of $\mathcal{T}$ defined by the embedding smooth map $\varphi : \mathcal{E} \rightarrow \mathcal{T}$ such that the pullback $\varphi^*(\Theta) = \varphi^*(d\Phi - I_a dE^a) = 0$, i.e., on $\mathcal{E}$, the first law of thermodynamics (1) is satisfied as a consequence of the definition of the smooth map φ, which also implies that $\varphi : \{Z^A\} \rightarrow \{E^a\}$, i.e. $\Phi = \Phi(E^a)$ and $I^a = I^a(E^b)$. Moreover, the smooth map induces a metric g on $\mathcal{E}$ by means of $g = \varphi^*(G)$. Then, from Eqs. (7), (8), and (9), we obtain

$$g^I_{ab} = \beta_\Phi \Phi \delta_a^{\ c} \frac{\partial^2 \Phi}{\partial E^b \partial E^c} , \tag{10}$$

$$g^{II}_{ab} = \beta_\Phi \Phi \eta_a^{\ c} \frac{\partial^2 \Phi}{\partial E^b \partial E^c} , \tag{11}$$

$$g^{III} = \sum_{a=1}^{n} \beta_a \left(\delta_{ad} E^d \frac{\partial \Phi}{\partial E^a} \right)^{2k+1} \delta^{ab} \frac{\partial^2 \Phi}{\partial E^b \partial E^c} dE^a dE^c , \tag{12}$$

respectively, where $\delta_a^{\ c} = \mathrm{diag}(1, \cdots, 1)$, $\eta_a^{\ c} = \mathrm{diag}(-1, 1, \cdots, 1)$. To obtain the components of the metrics g^I and g^{II}, we have chosen $\xi_{ab} = \beta_{ab}$ and used the quasi-homogeneous Euler identity (4), which generates the conformal factor $\beta_\Phi \Phi$. This choice is important in order to obtain the same metric for both homogeneous and quasi-homogeneous functions. Otherwise, the conformal term would be $\xi_{ab} E^a I^b$ that could generate singularities at the level of the curvature in the case of quasi-homogeneous systems. In the case of the metric g^{III}, we have chosen the arbitrary constants ξ_a as $\xi_a = \beta_a$. This choice will allow us to apply Euler's identity to analyze the singularities of g^{III}.

4. Systems with two degrees of freedom

To illustrate the results of the previous section, we will consider now the case of a system with two thermodynamic degrees of freedom ($n = 2$). Then, the fundamental equation reads $\Phi = \Phi(E^1, E^2)$. From Eqs. (10)-(12), we obtain in this case

$$g^I = \beta_\Phi \Phi \left[\Phi_{,11}(dE^1)^2 + 2\Phi_{,12} dE^1 dE^2 + \Phi_{,22}(dE^2)^2\right] \tag{13}$$

$$g^{II} = \beta_\Phi \Phi \left[-\Phi_{,11}(dE^1)^2 + \Phi_{,22}(dE^2)^2\right] , \tag{14}$$

$$\begin{aligned} g^{III} &= \beta_1(E^1\Phi_{,1})^{2k+1}\Phi_{,11}(dE^1)^2 + +\beta_2(E^2\Phi_{,2})^{2k+1}\Phi_{,22}(dE^2)^2 \\ &\quad + \left[\beta_1(E^1\Phi_{,1})^{2k+1} + \beta_2(E^2\Phi_{,2})^{2k+1}\right]\Phi_{,12} dE^1 dE^2 , \end{aligned} \tag{15}$$

where $\phi_{,a} = \frac{\partial \phi}{\partial E^a}$, etc. To investigate the singularity structure of the above metrics, we compute the corresponding curvature scalars. In doing this, we demand that the singularities of g^{III} are related to those of g^I and g^{II} so that all the metrics can be used to describe the same system. It then follows that this condition fixes the value of the integer k entering the metric g^{III} as $k = 0$. Then, a straightforward computation leads to

$$R^I = \frac{N^I}{D^I} , \quad D^I = 2\beta_\Phi \Phi^3 \left[\Phi_{,11}\Phi_{,22} - (\Phi_{,12})^2\right]^2 , \tag{16}$$

