Phase transitions in geometrothermodynamics

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Received: date / Accepted: date

Abstract Using the formalism of geometrothermodynamics, we investigate the geometric properties of the equilibrium manifold for diverse thermodynamic systems. Starting from Legendre invariant metrics of the phase manifold, we derive thermodynamic metrics for the equilibrium manifold whose curvature becomes singular at those points where phase transitions of first and second order occur. We conclude that the thermodynamic curvature of the equilibrium manifold, as defined in geometrothermodynamics, can be used as a measure of thermodynamic interaction in diverse systems with two and three thermodynamic degrees of freedom.

Keywords Geometrothermodynamics · phase transitions · black holes

PACS 05.70.-a · 02.40.-k

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1 Introduction

Although thermodynamics is based entirely upon empirical results which are satisfied under certain conditions in almost any macroscopic system, the geometric approach to thermodynamics has proved to be useful and illuminating. In very broad terms, one can say that the following three branches of geometry have found sound applications in equilibrium thermodynamics: analytic geometry, Riemannian geometry, and contact geometry.

To illustrate the role of analytic geometry, let us consider a thermodynamic system specified by an equation of state of the form \( f(P, V, T) = 0 \). In the \( PVT \)−space, the equation of state defines a surface whose points represent the states in which the system can exist in thermodynamic equilibrium. Given a surface in a 3-dimensional space, its properties and structure are investigated in the framework of analytic geometry. Probably, one of the most important contributions of analytic geometry to the understanding of thermodynamics is the identification of points of phase transitions with extremal points of the surface (or its projections on the coordinate planes) determined by the state equation \( f(P, V, T) = 0 \). More detailed descriptions of these contributions can be found in any good textbook on thermodynamics (see, for instance, [3,4]).

Riemannian geometry was first introduced in statistical physics and thermodynamics by Rao [5], in 1945, by means of a metric whose components in local coordinates coincide with Fisher's information matrix. Rao's original work has been followed up and extended by a number of authors (see, e.g., [6] for a review). On the other hand, Riemannian geometry in the space of equilibrium states was introduced by Weinhold [7] and Ruppeiner [8,9], who defined metric structures as the Hessian of the internal energy and the entropy, respectively.

Contact geometry was introduced by Hermann [10] into the thermodynamic phase space in order to take into account the invariance of ordinary thermodynamics with respect to Legendre transformations, i.e., to the choice of thermodynamic potential. In order to incorporate Legendre invariance in Riemannian structures at the level of the phase space and the equilibrium space, the formalism of geometrothermodynamics (GTD) [11] was recently proposed and applied to different systems. The main motivation for introducing the formalism of GTD was to formulate a geometric approach which takes into account the fact that in ordinary thermodynamics the description of a system does not depend on the choice of thermodynamic potential. One of the main goals of GTD has been to interpret in an invariant manner the curvature of the equilibrium space as a manifestation of the thermodynamic interaction. This would imply that an ideal gas and its generalizations with no mechanic interaction correspond to a Riemannian manifold with vanishing curvature. Moreover, in the case of interacting systems with non-trivial structure of phase transitions, the curvature should be non-vanishing and reproduce the behavior near the points where phase transitions occur. These intuitive statements represent concrete mathematical conditions for the metric structures of the spaces of phase and equilibrium. The main goal of the present work is to present metric structures which satisfy these conditions for systems with no thermodynamic interaction as well as for systems characterized by interaction with first and second order phase transitions.

This paper is organized as follows. In Section 2 we present the fundamentals of GTD. In Section 3 we analyze the case of systems with two and three degrees of freedom which are characterized by second order phase transitions. A metric is derived for
the equilibrium manifold which correctly reproduces the phase transitions in terms of curvature singularities. Section 5 is dedicated to the investigation of a thermodynamic metric which reproduces the first order phase transitions of realistic gases and fluids. Finally, Section 6 is devoted to discussions of our results and suggestions for further research. Throughout this paper we use units in which \( G = c = \hbar = k_B = 1 \).

