The geometry of thermodynamics

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Abstract. We present a review of the main aspects of geometrothermodynamics, an approach which allows us to associate a specific Riemannian structure to any classical thermodynamic system. In the space of equilibrium states, we consider a Legendre invariant metric, which is given in terms of the fundamental equation of the corresponding thermodynamic system, and analyze its geometric properties in the case of the van der Waals gas, and black holes. We conclude that the geometry of this particular metric reproduces the thermodynamic behavior of the van der Waals gas, and the Reissner-Nordström black hole, but it is not adequate for the thermodynamic description of Kerr black holes.

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INTRODUCTION

Differential geometry is a very important tool of modern science, specially of mathematical physics and its applications in physics, chemistry and engineering. In the case of thermodynamics, Gibbs [1] and Caratheodory [2], followed by Hermann [3] and later by Mrugala [4, 5], proposed a differential geometric approach based upon the contact structure of the thermodynamic phase space $\mathcal{T}$. This space is $(2n+1)$—dimensional and is coordinatized by $n$ extensive variables $E^a$ and $n$ intensive variables $I^a$, together with the thermodynamic potential $\Phi$. The first law of thermodynamics is incorporated into this approach in a very natural way through differential forms. A particular $n$—dimensional subspace of $\mathcal{T}$ is the space of thermodynamic equilibrium states $\mathcal{E}$. On $\mathcal{E}$, the laws of thermodynamics are valid and thermodynamics systems are specified by means of a fundamental equation.

In an attempt to describe thermodynamic systems in terms of geometric objects, Weinhold [6] introduced ad hoc on the space of equilibrium states a metric whose components are given as the Hessian of the internal thermodynamic energy. This metric turns out to be positive as a consequence of the second law of thermodynamics. This approach has been intensively used to study, from a geometrical point of view, the properties of the space generated by Weinhold’s metric [7, 8], the thermodynamic length [9, 10, 11], the chemical and physical properties of various two-dimensional thermodynamic systems [12, 13, 14, 15, 16], and the associated Riemannian structure [17, 18, 19].

In an attempt to understand the concept of thermodynamic length, Ruppeiner [17] introduced a metric which is given as the Hessian of the entropy and is conformally...
equivalent to Weinhold’s metric, with the inverse of the temperature as the conformal factor. The physical meaning of Ruppeiner’s geometry lays in the fluctuation theory of equilibrium thermodynamics. It turns out that the second moments of fluctuation are related to the components of the inverse of Ruppeiner’s metric. The corresponding geometry has been investigated for several thermodynamic systems such as the ideal (classic and quantum) gas, one-dimensional Ising model, multicomponent ideal gas, van der Waals gas, etc. It was shown that Ruppeiner’s metric contains important information about the phase transition structure of thermodynamic systems, indicating the location of critical points and phase transitions on those particular surfaces where the scalar curvature diverges. In the case of systems with no statistical mechanical interactions (e.g. an ideal gas), the scalar curvature vanishes and consequently the geometry of the associated two-dimensional space is flat. For this reason the thermodynamic length is considered as a measure of statistical mechanical interactions within a thermodynamic system. These results have been reviewed in [20] and more recent results are included in [21, 22]. Due to the conformal equivalence, Weinhold’s metric contains similar information about the structure of phase transitions as has been shown recently in [16]. Ruppeiner’s metric has found applications also in the context of thermodynamics of black holes [23, 24, 25, 26].

An alternative approach has been used in classical statistical mechanics to analyze the geometry of thermodynamic systems. The starting point is the probability density distribution which includes the partition function of the corresponding system. It can be shown [27, 28, 29] that from the information contained in the partition function a metric structure can be derived, the so-called Fisher-Rao metric which describes the properties of the statistical system. Although their conceptual origin is quite different, it can be shown [21] that Weinhold and Ruppeiner metrics are related to the Fisher-Rao metric by means of Legendre transformations of the corresponding thermodynamic variables. One common disadvantage of all these metrics is that they are not Legendre invariant, leading to the unphysical result that their properties depend on the thermodynamic potential used in their construction.