$$R^{II} = \frac{N^{II}}{D^{II}} , \quad D^{II} = 2\beta_\Phi \Phi^3 \left(\Phi_{,11}\Phi_{,22}\right)^2 , \tag{17}$$

$$\begin{aligned} R^{III} &= \frac{N^{III}}{D^{III}} , \\ D^{III} &= \left[\beta_\Phi^2 \Phi^2 (\Phi_{,12})^2 - 4\beta_1\beta_2 E^1 E^2 \Phi_{,1}\Phi_{,2}\Phi_{,11}\Phi_{,22}\right]^3 , \end{aligned} \tag{18}$$

respectively, where we have used the Euler identity

$$\beta_1 E^1 \Phi_{,1} + \beta_2 E^2 \Phi_{,2} = \beta_\Phi \Phi , \tag{19}$$

to reduce the form of the function D^{III}. The functions N^I, N^{II} and N^{III} depend on Φ and its derivatives.

The singularities of the equilibrium space metrics are determined by the zeros of the functions D^I, D^{II} and D^{III}. Notice that the term $\beta_\Phi \Phi$ appears as a result of applying Euler's identity at the level of the metric with the identification $\xi_{ab} = \beta_{ab}$. Otherwise, with the choice $\xi_{ab} = \delta_{ab}$, we would obtain the term $E^1\Phi_{,1} + E^2\Phi_{,2}$ in the functions D^I and D^{II}, which could lead to additional singularities. This has been correctly pointed out in [14]. The identification of the arbitrary constants ξ_{ab} as the quasi-homogeneous coefficients β_a avoids this type of singularities.

We now analyze the zeros of the above functions. The condition $D^I = 0$ implies that $\Phi_{,11}\Phi_{,22} = (\Phi_{,12})^2$ so that and $D^{II} \neq 0$ and

$$D^{III} = (\Phi_{,12})^6 \left[\beta_\Phi^2 \Phi^2 - 4\beta_1\beta_2 E^1 E^2 \Phi_{,1}\Phi_{,2}\right]^3 . \tag{20}$$

It is then easy to see that the expression inside the parenthesis is zero only if Φ depends on one variable only, which is equivalent to setting $\Phi_{,12} = 0$. The condition $D^{II} = 0$, i.e., $\Phi_{,11} = 0$ or $\Phi_{,22} = 0$, implies that D^I and D^{III} are zero only for $\Phi_{,12} = 0$. We conclude that all the singularities are determined by the zeros of the second-order derivatives of Φ, namely,

$$I: \ \Phi_{,11}\Phi_{,22} - (\Phi_{,12})^2 = 0 , \tag{21}$$

$$II: \ \Phi_{,11}\Phi_{,22} = 0 , \tag{22}$$

$$III: \ \Phi_{,12} = 0 . \tag{23}$$

We can now establish the relationship between the above singularities and the thermodynamic properties of the system under consideration. The singularity I implies that the stability condition of a system with two degrees of freedom is not satisfied [15], which is usually associated with a first order phase transition. Furthermore, the singularities II and III can be associated with second order phase transitions. Indeed, the response functions of a thermodynamic system define second order phase transitions and are essentially determined by the behavior of the independent variables E^a in terms of their duals I_a, i.e.,

$$C^{ab} = \frac{\partial E^a}{\partial I_b} = \frac{1}{\Phi_{,ab}} , \tag{24}$$

which is obtained by using the definition $I_b = \Phi_{,b}$. Consequently, the zeros of the second order derivatives of Φ can be associated with second order phase transitions.

Some examples of the application of the above procedure to determine the phase transition structure of homogeneous systems have been presented in [26,27]. To illustrate the case of a quasi-homogeneous system, consider the phantom Reissner-Nordström-AdS black hole [29] with mass M, charge q, and cosmological constant Λ, whose fundamental equation can be written as [30]

$$M = \frac{1}{2} S^{3/2} \left(\frac{1}{S} - \frac{\Lambda}{3} + \eta \frac{q^2}{S^2}\right) , \tag{25}$$

where $\eta = \pm 1$ and the entropy has been normalized as $S/\pi \to S$. The application of the GTD formalism leads to singularity conditions (21)-(23), which in this case read

$$I: \ M_{,SS}M_{,qq} - (M_{,Sq})^2 = \frac{\eta}{8S^3}(\eta q^2 - \Lambda S^2 - S) = 0 , \tag{26}$$