2 General framework

The starting point of GTD is the \((2n + 1)\)-dimensional thermodynamic phase space \( T \) which can be coordinatized by the set of independent coordinates \( \{ \Phi, E^a, I^a \} \), \( a = 1, \ldots, n \), where \( \Phi \) represents the thermodynamic potential, and \( E^a \) and \( I^a \) are the extensive and intensive thermodynamic variables, respectively. The positive integer \( n \) indicates the number of thermodynamic degrees of freedom of the system. Let the fundamental Gibbs 1–form be defined on \( T \) as

\[
\Theta = d\Phi - \delta_{ab} I^a dE^b,
\]

with \( \delta_{ab} = \text{diag}(1, \ldots, 1) \). The pair \((T, \Theta)\) is called a contact manifold \([10,12]\) if \( T \) is differentiable and \( \Theta \) satisfies the condition

\[
\Theta \wedge (d\Theta)^n \neq 0.
\]

Consider also on \( T \) a non–degenerate Riemannian metric \( G \) which is invariant with respect to Legendre transformations \([13]\) \((\Phi, E^a, I^a) \rightarrow (\tilde{\Phi}, \tilde{E}^a, \tilde{I}^a)\),

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

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. Legendre transformations are a special case of contact transformations which leave invariant the contact structure of \( T \). Legendre invariance guarantees that the geometric properties of \( G \) do not depend on the thermodynamic potential used in its construction. The set \((T, \Theta, G)\) defines a Riemannian contact manifold which is called the thermodynamic phase space (phase manifold), and represents an auxiliary structure which is necessary to implement in a consistent manner the properties of ordinary thermodynamics.

The space of thermodynamic equilibrium states (equilibrium manifold) is an \( n \)–dimensional Riemannian submanifold \( E \subset T \) induced by a smooth map \( \varphi : E \rightarrow T \), i.e. \( \varphi : (E^a) \mapsto (\Phi, E^a, I^a) \) with \( \Phi = \Phi(E^a) \) such that \( \varphi^*(\Theta) = \varphi^*(d\Phi - \delta_{ab} I^a dE^b) = 0 \) holds, where \( \varphi^* \) is the pullback of \( \varphi \). This implies the relationships

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

The first of these equations corresponds to the first law of thermodynamics, whereas the second one is usually known as the condition for thermodynamic equilibrium \([3]\). In the GTD formalism, the last equation also means that the intensive thermodynamic variables are dual to the extensive ones. Notice that the mapping \( \varphi \) as defined above implies that the equation \( \Phi = \Phi(E^a) \) must be explicitly given. In standard thermodynamics this is known as the fundamental equation from which all the equations of state can be derived \([3,4]\). In this representation, the second law of thermodynamics is equivalent to the convexity condition on the thermodynamic potential \( \partial^2 \Phi/\partial E^a \partial E^b \geq 0 \), if \( \Phi \) coincides with the internal energy of the system \([10]\). The smooth map \( \varphi \) induces in a canonical manner a metric \( g \) (thermodynamic metric) in the equilibrium manifold \( E \) by

\[
g_{ab} = \delta_{ab} + \delta_{ij} \delta_{kl} \tilde{E}^i \tilde{E}^j \tilde{I}^k \tilde{I}^l.
\]
means of \( g = \varphi^*(G) \). Consequently, \( E \) is a Riemannian manifold with a non-degenerate 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

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

which are known as Euler’s identity and Gibbs–Duhem relation, respectively.

From the above discussion we conclude that to describe a thermodynamic system in GTD it is necessary to specify a metric \( G \) for the phase manifold \( T \) and a fundamental equation \( \Phi = \Phi(E^a) \). These ingredients allow us to construct explicitly the pair \( (E, g) \) that constitutes the equilibrium manifold whose geometric properties should be related to the thermodynamic properties of the specific system. In the following sections we will present metrics \( G \) which generate equilibrium manifolds for different thermodynamic systems.