Recently, the formalism of geometrothermodynamics (GTD) was developed in [30, 31] in order to incorporate the concept of Legendre invariance into the geometric description of thermodynamics. It unifies in a consistent manner the contact structure of \( \mathcal{T} \) with the metric structures on \( \mathcal{E} \). One of the main results of GTD is that it allows to introduce Legendre invariant metrics on \( \mathcal{T} \) which are then consistently projected on \( \mathcal{E} \), generating in this way metrics which can be used to describe the properties of thermodynamic systems in terms of geometric properties.

In this work, we present a simple Legendre invariant metric which is then applied to different thermodynamic systems in order to analyze their geometric properties. We first present a short review of the main constituents of GTD, and consider a specific Legendre invariant metric. Then, we study the geometric properties of the metric corresponding to the van der Waals gas and to the ideal gas, as a special case of the first one. It follows that the geometry reproduces the thermodynamic behavior in both cases. Furthermore, we consider black holes as thermodynamic systems and analyze their geometric properties. The last section of this work is devoted to discussions of our results and suggestions for further research.
GEOMETROTHERMODYNAMICS

Let the thermodynamic phase space $\mathcal{T}$ be coordinatized by the thermodynamic potential $\Phi$, extensive variables $E^a$, and intensive variables $I^a$ $(a = 1, \ldots, n)$. Let the fundamental Gibbs 1-form be defined on $\mathcal{T}$ as $\Theta = d\Phi - \delta_{ab}I^a dE^b$, with $\delta_{ab} = \text{diag}(1, 1, \ldots, 1)$, satisfying the condition $\Theta \wedge (d\Theta)^n \neq 0$. Consider also on $\mathcal{T}$ the Riemannian metric $G = (d\Phi - \delta_{ab}I^a dE^b)^2 + (\delta_{ab}E^a I^b) (\delta_{cd} dE^c dI^d)$, \(1\)

which is non-degenerate and invariant with respect to Legendre transformations of the form \(\Phi, E^a, I^a \rightarrow \Phi, \tilde{E}^a, \tilde{I}^a\) \(2\)

\[\Phi = \tilde{\Phi} - \delta_{kl} \tilde{E}^k \tilde{I}^l, \quad E^i = -\tilde{I}^i, \quad E^j = \tilde{E}^j, \quad I^i = \tilde{E}^i, \quad I^j = \tilde{I}^j, \]

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 $i = \{1, \ldots, n\}$ and $i = \emptyset$ we obtain the total Legendre transformation and the identity, respectively. We say that the set $(\mathcal{T}, \Theta, G)$ defines a Legendre invariant manifold with a contact Riemannian structure.

The space of thermodynamic equilibrium states is an $n$–dimensional Riemannian submanifold $\mathcal{F} \subset \mathcal{T}$ induced by a smooth mapping $\varphi : \mathcal{F} \rightarrow \mathcal{T}$, i.e. $\varphi : (E^a) \rightarrow (\Phi, E^a, I^a)$ with $\Phi = \Phi(E^a)$ such that

\[\varphi^*(\Theta) = 0, \quad \varphi^*(G) = g = \Phi \frac{\partial^2 \Phi}{\partial E^a \partial E^b} dE^a dE^b, \]

where $\varphi^*$ is the pullback of $\varphi$ and $g$ is the Riemannian metric induced on $\mathcal{F}$. The first of these equations implies that on $\mathcal{F}$ the following relationships hold

\[d\Phi = \delta_{ab}I^a dE^b, \quad \frac{\partial \Phi}{\partial E^a} = \delta_{ab} I^b, \]

which correspond to the first law of thermodynamics and the conditions for thermodynamic equilibrium, respectively \(3\). The metric $g$ on $\mathcal{F}$ is Legendre invariant because it is induced by a smooth mapping from the Legendre invariant metric $G$ of $\mathcal{T}$. The explicit components of $g$ can be computed from the fundamental equation $\Phi = \Phi(E^a)$, which is given as part of the smooth mapping $\varphi$. Since the fundamental equation characterizes completely a thermodynamic system, the metric $g$ is also a characteristic which is different for each thermodynamic system. It is in this sense that we propose to analyze the relationship between the thermodynamic properties of a system, specified through the fundamental equation $\Phi = \Phi(E^a)$, and the geometric properties of the corresponding metric $g$.

