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Geometrothermodynamics, from ordinary systems to black holes

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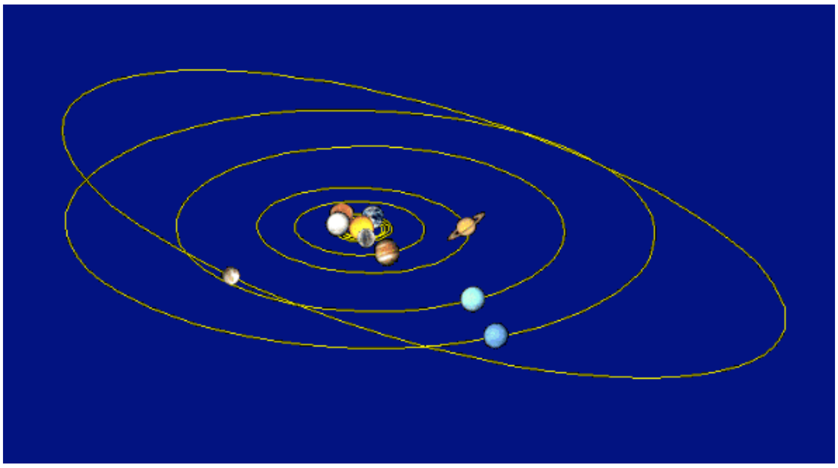

“ *ἀεὶ ὁ θεὸς γεωμετρεῖ* ”

(*God always geometrizes*)

Plato

Abstract

Thermodynamics was born in the nineteenth century together with the industrial revolution and it was mainly concerned with the macroscopic description of energy conversion involving heat and other forms of energy, most notably mechanical work. Later on it was developed as a theory on its own and nowadays it has achieved the state of an independent discipline of physics which can explain most of the collective phenomena from a very large perspective, provided a coherent notion of equilibrium is fulfilled. In fact, its applications range from the physics of fluids to superfluidity and superconductivity, from economics to cosmology, to biology, chemistry, information theory, sociology, and so on [1, 2].

The great generality of thermodynamics is due to the fact that its axioms, usually called "*laws*", are based on well established empirical results and are applicable to most of the systems in nature, thus making thermodynamics a fundamental underlying theory, in the sense that it sets limits (inequalities) on permissible physical processes and establishes relationships among apparently unrelated properties. According to Einstein "*a theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts*" [3].

Despite its generality, some aspects of thermodynamics still seem to be obscure and other points are not evident in the classical description, as for example the definition of thermodynamic equilibrium for systems which have non-negligible long-range interactions, i.e. non-extensive systems. Moreover, the mathematical formalism in which a thermodynamic course is presented is so related to the phenomenological description of the theory that some of the beautiful general aspects remain hidden and most of the origin of the thermodynamic relations appears unclear. In this sense, one would be tempted to agree with Arnold's ironical statement "*every mathematician knows it is impossible to understand an elementary course in thermodynamics*" [4].

On this regard, it must be said that the first attempts to give thermodynam-

ics a clear mathematical formulation date back to the original works of Gibbs [5] and Carathéodory [6]. Since then, several attempts have been made to describe thermodynamic systems by means of geometry, in particular following two distinct directions, i.e. the contact geometry of the phase space [7, 8, 9, 10, 11], associated with the first law, and the Riemannian geometry of the equilibrium space [12, 13, 14, 15, 16, 17, 18], associated with fluctuations and the second law.

Understanding the geometric description of thermodynamics appears to be of great interest for (at least) three reasons. One is that geometry provides a language in which every fundamental theory of physics can be rephrased and geometrical tools can be used to infer new physical ideas. This is not only an argument of beauty, but it has concrete applications, some of which have been proven to be particularly successful, especially in particle physics, where the use of symmetry and symmetry breaking has mapped out the route to the development of the Standard Model of particles. The second reason is that the discovery of the fundamental relation between the laws of thermodynamics and those of black hole mechanics made by Hawking [19] and Bekenstein [20] has focused the attention on the interplay between geometrical aspects of gravitation and their thermodynamic counterparts, such as e.g. the area of the event horizon and the entropy of a black hole. It is thus commonly believed that a deeper understanding of the geometrical meaning of information theory and thermodynamics could possibly shed some light on the relationship between thermodynamics and gravity. In fact, Einstein's equations basically established that Gravity *is* Geometry, which can be summarized in the fact that gravity affects the geometry of spacetime: $R_{\mu\nu} = 0$. On the other side, by adding a non vanishing stress-energy tensor on the right hand side of such equations, i.e. by taking $G_{\mu\nu} = T_{\mu\nu}$, one gets that Matter, as a source of gravity, *is* Geometry. However, the properties of Matter can be understood in terms of Thermodynamics. Therefore the scheme shall be closed by some equations describing how Geometry *is* Thermodynamics. In this sense, the recent works of Verlinde [21], Zhao [22] and Padmanabhan [23] have suggested the intriguing hypothesis that spacetime can be an emergent feature, which can be derived from the laws of thermodynamics.

For all these reasons the subject of this work is to provide a general and consistent approach to a geometric description of equilibrium thermodynamics, an approach which has the great advantage of unifying the contact and the Riemannian descriptions existing in the literature, thus giving a model which possibly encompasses all the aspects of ordinary thermodynamics and which can eventually also set the basis for a further extension to the thermodynamics of systems with long-range interactions or even systems out of equilibrium. This rather new geometric approach, known as Geometrothermodynamics (GTD), has been introduced by Quevedo [24] and has been proven to be succesful in describing many different thermodynamic systems, from ordinary to exotic ones, such as black holes and cosmological models [25, 26, 27, 28, 29, 30, 31, 32, 33, 34].

In this work, after a brief review of the historical development of the geometric ideas in thermodynamics, we will focus on the symmetries underlying the mathematical formulation of thermodynamics. Such a topic will directly lead us to introduce the abstract manifolds on which we will describe thermodynamics and it will result clear that the concepts of Legendre symmetry and symmetry under change of representation will play a major role. Therefore, we will construct a new metric structure that shares such symmetries and argue that the resulting geometry allows to deal both with processes that can only be correctly defined in the phase space, such as coexistence curves, as well as with objects that are more naturally defined in the equilibrium space, such as standard thermodynamic processes and continuous phase transitions. Based on these facts, we will argue that the new metric derived here is the natural geometric counterpart of standard homogenous thermodynamics and show that this assumption turns out to be correct for a wide variety of ordinary examples. Finally, having discussed in detail the context of systems for which the hypothesis of extensivity does not apply, we will turn in the last chapters to address the question of thermodynamics of black holes and explain to what extent thermodynamic geometry can help to understand such particular systems. The thesis is organized as follows.

In Chapter 1 we will present a brief review of standard thermodynamics, with a special emphasis on phase transitions, in order to highlight the differences between first order phase transitions and continuous phase transitions, which will serve as a guideline for the construction of the corresponding geometric model. Moreover, we will give a historical background on the development of the geometric formulation of thermodynamics so far and introduce the notation that we shall use in the following chapters.