$$II: \ M_{,SS}M_{,qq} = \frac{\eta}{8S^3}(3\eta q^2 - \Lambda S^2 - S) = 0 , \tag{27}$$

$$III: \ M_{,Sq} = -\frac{\eta q}{2S^{3/2}} = 0 . \tag{28}$$

Condition III cannot be satisfied in general. The singularity II coincides with the divergence of the heat capacity

$$C_q = T\left(\frac{\partial M}{\partial T}\right)_q = \frac{2S(-\eta q^2 - \Lambda S^2 + S)}{3\eta q^2 - \Lambda S^2 - S} , \tag{29}$$

which is interpreted as a second order phase transition [18,28]. Finally, the singularity I corresponds to a bread down of the stability condition, which is usually associated with a first order phase transition in classical thermodynamics [15].

To explain how the application of the quasi-homogeneity condition avoids the appearance of new singularities, we demand that the fundamental equation (25) be a quasi-homogeneous function. To this end, we perform the transformation $M \to \lambda^{\beta_M} M$, $S \to \lambda^{\beta_S} S$, $q \to \lambda^{\beta_q} q$, and $\Lambda \to \lambda^{\beta_\Lambda}\Lambda$ in (25) and obtain the conditions $\beta_M = \beta_S/2$, $\beta_\Lambda = -\beta_S$, and $\beta_q = \beta_S/2$. Then, the Euler identity (4) allows us to replace the sum

$$\beta_S S M_{,S} + \beta_\Lambda \Lambda M_{,\Lambda} + \beta_q q M_{,q} = \frac{\beta_S}{12 S^{1/2}}(3\eta q^2 - \Lambda S^2 + 3S) \tag{30}$$

by the conformal factor $\beta_M M$ that appears in the denominators (16) and (17). Notice that in this context the quasi-homogeneity condition implies that Λ should be considered as thermodynamic variable [30].

Thus, this simplification obtained from using the Euler identity is a consequence of the choice $\xi_a = \beta_a$ and $\xi_{ab} = \beta_{ab}$ for quasi-homogeneous systems. If, instead, we use the homogeneous choice $\xi_a = 1$ and $\xi_{ab} = \delta_{ab}$ in the case of the phantom Reissner-Nordström-AdS quasi-homogeneous black hole, instead of the conformal factor $\beta_M M$, we would obtain the term

$$SM_{,S}+\Lambda M_{,\Lambda}+qM_{,q}=\frac{1}{12S^{1/2}}(9\eta q^2-5\Lambda S^2+3S) \tag{31}$$

in the denominators (16) and (17), leading to new singularities that do not correspond to first or second order phase transitions.

5. Conclusions

In this work, we analyze homogeneous and quasi-homogeneous systems in the context of GTD. The Euler identity is used to obtain the explicit form of the three Legendre invariant metrics that are known in GTD for the equilibrium space. To this end, it is important to choose the arbitrary constants, which are not fixed by the Legendre invariant condition, in terms of the quasi-homogeneity coefficients of the corresponding fundamental equation. As a result, we obtain metrics that have the same functional dependence and can be used for homogeneous and quasi-homogeneous systems as well. This unified representation of the GTD metrics is tested in the case of a system with two degrees of freedom. The condition that all the three metrics can be applied simultaneously to any thermodynamic system fixes the only remaining integer constant k of the metric g^{III}.

The unified representation of the GTD metrics allows us to analyze the singularities of the equilibrium space, in general, for any fundamental equation. As a result, we obtain that all the singularities are given in terms of the second derivatives of the fundamental equation. In particular, the singularities of the metric g^{I} coincide with the locations where the stability condition breaks down. Furthermore, the singularities of the metrics g^{II} and g^{III} are determined by the zeros of the second order derivatives of the fundamental equation. We show that, in general, these zeros coincide with the locations where the response functions diverge and second order phase transitions occur.

The results presented in this work allow us to explain and avoid the appearance of non-physical singularities of the GTD metrics as pointed out, for instance, in [14]. We conclude that the correct application of Euler's identity at the level of the equilibrium space metrics is important in order to consider all the consequences and obtain all the information from the Legendre invariant condition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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