In general, the thermodynamic potential is a homogeneous function of its arguments, i.e., $\Phi(\lambda E^a) = \lambda^\beta \Phi(E^a)$ for constant parameters $\lambda$ and $\beta$. Using the first law of thermodynamics, it can easily be shown that this homogeneity is equivalent to the relationships

\[\beta \Phi(E^a) = \delta_{ab} I^b E^a, \quad (1 - \beta) \delta_{ab} I^a dE^b + \delta_{ab} E^a dI^b = 0, \]

where $a, b = 1, \ldots, n$. Therefore, $G$ is also a characteristic which is dif-

form $\Phi, E^a, I^a \rightarrow \Phi, \tilde{E}^a, \tilde{I}^a$, with $\tilde{\Phi} = \Phi - \delta_{kl} \tilde{E}^k \tilde{I}^l$, $E^i = -\tilde{I}^i$, $E^j = \tilde{E}^j$, $I^i = \tilde{E}^i$, $I^j = \tilde{I}^j$. In particular, for $i = \{1, \ldots, n\}$ and $i = \emptyset$ we obtain the total Legendre transformation and the identity, respectively. We say that the set $(\mathcal{T}, \Theta, G)$ defines a Legendre invariant manifold with a contact Riemannian structure.

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\[\beta \Phi(E^a) = \delta_{ab} I^b E^a, \quad (1 - \beta) \delta_{ab} I^a dE^b + \delta_{ab} E^a dI^b = 0, \]
which are known as Euler’s identity and Gibbs-Duhem relation, respectively. Moreover, the second law of thermodynamics corresponds to the convexity condition on the thermodynamic potential \( \frac{\partial^2 \Phi}{\partial E^a \partial E^b} \geq 0 \) \[33, 34\].

It must be noticed that the metric \( g \) given in Eq.(4) is not the only one which is Legendre invariant. In fact, there exists an infinite number of Legendre invariant metrics on \( \mathcal{E} \). In this work, however, we limit ourselves to the analysis of this specific metric due to its simplicity and the fact that it is the simplest Legendre invariant generalization of Weinhold’s and Ruppeiner’s metrics \[31\].

**THE VAN DER WAALS GAS**

The van der Waals gas is a 2-dimensional thermodynamic system for which the extensive variables can be chosen as the entropy \( S \) and the volume \( V \). The corresponding dual intensive variables are the temperature \( T \) and pressure \( P \). Accordingly, the first law of thermodynamics reads \( d \Phi = T dS - P dV \), where the thermodynamic potential \( \Phi \) can be identified with the internal energy of the gas. The thermodynamic properties of the van der Waals gas can be completely derived from the fundamental equation

\[
\Phi(S,V) = \left( \frac{e^{S/k}}{V-b} \right)^{2/3} - \frac{a}{V},
\]

(7)

where \( k \) is a constant, usually related to the Boltzmann constant, and \( a \) and \( b \) are constants which are responsible for the thermodynamic interaction between the particles of the gas.

On the space of equilibrium states \( \mathcal{E} \), the Riemannian structure is determined by the metric (4) which in this particular case can be written as

\[
g_{vdW} = \frac{2}{9k^2} \Phi \left( \Phi + \frac{a}{V} \right) \left[ 2dS^2 - \frac{4k}{V-b} dSdV + \frac{5k^2}{(V-b)^2} dV^2 \right] - \frac{2a \Phi V}{V^3} dV^2.
\]

(8)

This metric defines a 2-dimensional differential manifold whose geometric properties can be derived from the analysis of the corresponding connection and curvature. The connection determines the form of the geodesics in this manifold, and deserves a separate and detailed study which will be reported elsewhere. The scalar curvature can be computed in a straightforward manner and we obtain

\[
R_{vdW} = \frac{a \mathcal{P}(\Phi,V,a,b)}{\Phi^4 (PV^3 - aV + 2ab)^2},
\]

(9)

where \( \mathcal{P}(\Phi,V,a,b) \) is a polynomial which is always different from zero for any real values of \( a \) and \( b \). In the limiting case \( a = b = 0 \), the fundamental equation reduces to that of an ideal gas and the curvature vanishes. But the curvature vanishes also in the limiting case \( a = 0 \) and \( b \neq 0 \). This is in agreement with the well-known property \[16\] that the constant \( a \) is responsible for the non-ideal thermodynamic interactions, whereas the constant \( b \) plays a qualitative role in the description of thermodynamic interactions.
Since the main characteristic of an ideal gas is the absence of thermodynamic interaction between the particles of the gas, we conclude that the curvature can be used as a measure of this interaction. Any generalization of an ideal gas is therefore characterized by a non-zero curvature.