### 3 Systems with second order phase transitions

The non-degenerate metric

\[
G = (d\Phi - \delta_{ab} I^a dE^b)^2 + (\delta_{ab} E^a I^b)(\eta_{cd} dE^c dI^d), \quad \eta_{ab} = \text{diag}(-1, 1, ..., 1)
\]

is invariant with respect to total Legendre transformations \( \varphi \) and, consequently, can be used to describe the geometric properties of the phase manifold \( T \). The smooth map \( \varphi : \{E^a\} \rightarrow \{\Phi(E^a), E^a, I^a(E^a)\} \), satisfying \( \varphi^*(d\Phi - \delta_{ab} I^a dE^b) = 0 \), induces the thermodynamic metric

\[
g = \varphi^*(G) = \left( \frac{\partial \Phi}{\partial E^c} \right) \left( \eta_{ab} \delta^{bc} \frac{\partial^2 \Phi}{\partial E^c \partial E^d} dE^a dE^d \right)
\]

that can be explicitly calculated once the fundamental equation \( \Phi = \Phi(E^a) \) is specified. Notice that by virtue of the equilibrium conditions \( \Phi \) and Euler’s identity \( \delta \), the conformal factor of the thermodynamic metric \( g \) turns out to be proportional to the thermodynamic potential \( \Phi \). This means that in general we can assume that the conformal factor is different from zero.

For concreteness we assume that \( E^1 = S \) is the entropy of a system with two thermodynamic degrees of freedom \( n = 2 \). Then, the dual intensive variable \( I^1 = \partial \Phi / \partial S = T \) represents the temperature, and the thermodynamic metric \( g \) reduces to

\[
g = (ST + E^2 I^2) \left[ -\Phi_{..S} dS^2 + \Phi_{..22} (dE^2)^2 \right],
\]

where a subscript represents derivation with respect to the corresponding coordinate.

To describe the phase transition structure of the system we use the heat capacity \( C = T(\partial T / \partial S) = \Phi_{..S} / \Phi_{..S S} \), so that phase transitions of second order occur at those points where \( C \) diverges. For the calculation of concrete examples it is necessary to specify the fundamental equation \( \Phi = \Phi(S, E^2) \). In particular, we are interested in analyzing the thermodynamic properties of black hole configurations \( \Phi \) for which usually \( \Phi = M \) is the mass (energy) of the black hole and \( E^2 \) is an additional extensive variable.
like electric charge, angular momentum, etc. In this case, the fundamental equation is essentially equivalent to the entropy–area relation $S = S(M, E^2) = kA$, where $A$ is the area of the horizon and $k$ is a constant that depends on the dimension of the spacetime. However, it turns out that it is not always possible to express the fundamental equation in the form $M = M(S, E^2)$ and the entropy–area relation $S = S(M, E^2)$ must be used. In ordinary thermodynamics this corresponds to a change from the energy representation to the entropy representation. GTD allows us to perform changes of representations in a simple manner. In fact, to obtain the entropy representation of the metric (7) we rewrite the first law of thermodynamics $dM = TdS + I^2dE^2$ as $dS = (1/T)dM - (I^2/T)dE^2$ and identify $M$ and $E^2$ as the new extensive variables, whereas $1/T$ and $-I^2/T$ represent the corresponding new dual intensive variables. Replacing these new variables in the general expression (6), we obtain the metric

$$g = (MS_{MM} + E^2S_2) \left[ -S_{MM}dM^2 + S_{22}(dE^2)^2 \right],$$

where $S = S(M, E^2)$ and $M = M(S, E^2)$.