In Chapter 2 we will see how first order phase transitions have a natural description within the contact structure of the thermodynamic phase space, thus motivating the introduction of such space in the following chapters. Especially, we will deal with the coexistence region and determine the geometrical counterparts of Maxwell equal area construction. We will also show how to extend this construction to generalized theories of thermodynamics, in which the potential is a homogeneous function of any degree. As a result, we will introduce a new definition of equilibrium between subsystems of a thermodynamic system, i.e. a generalized zeroth law of thermodynamics, which applies to the case of non-extensive systems in which the thermodynamic potential is not simply homogeneous of order one, such as e.g.

in the case of black holes [35], self-gravitating systems [36], quantum systems [37], nanoscale materials [38], but also the simple Ising model corrected with a long-range type of interaction [39]. This novel approach solves a long-standing problem in thermodynamic geometry (see e.g. [18]), that is, the problem of describing the coexistence region and it provides a natural generalization of Maxwell's construction.

In Chapters 3 and 4, after an introduction to Geometrothermodynamics with particular emphasis on the concepts of symmetries, we will introduce a new metric structure, both in the phase space and in the equilibrium space of thermodynamics, whose group of symmetries contains the symmetries of ordinary thermodynamics, which we will call the *natural metric* in the context of GTD. Afterwards, we will present the GTD analysis of some ordinary thermodynamic systems with the use of such geometry. It turns out that the Riemannian equilibrium manifold thus defined correctly describes the behavior of any thermodynamic systems as long as it is in a single phase, with the scalar curvature giving a measure of the thermodynamic stability with respect to fluctuations. In particular, we will see that the scalar curvature of the equilibrium manifold diverges along the spinodal curve, signalizing that the single phase description is no longer sufficient and we need to move to a larger space, i.e. the phase space. Moreover, the scalar curvature also gives a direct measure of the divergence of fluctuations near the critical point, corresponding to the divergence of the correlation length, that is, we will recover in our formalism a result first obtained by Ruppeiner in [14].

Furthermore, Chapters 5 and 6 are devoted to the discussion of phase transitions in black holes. After a general discussion of the various definitions of phase transitions in black holes existing in the literature, we will make clear that first order phase transitions *à la Van der Waals*, taking place especially in asymptotically AdS black holes [40, 41, 42, 43, 44, 45, 46, 47], can be treated equivalently with the Maxwell construction and the full equipment of the contact geometry of the phase space (as for ordinary thermodynamic systems), *provided a consistent definition of equilibrium between the two coexisting phases is given*, as explained in Chapter 2. Moreover, continuous phase transitions can be fairly well described by the means of the thermodynamic curvature of the metric introduced in Chapter 3. In addition, we will illustrate that phase transitions as defined by Davies [35] are better interpreted in ordinary thermodynamics as the changing from a stable phase to an unstable one. Moreover, we will argue that they are a completely different thermodynamic phenomenon, which is characteristic of systems with long-range interactions [48, 49]. Therefore, we will conclude that also the thermodynamic geometric description shall be different, thus explaining some puzzling results appearing in the literature [16, 50, 51, 52]. In order to describe such transitions, we will provide a different metric structure from the GTD framework which allows to take account of this situation. These ideas will be applied to the cases of the Reissner-Nordström and Kerr black holes in any spacetime dimensions and later to the Myers-Perry black hole in five dimensions, considering different values of the spins.

Finally, in Chapter 7 we will make a summary of the new results presented in this work and discuss further possible applications and future developments.

We hope that this work will be a concrete step towards a clearer mathematical description of thermodynamics and hopefully also towards a deeper understanding of the relation between the geometry of thermodynamics and the thermodynamics of systems in strong gravitational fields.

Papers

This thesis was performed at the University of Rome “Sapienza” and at the National Autonomous University of Mexico, UNAM.

The main results of this thesis are published in the following research articles

- **“Second order phase transitions and thermodynamic geometry: a general approach”**
  A. Bravetti & F. Nettel,
  submitted to J. Geom. Phys., arXiv:1208.0399v2 [math-ph].
- **“The conformal metric structure of Geometrothermodynamics”**
  A. Bravetti, C. S. Lopez-Monsalvo, F. Nettel & H. Quevedo,
  J. Math. Phys. **54**, 2, 345-349, (2013).
- **“Representation invariant Geometrothermodynamics: applications to ordinary thermodynamic systems"**
  H. Quevedo, F. Nettel, C. S. Lopez-Monsalvo & A. Bravetti,
  submitted to J. Geom. Phys., arXiv:1303.1428 [math-ph].
- **“Geometrothermodynamics of higher dimensional black holes”**
  A. Bravetti, D. Momeni, R. Myrzakulov & H. Quevedo,
  Gen. Rel. Grav. **45**, 8, 1603-1617, (2013).
- **“Geometrothermodynamics of Myers-Perry black holes”**
  A. Bravetti, D. Momeni, R. Myrzakulov & A. Altaibayeva,
  Adv. High Energy Phys. 2013, 549808, (2013).
- **“Legendre symmetry and first order phase transitions of homogeneous systems”**
  A. Bravetti, C. S. Lopez-Monsalvo, & F. Nettel,
  submitted to Phys. Lett. A, arXiv:1308.6740 [physics.gen-ph].

In addition, the following papers were published during the time of work of this thesis

- **“Updated constraints on $f(\mathcal{R})$ gravity from cosmography”**
  A. Aviles, A. Bravetti, S. Capozziello & O. Luongo,
  Phys. Rev. D **87**, 4, 044012, (2013).
- **“Cosmographic reconstruction of $f(\mathcal{T})$ cosmology”**
  A. Aviles, A. Bravetti, S. Capozziello & O. Luongo,
  Phys. Rev. D **87**, 064025, (2013).
- **“Dark energy from Geometrothermodynamics”**
  A. Bravetti, & O. Luongo,
  submitted to Int. J. Mod. Phys. D, arXiv:1306.6758 [gr-qc].

Contents

1 Introduction

Thermodynamics is the study of collective phenomena through the use of properties that characterize their behavior as a whole. For this reason it has acquired great importance in the modern treatment of various disciplines, ranging from physics to economics and also biology, chemistry and so on. One of the two most important ingredients of the theory is *equilibrium*, which is the main hypothesis that ensures that the system being analyzed can be treated through the laws of thermodynamics. Therefore, it enables us to speak about thermodynamic states, that is, states in which the great varieties of components in the system can be described by only a few parameters, namely temperature, pressure and volume [1, 2]. The second fundamental aspect about thermodynamics is the appearance of *phase transitions*. Phases of matter are regions of the thermodynamic configuration space characterized by a uniform change in the thermodynamic parameters of the system. On the contrary, phase transitions are abrupt changes in some of these parameters. It is important to underline that such transitions can only happen in the thermodynamic limit, i.e. they are not allowed in the mechanics of finite systems, but they are the most natural result of regarding a system as a collective phenomenon [53, 54, 55]. Since we will be dealing in this thesis with the concepts of equilibrium and phase transitions, it is better to give a brief resume, with a special focus on the properties that characterize phase transitions that we shall use in the next chapters.