The scalar curvature for the van der Waals gas is singular for all values of pressure and volume which satisfy the condition $PV^3 - aV + 2ab = 0$. One can show that this is a zero-volume singularity in the sense that it is characterized by the vanishing of the determinant of the metric $g$. It is a true curvature singularity since it cannot be removed by a change of coordinates, and we interpret it as an indication that our geometric approach is not valid as the singularity is approached. Remarkably, this limit coincides with the limit of applicability of classical thermodynamics [33]. Indeed, the condition $PV^3 - aV + 2ab = 0$ for the van der Waals gas is associated with the limit of thermodynamic stability, i.e., situations where thermodynamic processes cannot be described in the context of equilibrium thermodynamics. This shows that in order to avoid the curvature singularity it is necessary to introduce a different approach which take into account processes of non-equilibrium thermodynamics. This is, of course, a task that requires the application of more general geometric structures, and is beyond the scope of the present work.

On the other hand, the limit of thermodynamic stability is associated with the appearance of critical points and phase transitions. This opens the possibility of analyzing critical behavior and phase transitions of thermodynamic systems by studying the geometric properties of the curvature singularities. In particular, one could try to classify the behavior of the curvature near the singularities in terms of divergent polynomials or exponentials, and relate them with different types of critical points and phase transitions.

**BLACK HOLES**

According to the no-hair theorems of general relativity, electro-vacuum black holes are completely described by three parameters only: mass $M$, angular momentum $J$, and electric charge $Q$. These parameters satisfy the first law of black hole thermodynamics [35]

$$dM = TdS + \Omega_H dJ + \phi dQ,$$  

where $S$ is the entropy, which is proportional to the horizon area, $T$ is the Hawking temperature, which is proportional to the surface gravity on the horizon, $\Omega_H$ is the angular velocity on the horizon, and $\phi$ is the electric potential. In black hole thermodynamics the mass is considered as the thermodynamic potential so that any function of the form $M = M(S,J,Q)$ corresponds to a fundamental equation. The most general fundamental relation was derived originally by Smarr [36] in the form $M^2 = A/16\pi + Q^2/2 + (4\pi/A)(J^2 + Q^4/4)$, where $A$ is the horizon area. The identification of the entropy as the horizon area in the form $S = kA/4$, where $k$ is Boltzmann’s constant, generates the fundamental equation (we use units in which $k = 1$)

$$M = \left[ \frac{\pi J^2}{S} + \frac{S}{4\pi} \left( 1 + \frac{\pi Q^2}{S} \right)^2 \right]^{1/2},$$  

(11)
which corresponds to the Kerr-Newman black hole \[37\]

\[
\begin{align*}
  ds^2 &= -\frac{\Delta - a^2 \sin^2 \theta}{\Sigma} dt^2 - \frac{2a \sin^2 \theta (r^2 + a^2 - \Delta)}{\Sigma} dt d\varphi \\
  &\quad + \frac{(r^2 + a^2)^2 - a^4 \sin^2 \theta \Delta}{\Sigma} \sin^2 \theta d\varphi^2 + \frac{\Sigma}{\Delta} dr^2 + \Sigma d\vartheta^2, \\
  \Sigma &= r^2 + a^2 \cos^2 \theta, \quad \Delta = (r - r_+)(r - r_-), \quad r_{\pm} = M \pm \sqrt{M^2 - a^2 - Q^2},
\end{align*}
\]

where \(a = J/M\) is the specific angular momentum.