The above thermodynamic metrics (7) and (8) have been used to investigate the black hole configurations listed in Table 1. In all the cases GTD is mathematically consistent and reproduces the thermodynamic behavior of the black holes. In fact, the scalar curvature of the equilibrium manifold $(E, g)$ is in all cases different from zero, indicating the presence of non-trivial thermodynamic interaction. Furthermore, in Table 2 we present the heat capacity and the scalar curvature for each of the black holes contained in Table 1. It follows that at those points where the heat capacity diverges the scalar curvature of the equilibrium manifold becomes singular. Consequently, a second order phase transition is characterized by a curvature singularity. This shows that indeed the curvature of the equilibrium manifold can be considered as a measure of thermodynamic interaction.

The fact that our results are invariant with respect to Legendre transformations explains some contradictory results [21,22,23] that follow when the equilibrium manifold is equipped with metrics strongly associated to a particular thermodynamic potential.

The 4-dimensional Kerr-Newman black hole represents a thermodynamic system with three degrees of freedom. Indeed, from the entropy-area relation one can derive the fundamental equation

$$S = \pi \left( 2M^2 - Q^2 + 2\sqrt{M^4 - M^2Q^2 - J^2} \right),$$

which depends on the extensive variables $M$, $J$, and $Q$. The second order phase transitions are determined by the corresponding heat capacity:

$$C = \frac{4TM^3S^3}{2M^6 - 3M^4Q^2 - 6M^2J^2 + Q^2J^2 + 2(M^4 - M^2Q^2 - J^2)^3/2}.$$  

According to the general expression for the metric $g$, as given in Eq.(3), the equilibrium manifold is 3-dimensional and the corresponding Legendre invariant metric reduces to

$$g^{KN}_{ab} = (MS_{MM} + QS_{QQ} + JS_{JJ}) \left( \begin{array}{ccc} S_{MM} & 0 & 0 \\ 0 & -S_{QQ} & -S_{QJ} \\ 0 & -S_{QJ} & -S_{JJ} \end{array} \right).$$  

(11)
Function equation

Table 1 Black holes with two degrees of freedom. Here we use the following notations: RN = Reissner-Nordström, RNAdS = Reissner-Nordström-Anti-de-Sitter, KAdS = Kerr-Anti-de-Sitter, BTZ = Bañados-Teitelboim-Zanelli, BTZCS = Bañados-Teitelboim-Zanelli-Chern-Simons, BTZTF = Bañados-Teitelboim-Zanelli black hole with thermal fluctuations, EGB = Einstein-Gauss-Bonnet, EGBME = Einstein-Gauss-Bonnet black holes with modified entropy, EYMGB = Einstein-Yang-Mills-Gauss-Bonnet, EMGB = Einstein-Maxwell-Gauss-Bonnet, M = mass, \( S \) = entropy, Q = charge, J = angular momentum, \( A = -1/l^2 \) = cosmological constant, and \( \omega_{D-2} = 2\pi^{-\frac{D-2}{2}}/\Gamma(\frac{D-1}{2}) \) is the volume of the unit \((D-2)\)-sphere. \( k = \text{Chern-Simons coupling constant}, \alpha = \text{Gauss-Bonnet coupling constant}, \) and \( \hat{\alpha} = (D - 2)(D - 3)\alpha \).
Table 2 GTD of black holes with two degrees of freedom. Here we use the following notations: $r_+$ = radius of the exterior horizon, $r_-$ = radius of the interior horizon, $\beta = Q/M$, $\delta = \Delta/M$. The function $N$ represents in each case the numerator of the scalar curvature which is a well-behaved function at the points where the denominator vanishes. The results for charged rotating BTZ black holes are generalized in [20] For more details see Refs. [15,16,17].

Table 3 contains the fundamental equations for some ordinary thermodynamic systems which we investigated from the point of view of GTD.