1.1 Basic concepts of thermodynamics

1.1.1 The four laws of thermodynamics

Classical thermodynamics deals with equilibrium states and conservation of energy. Therefore the axioms of the theory establish the existence of such states, the possibility of measuring the change of energy from one form to another during an equilibrium (quasi-static) process, and to understand the final fate of the evolution of a system towards equilibrium. Such axiomatic structure is encoded in four axioms, usually referred to as *the four laws of thermodynamics*. We report them here in a schematic way, leaving aside any discussion on their justifications (see e.g. [1]).

The Zeroth Law: The zeroth law of thermodynamics describes thermal equilibrium between systems in contact and allows for a definition of temperature.

A system is said to be in thermal equilibrium if it experiences no net change in thermal energy. Suppose A, B and C are three different systems, then

"If systems A and B are in thermal equilibrium with system C, then system A is in thermal equilibrium with system B".

This principle implies (together with the assumption that the potential be a homogeneous function of order one, see Chapter 2) that the three systems must have the same temperature and hence it sets the basis for comparison of temperatures.

The First Law: The first law of thermodynamics can be stated in several different and equivalent ways. We choose here the following

"For a thermodynamic cycle, the net heat supplied to the system equals the net work done by the system on the surroundings".

This is equivalent to say that energy can neither be created nor destroyed, it can only change form. Let us see the mathematical and physical implications of this principle. Let ΔQ denote the net amount of heat absorbed by the system and ΔW the net amount of work done by the system. The first law of thermodynamics states that we can always define a state function U such that its difference from any given initial and final states does not depend on the thermodynamic process leading from one state to the other, but it is given by

$$\Delta U = \Delta Q - \Delta W \,. \tag{1.1}$$

The function U is called the *internal energy* of the system and it is defined only up to an additive constant. Moreover, in ordinary thermodynamics it must be an *additive* variable, which implies that were the system divided into two subsystems, then each subsystem would have half the total internal energy of the original system.

It is important for the following discussion to present the infinitesimal version of (1.1). In an infinitesimal transformation of the system, the infinitesimal change in the internal energy is given by

$$\mathrm{d}U = đQ - đW = đQ - P\,\mathrm{d}V \,, \tag{1.2}$$

where $\mathrm{d}U$ is an exact differential, in the sense that it is independent of the path, while $đQ$ and $đW$ are not, P is the external pressure and $\mathrm{d}V$ is the change in the volume occupied by the system.

The Second Law: The second law of thermodynamics can also be phrased in many equivalent ways. However, all of them are negative statements, which means that they state the impossibility of something to happen. Such type of statement is hard to be demonstrated in general. However, no exceptions to the second law have been found and due to its generality it is regarded as one of the most fundamental laws in Nature. One way of phrasing the second law is

"There is no thermodynamic transformation whose sole effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir".

Such formulation turns out to be equivalent to say that for any closed cycle of transformations one has

$$\oint \frac{đQ}{T} \leq 0\,, \tag{1.3}$$

where the equality only holds for *reversible* cycles. In particular, this implies that for reversible cycles the quantity $\mathrm{d}S \equiv đQ/T$ is an exact differential and therefore we can define another state variable S, which depends only on the initial and final state and not on the thermodynamic process in-between. This function S is called the *entropy* of the system. It follows immediately that S is an extensive variable, related to the intensive quantity T. Finally, for a reversible process, we can rewrite the first law of thermodynamics, equation (1.2), as

$$\mathrm{d}U = đQ - đW = T\,\mathrm{d}S - P\,\mathrm{d}V\,. \tag{1.4}$$

The Third Law: We have seen that the second law deals with the definition of entropy. We note that such function is defined up to an additive constant and apparently the definition can be different from system to system, provided they are made of different substances. The third law of thermodynamics determines the entropy of any thermodynamic system uniquely by stating that

"The entropy of a system at absolute zero is a constant, which may be taken to be zero".

It is clear that this statement is not related to any particular substance and it does not depend on the process necessary to reach the absolute zero. In fact, the third law guarantees that $S \to 0$ whenever $T \to 0$, no matter what the substance, nor what is the process to reach the absolute zero limit.

1.1.2 Homogeneity, Additivity, Extensivity and Long-range interactions

This section serves to make clear some concepts which will be repeated several times in this work and that may cause some confusion. We write here the definitions only, together with some useful references to a more detailed description. First of all we shall introduce the concept of homogeneity.

Definition 1. (Homogeneity) *We say that a function* $f(x^1, \ldots, x^n)$ *is* homogeneous of order β *in its variables if*

$$f(\lambda\, x^1, \ldots, \lambda\, x^n) = \lambda^\beta f(x^1, \ldots, x^n)\,, \quad \lambda \in \mathbb{R}^0\,. \tag{1.5}$$

We observe that in standard thermodynamics, both the entropy and the internal energy are homogeneous functions of order one.[1] In the particular case that the entropy and internal energy are homogeneous functions of order one, they also happen to satisfy another fundamental property, which is additivity.

Definition 2. (Additivity) *Given a system of* N *particles and a joint physical observable* $X(x_1, \ldots, x_N)$ *of the individual states of the particles, we say that* X *is* additive with respect to splitting of the system into subsystems *if for any two probabilistically independent subsystems* A *and* B *one has*

$$X(A + B) = X(A) + X(B)\,. \tag{1.6}$$

If an observable satisfies Eq. (1.6), then it follows immediately that for any system of N equal and independent particles

$$X(N) = N\, X(1)\,, \tag{1.7}$$

which means that X is an extensive quantity, according to the following definition.

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[1] In this work we limit our attention to homogeneous functions. However, our results can be easily generalized to the case of *quasi-homogeneous functions*, that is when the potential is homogeneous of different degree with respect to its variables (see e.g. [56] for a detailed analysis of quasi-homogeneous thermodynamics).

Definition 3. (Extensivity) *Given a system of N particles and a joint physical observable $X(x_1, \dots, x_N)$ of the individual states of the particles, we say that X is* (asymptotically) extensive *if*

$$\lim_{N\to\infty} \frac{X(N)}{N} < \infty \,. \tag{1.8}$$

For a more detailed treatment about the concepts of additivity and extensivity, we refer to [57, 58]. Here we limit to say that for ordinary systems, the entropy and the internal energy satisfy all the above mentioned properties.

Finally, we define those types of systems where the situation is more messed up.