The space of equilibrium states for the Kerr-Newman black hole is 3-dimensional with coordinates \(S, J,\) and \(Q\). The corresponding metric structure can be derived from the fundamental equation (11). Then

\[
\begin{align*}
  g_{ss} &= \frac{1}{64\pi^2 S^4 M^2} \left\{ -S^4 + \pi^2 (4J^2 + Q^4) [6S^2 + 8\pi SQ^2 + 3\pi^2 (4J^2 + Q^4)] \right\}, \\
  g_{sq} &= \frac{Q}{4S^2 M^2} [4\pi J^2 - (\pi Q^2 + S) M^2], \quad g_{sj} = -\frac{J}{4S^2 M^2} [4\pi J^2 + \pi Q^2 + S], \\
  g_{qq} &= \frac{1}{8\pi S^2 M^2} [4\pi^2 J^2 (3\pi Q^2 + S) + (\pi Q^2 + S)^3], \\
  g_{qj} &= -\frac{\pi J Q}{2S^2 M^2} (\pi Q^2 + S), \quad g_{jj} = \frac{1}{4S^2 M^2} (\pi Q^2 + S)^2.
\end{align*}
\]

The geometry behind this metric is very rich, and deserves a separate investigation. In this work we limit ourselves to the analysis of two special cases of this general metric, namely, the case \(J = 0\) which corresponds to the Reissner-Nordström metric, and \(Q = 0\) which corresponds to the Kerr black hole. In the first case, the metric can be written as

\[
g_{RN} = \frac{1}{2S^2} (\pi Q^2 + S) \left[ \frac{1}{8\pi S} (3\pi Q^2 - S) dS^2 - QdSdQ + SdQ^2 \right].
\]

In the last section we noticed that the limit of thermodynamic stability corresponds to the singularities of the corresponding metric in the space of equilibrium states. To see if this is also valid in this case we calculate the curvature scalar of the metric \(g_{RN}\), and obtain

\[
R_{RN} = -\frac{8\pi^2 Q^2 S^2 (\pi Q^2 - 3S)}{(\pi Q^2 + S)^3 (\pi Q^2 - S)^2}.
\]

This scalar presents two critical points. The first one is situated at \(S = \pi Q^2\), which according to the fundamental equation for this case, corresponds to an extremal black hole with \(M = Q\). The second point is at \(S = \pi Q^2 / 3\), where the scalar curvature vanishes identically, leading to a flat geometry. This point corresponds to the value \(M = 2Q/\sqrt{3}\), where the system undergoes a phase transition \[38\]. The behavior of the curvature near these two critical points resembles the critical thermodynamic behavior of the Reissner-Nordström black hole \[39\]. We conclude that in this particular case GTD correctly describes the thermodynamic behavior in terms of geometric concepts.
For the second limiting case with $Q = 0$ we obtain the thermodynamic metric

$$g_{Kerr} = \frac{\pi S}{S^2 + 4\pi^2 J^2} \left[ \left( \frac{3\pi^2 J^4}{S^4} + \frac{3J^2}{2S^2} - \frac{1}{16\pi^2} \right) dS^2 - \frac{J}{S^3} \left( 3S^2 + 4\pi^2 J^2 \right) dJ dS + dJ^2 \right].$$

(20)

A straightforward calculation shows that the curvature of this metric is zero. This would imply that statistical interaction is not present in Kerr black holes, a result that contradicts the results obtained from standard black hole thermodynamics, where it was shown that rotating black holes possess a non-trivial structure of phase transitions [38].

**CONCLUSIONS**

In this work, we reviewed the main concepts of geometrothermodynamics, and applied them to completely different thermodynamic systems, namely, the van der Waals gas and vacuum black holes. In the first case we saw that it is possible to reproduce the main aspects of the thermodynamic behavior by using the curvature of the corresponding metric in the space of equilibrium states. In the case of black holes we found that only the thermodynamics of Reissner-Nordström black hole can be reproduced by using the geometry of the space of equilibrium states. In the case of the Kerr black hole, however, the geometry is flat and leads to a non-interacting thermodynamic systems, whereas standard thermodynamics predicts a non-trivial behavior with phase transitions. Although this last result is negative, it must be emphasized that it was obtained by using a very particular Legendre invariant metric, which is probably the simplest consistent generalization of other known metrics that are not invariant with respect to Legendre transformations.

We expect that the application of a different metric will overcome this particular difficulty. In any case, a more detailed analysis is necessary. In particular, it will be interesting to find a criterion to select Legendre invariant metrics from the vast number of possible metrics. We expect that a variational principle applied on all metrics of the space of equilibrium states will be a plausible criterion. This task is currently under investigation and will be presented elsewhere.

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