Table 3 contains the results of our analysis. In the case of the ideal gas and its paramagnetic generalization, which have no thermodynamic interaction, the curvature vanishes and the equilibrium manifold becomes flat. In fact, one can show the general result that any generalization of the ideal gas whose fundamental equation can be separate in its variables as $S = S_1(U) + S_2(V) + S_3(E^3) + ...$ always generates a flat thermodynamic metric [24]. The 1-dimensional Ising model [25] generates a metric whose curvature is non-zero, indicating the presence of thermodynamic interaction, 

| BH | Heat Capacity | Scalar curvature |
|----|---------------|-----------------|
| RN | $(D-2)S \left( \frac{2\pi r_+ (r_+ - r_-)}{(r_+ - r_-)^2} + \frac{\pi^2 r_+^2}{16} \right)$ | $\frac{r_+^2 (r_+^2 - 6r_+^2 + 9r_-^2)}{28r_+^3 (r_+^2 - 3r_-^2)}$ |
| RNAdS | $\frac{D-1}{2} \frac{D-3}{(D-3)} \left( \frac{2\pi r_+ (r_+ - r_-)}{(r_+ - r_-)^2} + \frac{\pi^2 r_+^2}{16} \right)$ | $\frac{D-1}{2} \frac{D-3}{(D-3)} \left( \frac{2\pi r_+ (r_+ - r_-)}{(r_+ - r_-)^2} + \frac{\pi^2 r_+^2}{16} \right)$ |
| Kerr | $\frac{2\pi r_+^2 (r_+ - r_-)^2}{r_+^2 - 6r_+^2 - 3r_-^2}$ | $\frac{2\pi r_+^2 (r_+ - r_-)^2}{r_+^2 - 6r_+^2 - 3r_-^2}$ |
| KAdS | $\frac{\pi^2 r_+^2}{3^2 + 24\beta^2 + 36\beta^2 + 24\beta^2 + 36\beta^2}$ | $\frac{\pi^2 r_+^2}{3^2 + 24\beta^2 + 36\beta^2 + 24\beta^2 + 36\beta^2}$ |
| BTZ | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ |
| BTZCS | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ |
| BTZTF | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ | $\frac{4\pi r_+^2 (r_+^2 - r_-^2)}{6^2 + 6^2 + 18^2 + 24\beta^2 + 36\beta^2}$ |
| EGB | $-3S \left( \frac{35 - Q^2}{5S - 5Q^2} \right)$ | $-\frac{3\pi^2}{2}(35S^3 + 10S^2 Q^2 - 4S^3 Q^4)$ |
| EGBME | $-\sqrt{\frac{1 - 4\beta^2}{\sqrt{1 - 4\beta^2}} \sqrt{1 - 4\beta^2}} \left( 1 + \frac{\sqrt{1 - 4\beta^2}}{\sqrt{1 - 4\beta^2}} \right) \left( 1 + 4\beta^2 \right)$ | $-\sqrt{\frac{1 - 4\beta^2}{\sqrt{1 - 4\beta^2}} \sqrt{1 - 4\beta^2}} \left( 1 + \frac{\sqrt{1 - 4\beta^2}}{\sqrt{1 - 4\beta^2}} \right) \left( 1 + 4\beta^2 \right)$ |
| EYMGB | $S \left( \frac{S - Q^2}{Q^2 - 5S} \right)$ | $\left( Q^2 - \frac{1}{2} S \right)^2 + Q^2 S^2 + 2Q^2 S^2 \ln S - S$ |
| EMGB | $3S \left( \frac{S + S^2 - Q^2}{5S^2 - 3S^2 - 2AS^2} \right)$ | $-\left( 2Q^2 + 3S^2 + AS^2 \right) \left( 5S^2 - 3S^2 - 2AS^2 \right)$ |
System | Fundamental equation
--- | ---
IG | \[ S = N \left( \ln V_N + \frac{3}{2} \ln \frac{U_N}{N} \right) \]
PaIG | \[ S = N \left[ \ln V_N + \frac{3}{2} \ln \frac{U_N}{N} - \frac{3}{2} \ln \left( 1 - \frac{2M^2}{N} \right) - \frac{3}{2} \frac{M^2}{N} \right] \]
1IM | \[ F = -J - T \ln \left( \cosh \frac{H}{T} + \sqrt{\sinh^2 \frac{H}{T} + e^{-4J}} \right) \]