Definition 4. (Long-range interaction) *We say that a system of N particles in d dimensions has a* long-range interaction *if the pair interaction potential that gives the interaction between the particles decays as $1/r^\nu$, where $\nu \leq d$ and r is the distance between any two particles.*

As an example, the Newtonian potential decays with $\nu = 1$. Therefore, a system of N particles in three dimensions interacting between them with a Newtonian potential is a system with long-range interactions. It turns out that in systems with long-range interactions, the interaction part of the potential does not vanish in the thermodynamic limit $N \to \infty$, and thus for such systems the (Boltzmann-Gibbs-Shannon) entropy and the (related) internal energy are not extensive, which means that the thermodynamic limit for these quantities does not hold and one needs to work with non-additive extensions of thermodynamics (see e.g. [57] and references therein).

1.1.3 Stability Conditions

In this section we give a brief account of the consequences of the second law in equilibrium thermodynamics. Our aim here is to highlight the distinction between global and local stability conditions and its importance in our geometric description below. We follow the arguments contained in [1], so that we will skip the proofs of our statements.

Having established by the second law that the system evolves towards a state of maximum entropy, we discuss now what are the mathematical implications of such assumption. Indeed the maximum principle has two types of implications on the stability of the thermodynamic equilibrium. The first type are *global* stability conditions, which basically state that the entropy and all its Legendre transforms have to be concave functions of their natural variables (U, V), that is, they have to lie above their tangent plane at every point. We remark that this can be also rephrased by stating that the internal energy and all its Legendre transforms must be convex functions of the variables (S, V), that is, they have to lie below their tangent plane at every point. On the contrary, *local* stability conditions can also be deduced from the maximum principle. Being the state of equilibrium the one for which the entropy has a local maximum, supposing that the entropy is twice-differentiable, one can derive local conditions, i.e. *the Hessian of the entropy has to be* (*semi*)*-negative definite.* Equivalently, this can be rewritten in terms of the energy by saying that the Hessian of the internal energy (more frequently the Gibbs free energy is used) has to be (semi)-positive definite.

It turns out that the local stability conditions are equivalent to some statements about the so-called *second order response functions.* Indeed, in thermodynamics one defines the quantities

$$C_V \equiv T \left(\frac{\partial S}{\partial T}\right)_V \qquad C_P \equiv T \left(\frac{\partial S}{\partial T}\right)_P \tag{1.9}$$

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \qquad \alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P . \tag{1.10}$$

The first two quantities are known as the *heat capacity at constant volume* and the *heat capacity at constant pressure* respectively, while the other two are the *isothermal compressibility* and the *coefficient of expansion* [1]. The name second order response functions descends from the fact that they are related to the second order derivatives of the potentials and therefore the local conditions on the Hessian of the potential imply conditions on these functions. In particular, *all of them must be greater than* (*or equal to*) *zero for the system to satisfy the local stability.*

In principle, some further relationships among them must also be satisfied, but they will not be important for the discussion here so we refer to [1] for more details. Moreover, additional second order response functions can be introduced, depending on the thermodynamic potential being used, but for ordinary systems it turns out that only three of them are sufficient to completely describe the local stability of the system. However, for systems with long-range interactions, one can get different local results depending on the ensemble, therefore it is useful to define all of the local quantities, as we will do in Chapter 5.

We remark that the global stability conditions are much stronger than the local ones. Therefore, fulfillment of the global conditions imply the fulfillment of the local ones, while the converse is not true, so that in principle a system can be in a so-called *metastable state*, one in which the global stability conditions do not hold whereas the local ones do. This fact will turn out to be particularly important for instance in our discussion about first order phase transitions. In fact, as we shall see, the region where the local stability conditions for e.g. a Van der Waals fluid fail is strictly contained inside the region where the global stability conditions are broken (see Figure 1.4 below). Therefore, from the point of view of ordinary thermodynamics (for which the potential is *additive*), it is thermodynamically favored for the system to phase separate and follow the concave hull of the entropy (resp. the convex hull of the energy) *long before* the region of local instability is reached. This implies that ordinary thermodynamic systems (viz. systems for which the potential is additive with respect to splitting into subsystems) never reach the metastable region following an equilibrium process, nor of course the region of local instability. However, if we are to relax the hypothesis of additivity (as we shall do in Chapter 2 by considering potentials that are homogeneous of any order), then the breaking of the global stability conditions not necessarily implies that phase separation is thermodynamically favored. In sum, a system whose potential is not homogeneous of order one can reach the region of local instability by a process at equilibrium. One of the most interesting consequences of this fact is that such type of systems (basically all systems with long-range interactions) can undergo equilibrium regions with negative (microcanonical) heat capacities and ensemble inequivalence [48, 49].

1.1.4 The ideal gas

Models in thermodynamics are a powerful tool in order to investigate general features. Among them, a major role is played by the ideal gas system. An ideal gas is a gas whose particles have no interaction between themselves. This is of course an idealization, but it can be thought as the situation occurring when the density of particles is very low. In this sense every gas is an ideal gas in some limit. We are interested here to provide the fundamental equation for the ideal gas that will be used in the following chapters and to mention the fact that an ideal gas show no phase transitions.

The fundamental equation for a monatomic ideal gas that will be used in this thesis can be either written in the entropy representation as

$$s(u,v) = \frac{3}{2}\ln u + \ln v\,, \tag{1.11}$$

where s, u and v are the molar quantities, i.e. the extensive quantities divided by the number of moles, and we have set the universal gas constant to $R = 1$ [1]. Equivalently, one can give all the thermodynamic information about an ideal gas in the energy representation as

$$u(s,v) = \left(\frac{1}{v}\,e^{s}\right)^{\frac{2}{3}} . \tag{1.12}$$

As already commented, an ideal gas has no inter-particle interaction, therefore this system will be the basic model to test and build our geometric counterpart of the concept of thermodynamic interaction (see Chapter 4 for the geometric description of an ideal gas).

1.1.5 The Van der Waals model

The second model system which is ubiquitous in thermodynamics is the Van der Waals gas. This model describes, at least qualitatively, the properties of real gases, that is, it reproduces the correct shapes for the isotherms and the instabilities corresponding to both first order phase transitions, i.e. separation of the system into different phases, and continuous phase transitions, i.e. critical points where fluctuations diverge and the thermodynamic description breaks down. Therefore it will play a central role in our general discussion of both the contact description of first order phase transitions (which will be the content of the next section and of Chapter 2) and the Riemannian description of continuous phase transitions (which will be discussed in detail in Chapters 3 and 4). Here we give the fundamental equation of the Van der Waals gas, as usual first in the entropy representation as

$$s(u,v) = \frac{3}{2}\ln\left(u + \frac{a}{v}\right) + \ln\left(v - b\right) . \tag{1.13}$$

and then in the energy representation as

$$u(s,v) = \frac{a(v-b)^{\frac{2}{3}} - v\,e^{\frac{2}{3}s}}{v(v-b)^{\frac{2}{3}}} , \tag{1.14}$$

where molar quantities are always being used and the gas constant is set to one. It is worth remarking that (1.14) is a generalization of the ideal gas equation, in which two new parameters appear, a which is representative of the inter-particle interaction and b that takes into account the fact that particles are hard spheres, i.e. they cannot occupy the same volume of space.