Table 3 Ordinary thermodynamic systems. We use the following notations: IG = ideal gas, PaIG = paramagnetic ideal gas, 1IM = 1–dimensional Ising model, \( U \) = energy, \( V \) = volume, \( N \) = total number of molecules, \( M \) = magnetization, \( H \) = magnetic field, \( T \) = Temperature, \( J \) = spin interaction parameter, \( F \) = Helmholtz free energy.

and regular everywhere, indicating the lack of second order phase transitions. Consequently, GTD reproduces at the level of the curvature the properties associated with the thermodynamic interaction between the particles of the mentioned thermodynamic systems.

### Table 4 GTD of some ordinary systems.

Here \( I = I(T, H, J) \) is function with non-zero values. The Ricci scalar for the Ising model cannot be put in a compact form, but a numerical analysis shows that it is everywhere regular.

| System | Heat Capacity | Curvature scalar |
| --- | --- | --- |
| IG | \( \frac{3}{2} N \) | \( R = 0 \) |
| PaIG | \( \frac{3}{2} N \left( 1 - \frac{2M^2}{N^2} \right) \) | \( R = 0 \) |
| 1IM | \(- \frac{1}{T^2} \left\{ \frac{M(T,H)}{T^2[1+cosh \frac{H}{T}]} - \frac{N(T,H)^2}{T^2[1+cosh \frac{H}{T}]} \right\} \) | \( R \neq 0 \) |

4 Systems with first order phase transitions

Consider the non–degenerate and Legendre invariant metric

\[ G = (d\Phi - \delta_{ab} I^a dE^b)^2 + (\delta_{ab} E^a I^b)(\delta_{cd} dE^c dI^d), \quad (13) \]

for the phase manifold \( \mathcal{T} \). This metric is invariant with respect to total Legendre transformations and, consequently, can be used to describe the geometric properties of \( \mathcal{T} \). If we assume that the equilibrium manifold \( \mathcal{E} \subset \mathcal{T} \) has as coordinates the extensive variables \( \{E^a\} \), the smooth embedding map \( \mathcal{E} \to \mathcal{T} \), satisfying \( \varphi^* (d\Phi - \delta_{ab} I^a dE^b) = 0 \), can be used to generate in a canonical way the thermodynamic metric

\[ g = \varphi^* (G) = \left( E^c \frac{\partial \Phi}{\partial E^c} \right) \left( \frac{\partial^2 \Phi}{\partial E^a \partial E^b} dE^a dE^b \right) \quad (14) \]
for the equilibrium manifold $E$. In the case of a thermodynamic systems with only
two degrees of freedom ($n = 2$), let us introduce the extensive variables $\Phi = U =$
internal energy, $E^1 = S =$ entropy, and $E^2 = V =$ volume, together with the intensive
variables $T =$ temperature, and $P =$ pressure. The first law of thermodynamics \[\text{(3)}\]
reads $dU = TdS - PdV$ and the explicit form of the thermodynamic metric is
\[ g = (ST - PV) \left( U_{ss} dS^2 + 2U_{sv} dSdV + U_{vv} dV^2 \right) \] (15)
or, equivalently, in the entropy representation
\[ g = \frac{1}{T} (U + VP) \left( S_{uu} dU^2 + 2S_{uv} dUdV + S_{vv} dV^2 \right) . \] (16)

Probably, the best–known thermodynamic system with a very rich structure of first
order phase transitions is the van der Waals fluid \[\text{(3)}.\] For the sake of generality, we
will use here the van der Waals fundamental equation together with the theorem of
corresponding states in order to recast the fundamental equation in an invariant form
applicable to all fluids
\[ S = \ln \left( \frac{3}{V} - 1 \right) + \frac{3}{2} \ln \left( \frac{U}{V} + 3 \right) , \] (17)
where $U = U/U_c$ and $V = V/V_c$, with $U_c = 4a/9b$, \( V_c = 3b \), and $a$ and $b$ are the
van der Waals constants. The heat capacity following from this fundamental equation
turns out to be constant and, consequently, no second order phase transitions can
occur. However, the critical points determined by the roots of the equation
\[ PV^3 - 3V + 2 = 0 \] (18),
correspond to first order phase transitions \[\text{(3)}.\] where $P = P/P_c$, with $P_c = a/27b^2$, is the
reduced pressure.