1.1.6 Phase transitions

Since all the geometric description in this work will be basically dealing with phase transitions, let us pause a little to recall the properties and the characterization of phase transitions in ordinary thermodynamics.

Phase transitions are among the most interesting phenomena in nature, with applications that range from particle physics to cosmology, from social science to geology, from information theory to economics and more [53, 54, 55]. For this reason they have been investigated in a number of ways. In ordinary thermodynamics, they can be classified into two major classes. First order phase transitions, which happen along a line of coexistence between two (or more) competing phases and present discontinuities in some first derivatives of the thermodynamic potential, and continuous phase transitions (or second order phase transitions, according to the old Ehrenfest classification [59]), which on the contrary happen only at a point, usually referred to as the critical point. Physically, the process taking place during the two types of transitions is completely different. In the first case, two phases (represented by equal minima of the Gibbs potential) are competing, which means that the system has split into two coexisting phases. In this type of transition, the equilibrium thermodynamic description requires a special adjustment, namely the Maxwell equal area law, after which equilibrium and stability are recovered [1].

On the contrary, near a continuous phase transition, there is an incredible increase in the fluctuations of the system, so that the thermodynamic (equilibrium, mean value) description eventually breaks down. Mathematically, this is represented by the fact that the thermodynamic potential becomes non analytic and the second order response functions diverge (hence the name “second order phase transitions”). It is important for the discussion in Chapter 5 to remark also another fact about continuous phase transitions, that is, a continuous phase transition implies the divergence of (all) second order response functions, in a specific way encoded in the so-called *critical exponents* [55]. On the other side, the divergence of one of the response functions along a line or a point does not necessarily implies a continuous phase transition (it may correspond to a change in the stability in some of the ensembles and it is of particular interest in systems showing ensemble inequivalence [48, 49]). In any case, the failure of the equilibrium hypothesis at the critical point hints at the fact that some additional ingredient must be taken into account in this region. It turns out naturally that including fluctuations from the mean values of the thermodynamic quantities, the situation is completely resolved [2, 15].

First order phase transitions

First order phase transitions are a fully thermodynamic phenomenon, in the sense that they can be described using the basic theory of thermodynamics [1]. In fact, nothing special happens except for the equilibrium between different phases. The only requirement to do thermodynamics on a first order phase transition is to take special care over the region of coexistence. This is because the coexistence region is not predicted by the fundamental equation, nor by the equations of state in their analytical form, but it results from the presence of two (or more) equal minima of the Gibbs potential, which means that the system separates into two (or more) phases that coexist at equilibrium (see Figure 1.1 below). Therefore one has a thermodynamic process taking a phase to another along which the system is split into a mixture of the two phases. Thus the analytic treatment fails over this region and even the phase diagrams show some discrepancies (this is a basic example of ensemble inequivalence, see e.g. [48, 49]). The resolution of this problem in ordinary thermodynamics is the introduction of a "correction" to the unstable isotherms, the so-called *Maxwell equal area law*, by means of which the laws of thermodynamics are recovered and the coexistence can be described. There is only a little price to be paid for doing such construction, that is, the thermodynamic potential becomes non analytic at some points and the Legendre transformation is not defined along the

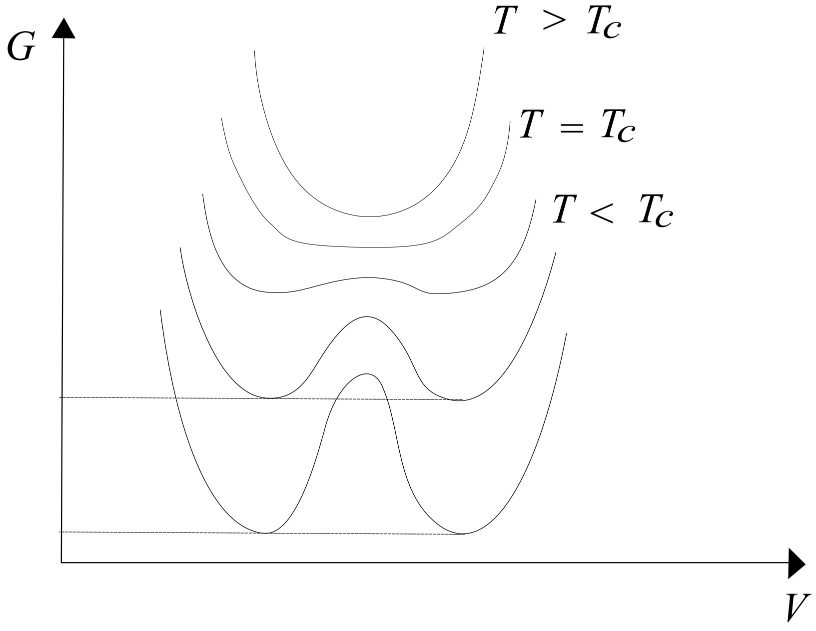

Figure 1.1: In the coexistence region $T < T_c$ the Gibbs potential has two equal minima, corresponding to two different phases that are equally probable. In this region the Legendre transformation is ill-defined as the convexity of G is lost, corresponding to an unstable region of the potential.

line of coexistence. The situation is depicted in Figs. 1.1, 1.2 and 1.3. Figure 1.1 shows that in the region of coexistence, the Gibbs potential has two equal minima, representing the two different phases that coexist over this region. In Figure 1.2 the unstable isotherms are shown, together with the Maxwell law. Details about these features can be found in any book of thermodynamics, see e.g. [1].

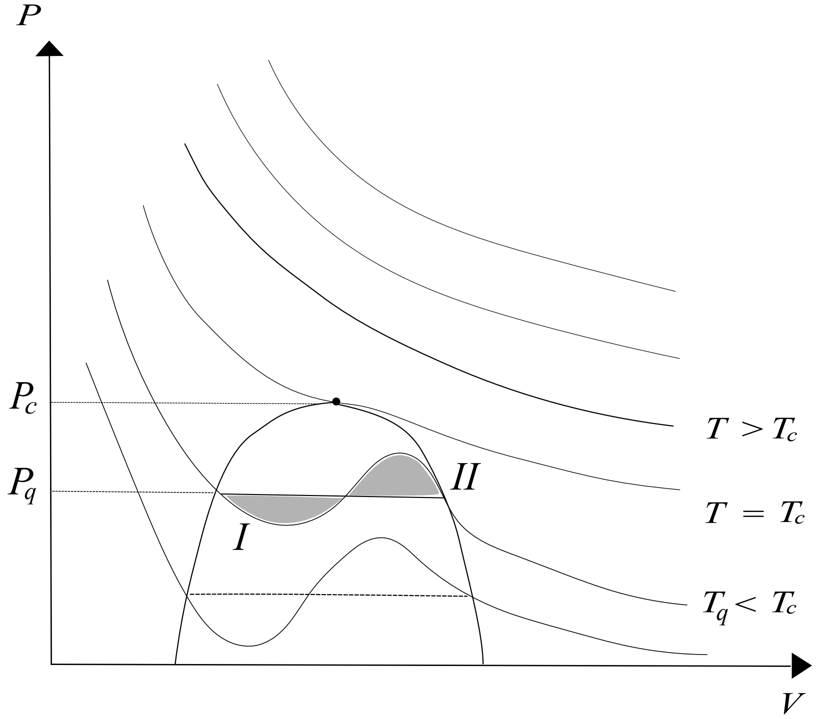

Figure 1.2: This figure shows typical isotherms in a $P-V$ diagram. The coexistence (horizontal) line constructed according to the Maxwell equal area law is indicated as well as the critical point (P_c, T_c) where a continuous phase transition takes places.

Let us now focus on another feature, i.e. the $P-T$ diagram of a typical first order phase transition (see Fig. 1.3). In this diagram it is particularly clear that when we are at a given temperature and a given pressure along the coexistence region, this corresponds to a single point in the $P-T$ diagram (c.f. Maxwell line in Fig. 1.2 and point q in Fig. 1.3).

On the other side, we see from Figure 1.2 that the system is evolving and that in $P-V$ coordinates the "point" q is not just a point, but it corresponds to all the segment of coexistence at the given temperature T_q. This is indicating that in the $P-T$ description we are missing some information and that the general aspects of the process can only be accounted for if we look at both diagrams. In Chapter 2 we will interpret this fact as a signal that a phase coexistence cannot be fully described on a two dimensional manifold, i.e. cannot be described on the manifold of equilibrium states usually introduced in the intrinsic treatments of

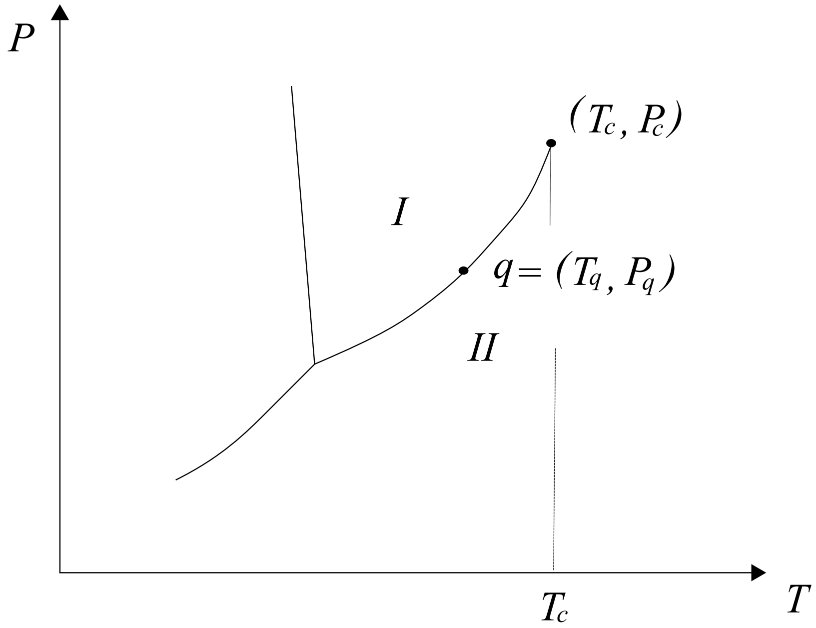

Figure 1.3: We observe that the coexistence line constructed according to Maxwell law in the $P - V$ diagram corresponds to a single point q in the $P - T$ diagram.

thermodynamic geometry. This is a first point hinting at the direction that we must introduce some larger structure in order to include first order phase transitions and in general all types of transitions which show ensemble inequivalence [48, 49].

On the other hand, Figure 1.4 shows another crucial aspect happening along the coexistence curve, i.e. the failing of the Legendre transformation. This means that along the region of coexistence one cannot switch for example from the description in the U potential to the description in the G potential. We remark that this is the only region of the thermodynamic space in which that happens. In fact, in all other regions the two descriptions are fully equivalent. We also interpret this result as indicating that in the region of coexistence the $P - V$ diagram is not equivalent to the $P - T$ diagram, that is, the two ensembles are inequivalent. Therefore if one wants to recover the full information, then one should consider both. Again this is indicating that in the context of thermodynamic geometry we cannot limit to the (2-dimensional) equilibrium manifold, but we need a larger space.

Let us summarize at this point the properties that such a larger space should have. First, it must take account of the Maxwell equal area construction, so that we can be sure of being working on real equilibrium states and not on metastable ones. Second, such space should contain the information given by all the possible thermodynamic variables, since we have just learnt that only two of them are not sufficient on the coexistence region. Finally, the geometric objects defined on such

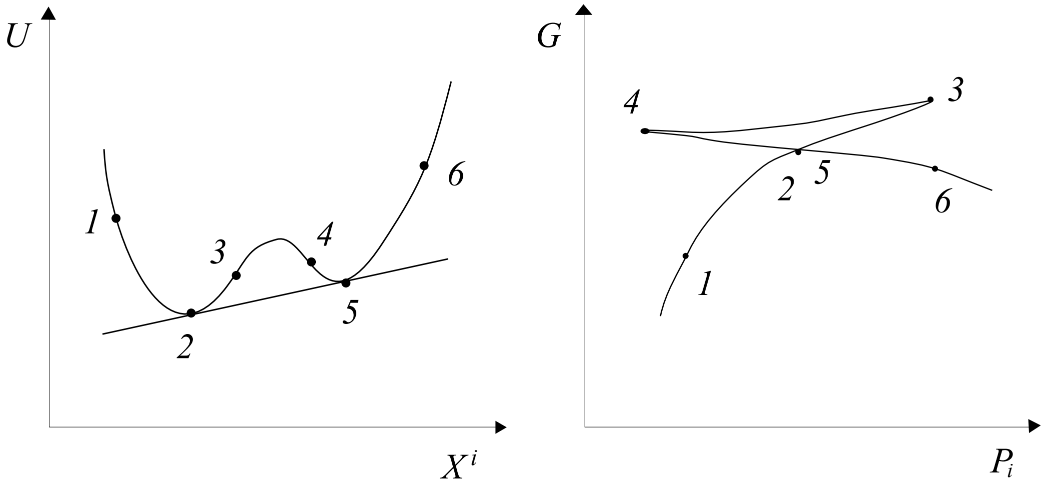

Figure 1.4: Failure of the Legendre transformation in the coexistence region as one applies the transformation from U depending on the extensive variables X^i to the potential G depending on the intensive variables P_i.

space should be symmetric with respect to Legendre transformations and changes in the representation, excluding at most the region of coexistence, where we know that the Legendre transformation fails. It would be also natural that the larger space include the equilibrium (2-dimensional) space and that the two descriptions coincide out of the coexistence region. The analysis of the construction of such space will be the content of Section 1.2.2 and the importance for the description of first order phase transitions will be highlighted in Chapter 2.