From the fundamental equation \[\text{(17)}\] it is then straightforward to compute the
thermodynamic metric in the entropy representation:
\[ g^{vdW} = -\frac{9}{4(3V - 1)(U/V + 3)^3} \left\{ V^4 U^2 - 6V^2 U dU dV + 
+ 9 \left[ \frac{2(U + 3)(U^4 - 6V^2 + 6V - 1)}{3(3V - 1)^2} - 1 \right] dV^2 \right\} . \] (19)
The 2–dimensional equilibrium manifold turns out to be curved in general, indicating
that the particles of the fluid interact thermodynamically. Furthermore, the scalar
curvature of the above metric can be written in the form
\[ R = \frac{\Lambda^{vdW}}{(P/V^3 - 3V + 2)^2} \] (20)
where $\Lambda^{vdW}$ is a function of $U/V$, and $V$ that is well–behaved at the points where the
denominator vanishes. We see that the scalar curvature diverges at the critical points
determined by Eq.\[\text{(18)}.\] Consequently, a first order phase transition can be interpreted
geometrically as a curvature singularity. This is in accordance with our intuitive inter-
pretation of thermodynamic curvature.
It is worth noticing that the metric (14) can also be used to describe the properties of ordinary systems. Indeed, a straightforward computation of the corresponding thermodynamic metrics, using the fundamental equations of the ordinary systems listed in Table 3 leads to results equivalent to those reviewed in Table 4.

5 Conclusions

Geometrothermodynamics is a differential geometric formalism whose objective is to describe in an invariant manner the properties of thermodynamic systems in terms of geometric concepts. To a specific thermodynamic system, GTD assigns a particular equilibrium manifold $E$ whose geometric properties should be related to the thermodynamic properties of the system. In particular, we expect that the curvature of the equilibrium manifold is related to the thermodynamic interaction between the particles that constitute the system.

In this work, we analyzed two different thermodynamic metrics which can be canonically derived from the non-degenerate Legendre invariant metric

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

of the phase manifold $T$, where $\chi_{ab}$ is an arbitrary constant diagonal tensor. If $\chi_{ab} = \eta_{ab}$, the resulting thermodynamic metric can be used to describe the properties of systems characterized by second order phase transitions. This was shown in particular for several black hole configurations in diverse theories and dimensions. In the Euclidean case, $\chi_{ab} = \delta_{ab}$, the corresponding thermodynamic metric was shown to correctly reproduce the structure of phase transitions of first order in the specific case of a fundamental equation which describes realistic gases and fluids.

The formalism of GTD indicates that phase transitions occur at those points where the thermodynamic curvature is singular. The singularities represent critical points where the geometric description of GTD does not hold anymore and must give place to a more general approach. In ordinary thermodynamics the situation is similar; near the points of phase transitions equilibrium thermodynamics is not valid and non-equilibrium models must be implemented. It would be interesting to study non-equilibrium thermodynamic models in the context of a generalized GTD.

Our results show that the metric structure of the phase manifold $T$ determines the type of systems that can be described by a specific thermodynamic metric: An Euclidean structure describes systems with first order phase transitions, whereas a pseudo-Euclidean structure describes systems with second order phase transitions. At the moment we do not have an explanation for this result. It is clear that the phase manifold contains information about thermodynamic systems; however, it will be necessary to further explore its geometric properties in order to understand where the thermodynamic information is encoded. In this context, the use of variational principles could be of interest [24].

Acknowledgements II. Quevedo and S. Taj would like to thank ICRANet for support.

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