Continuous phase transitions

Continuous phase transitions are transitions between two different phases that happen without discontinuity in any of the basic thermodynamic state functions, that is the reason for the name “continuous”. However, it can be shown that second order derivatives of the potential are discontinuous at such points, therefore according to the old Ehrenfest classification [59] they are sometimes also called “second order phase transitions”. In this work we will call them continuous, because this term is the most modern and it encompasses better the phenomenon (see [53, 54] for a full introduction to the theme). Moreover, this term will help us to better understand the difference between continuous phase transitions in standard thermodynamics, happening at critical points, and those transitions that are often referred to as second order phase transitions in the literature of black holes thermodynamics, which will be the content of Chapter 5, which will be named *Davies phase transitions* here.

Continuous phase transitions happen at single points in the phase diagram, called *critical points*, and they are usually associated with a change in the symmetry of the system. For example, the critical point at the end of the liquid-vapor line of coexistence of a Van der Waals fluid is point (T_c, P_c) in Figure 1.3. The microscopic aspect characterizing a continuous phase transition is completely different from the one occurring at a first order phase transition. In fact, the fluctuations on the value of the thermodynamic parameters become very large in the critical region and they diverge at the critical point, due to the divergence of correlations [54, 55]. This fact has some remarkable consequences on the thermodynamic description. The first direct consequence is that fluctuations out of the average values play a major role in this region, so that the system cannot be analyzed by considering only the mean values of the thermodynamic functions. This is so important that it is the understanding of this fact that lead to the solution of the problem with the wrong quantitative predictions of the mean field theories, such as the Van der Waals description or the Curie description or, more generally, the Landau treatment of critical behavior [2, 53, 54, 55]. Such a revolution gave birth to the modern treatment of critical behavior, including Renormalization Group techniques, scaling laws and universality (see e.g. [53, 54, 55] and references therein). In fact, the second and perhaps most striking consequence of large correlations in the critical region, is the fact that the parameters of the system exhibit some scaling laws, i.e. the thermodynamic response functions diverge according to some precise power laws, whose exponents (the *critical exponents*) can be calculated explicitly. Furthermore, many different thermodynamic systems are found to have the same critical exponents, that is because the appearence of long-range correlations make the microscopic differences between the systems irrelevant and therefore they all look the same from the thermodynamic perspective. Indeed, it turns out that differences in the values of exponents are only due to spatial dimensions of the system, type of the order parameter and symmetries. Systems having the same critical exponents are said to belong to the same *universality class.*

Therefore in the case of continuous phase transitions the thermodynamic analysis is telling us that we must include fluctuations over the equilibrium values in the geometric picture in order to correctly reproduce the behavior of the system. As we shall see in Section 1.2, fluctuations have a natural geometric representation resulting from both statistical mechanics and thermodynamic fluctuation theory [10, 15]. Furthermore in Chapter 3, based on the symmetry assumptions of GTD, we shall derive a new Riemannian structure for thermodynamics that includes fluctuations in a natural way and therefore permits the description of continuous phase transitions.

1.2 Thermodynamics and Geometry: historical background

In this section we give a brief historical overview about the different approaches to the geometrization of thermodynamics and at the same time we introduce the main geometric concepts that we are going to use throughout the rest of the work. Moreover, from the discussion here, it will result that Geometrothermodynamics comes as a synthesis of the different approaches, with a special emphasis on the role played by the thermodynamic phase space and the introduction of the concept of symmetry, which had never been addressed before.

1.2.1 Gibbs sufraces

The study of geometric properties of thermodynamics has started with the works of Gibbs [5], who considered thermodynamic systems as surfaces embedded on the euclidean space, defined by their fundamental equation. Thus for example the ideal gas at constant number of molecules can be regarded as the two-dimensional surface in $\mathbb{R}^3$ given by the fundamental equation $s(u, v) = 3/2 \ln u - \ln v$. Due to the second law of thermodynamics, it turns out that such surfaces must be concave (or convex, depending on the thermodynamic potential used to define them) throughout all the domain of definition. In particular, no notion of distance has ever been included in such space by Gibbs. However, some later work by Gilmore and Salomon pointed in this direction [60]. In particular, they described Gibbs surfaces by means of the first and second fundamental forms. It turned out that such description does not allow one to include fluctuations from equilibrium and hence it fails to account for phase transitions [61].

Riemannian geometry was first introduced in statistical physics and thermodynamics by Rao [62], in 1945, by means of a metric whose components in local coordinates coincide with Fisher's information matrix. Remarkably, such structure can be used to calculate the informational difference between measurements. The original work of Rao has been followed up and extended by a number of authors (see e.g. [63] for a review).

Later, in the 1970s, Weinhold [12, 13] introduced a scalar product on the tangent space at every point of an abstract space constituted by all the admissible thermodynamic states of the system, the so-called *equilibrium manifold*. Such product was defined by the Hessian matrix of the internal energy of the system. The great advantage in the introduction of this new structure is that many of the thermodynamic relations can be elegantly recovered from the properties of the scalar product, which points at a more rich geometric structure in thermodynamics. However, Weinhold himself never introduced the concept of distance in the equilibrium manifold. It was Ruppeiner [14] who then introduced a metric structure inspired by the scalar product on the tangent space of Weinhold, but derived from a completely different perspective. In fact, Ruppeiner's intrinsic metric on the abstract equilibrium manifold is defined as (minus) the Hessian of the entropy and it is derived directly from thermodynamic fluctuation theory [14]. As a consequence of its definition, the distance between equilibrium states has a natural interpretation as the probability of fluctuations between the two states. Moreover, Ruppeiner developed a fully covariant fluctuation theory which is consistent with the introduction of the thermodynamic metric based on the Hessian of the entropy and showed that the scalar curvature of this Riemannian structure gives a macroscopic measure of the correlation volume of the system, which opens the possibility to understand microscopic properties of matter by means of macroscopic functions, that is, what Ruppeiner called a "build down approach" (see [15] for a detailed review). All these approaches are based on the intrinsic properties of the equilibrium manifolds: on the one side the equilibrium surfaces introduced by Gibbs and defined by the fundamental equation, and on the other side the abstract equilibrium manifold used in the approaches of Weinhold and Ruppeiner. It was also shown that after introducing the notion of distance on the abstract manifold, the two types of description are inequivalent. Therefore, one should choose one description or the other, based on the aspects one is more interested to describe [61].

Besides, a completely different approach to the geometrization of thermodynamics was pursued first by Hermann [7] and later by Mrugala and his collaborators [8, 9, 10]. In this approach, the phase space of thermodynamics is introduced as a manifold in which all the thermodynamic quantities are independent variables. The geometric structure of such manifold is given by the first law, contrary to the intrinsic descriptions of Gibbs, Weinhold and Ruppeiner, where the second law rules the geometric properties of the manifold. It turns out that the first law defines a contact structure on the phase space of thermodynamics, and that the abstract equilibrium manifold where the intrinsic description of thermodynamics is performed emerge as a particular class of integral submanifolds of the contact distribution.

Below we review all these concepts briefly and give a detailed list of references, in order to introduce the notation which will be used in the following chapters. In particular, we distinguish between the contact structure of the phase space and the Riemannian structure of the equilibrium space, the two most important concepts in the theory of Geometrothermodynamics.

1.2.2 The contact formulation of classical thermodynamics

In this section we introduce contact geometry and its applications to thermodynamics. The introduction of contact geometry in thermodynamics as the natural landscape to work with the Pfaffian equation representing the first law is due to Hermann [7] and was later developed by Mrugala [8, 9, 10]. We present here the general features, with a special interest on the symmetries of the contact structure, which will be the guideline to the introduction of a compatible metric structure discussed in Chapter 3.

Contact manifolds and the thermodynamic phase space $\mathcal{T}$

Definition 5. *A* $(2n+1)$*-dimensional manifold* $\mathcal{T}$ *is said to be a* contact manifold *if it is endowed with a maximally non-integrable family of hyperplanes*

$$\xi = \ker(\Theta) \tag{1.15}$$

defined through some 1-form Θ *satisfying the non-integrability condition*

$$\Theta \wedge (\mathrm{d}\Theta)^n \neq 0\,, \tag{1.16}$$

where $\wedge$ *denotes the exterior product and* $(\mathrm{d}\Theta)^n = \mathrm{d}\Theta \wedge \cdots \wedge \mathrm{d}\Theta$ *(*n *times).*

The above condition means that Θ is non-degenerate. The 1-form Θ is called the *contact form.* Note that the contact form Θ is not unique. Indeed, any other 1-form defining the same family of hyperplanes, equation (1.15), is necessarily conformally equivalent to Θ. Thus, a contact structure is an *equivalence class* $[\Theta]$ of 1-forms satisfying (1.16) and related by a conformal transformation, i.e. for any two 1-forms Θ_1 and Θ_2 in $[\Theta]$

$$\Theta_1 \sim \Theta_2 \quad \text{iff} \quad \Theta_2 = \Omega\,\Theta_1 \tag{1.17}$$

for some real and non-vanishing function Ω. As we will shortly show, each member of the class corresponds to a different thermodynamic representation. To this end, let us consider the class of maps which leave invariant the contact structure. Let $f : \mathcal{T} \longrightarrow \mathcal{T}$ be a diffeomorphism of the thermodynamic phase space. If f preserves the contact structure, i.e

$$f^*(\Theta) = \Omega(Z^A)\Theta = \Theta' \quad \text{where} \quad \Omega \neq 0\,, \tag{1.18}$$

we call f a *contactomorphism* [64]. Note that $\Theta' \in [\Theta]$.

According to the Darboux theorem [65], there always exist local contact coordinates $Z^A = (\Phi, E^a, I_a)$, $a = 1, \dots, n$ in which Θ has the canonical form

$$\Theta = \mathrm{d}\Phi - I_a \mathrm{d}E^a \,, \tag{1.19}$$

where the summation convention over repeated indices has been assumed. The non-degeneracy condition (1.16) can be geometrically interpreted in several ways, the simplest one resulting from (1.19), from which we see that $\Theta \wedge (\mathrm{d}\Theta)^n$ is the volume form on $\mathcal{T}$.

There is a particular set of contactomorphisms which is of thermodynamic relevance. That is, those defined by interchanging the thermodynamic potential with one of the extensive variables. In fact, a particular case of such set is the change of representation from the internal energy to the entropy representation or viceversa. If we express Θ in Darboux coordinates as in equation (1.19), the transformation exchanging Φ with the ith extensive variable is

$$f^*_{(i)}(\Theta) = \Theta_{(i)} = -\frac{1}{I_{(i)}}\Theta = \mathrm{d}E^{(i)} - \frac{1}{I_{(i)}}\mathrm{d}\Phi + \sum_{j\neq i} \frac{I_j}{I_{(i)}}\mathrm{d}E^j \,, \tag{1.20}$$

and using Darboux's theorem, we can write $\Theta_{(i)}$ in its canonical form

$$\Theta_{(i)} = \mathrm{d}\Phi' - I_{a'}\mathrm{d}E^{a'} \,, \tag{1.21}$$

from which we can read the transformation as

$$\Phi' = E^{(i)}, \quad E^{(i)'} = \Phi, \quad E^{j'} = E^j, \quad I_{(i)'} = \frac{1}{I_{(i)}} \quad \text{and} \quad I_{j'} = -\frac{I_j}{I_{(i)}} \,. \tag{1.22}$$

It follows immediately that the contact form in the $E^{(i)}$ representation can be rewritten as

$$\Theta_{(i)} = \mathrm{d}E^{(i)} - \frac{1}{I_{(i)}}\mathrm{d}\Phi + \sum_{j\neq i} \frac{I_j}{I_{(i)}}\mathrm{d}E^j \,, \tag{1.23}$$

which means that a conformal relation between the two thetas holds, i.e.

$$\Theta_{(i)} = -\frac{1}{I_{(i)}}\,\Theta \,. \tag{1.24}$$

Definition 6. *In thermodynamics the couple* $(\mathcal{T}, [\Theta])$ *represents* the thermodynamic phase space *and choosing a different thermodynamic representation corresponds to choose a different* 1*-form in the class* $[\Theta]$.

Let us see how. In the energy representation we have the contact coordinates

$$(\Phi, E^1, E^2, E^3, \ldots, I_1, I_2, I_3, \ldots) \leftrightarrow (U, S, V, N_1, \ldots, T, -P, \mu_1, \ldots)\,, \tag{1.25}$$

and the corresponding representative of the contact structure is

$$\Theta^U = \mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V - \mu_k \mathrm{d}N^k, \quad k = 1, \ldots, n-2\,. \tag{1.26}$$

On the other side, in the entropy representation we have

$$(\Phi, E^1, E^2, E^3, \ldots, I_1, I_2, I_3, \ldots) \leftrightarrow (S, U, V, N_1, \ldots, \frac{1}{T}, \frac{P}{T}, \frac{\mu_1}{T}, \ldots) \tag{1.27}$$

and

$$\Theta^S = \mathrm{d}S - \frac{1}{T}\mathrm{d}U - \frac{P}{T}\mathrm{d}V - \frac{\mu_k}{T}\mathrm{d}N^k, \quad k = 1, \ldots, n-2\,, \tag{1.28}$$

where all the symbols have their standard thermodynamic meaning [1]. It is important to notice that in each case all the $2n+1$ variables are treated as independent on the phase space $\mathcal{T}$ (we will see in the next subsection that this is not the case in the equilibrium manifold $\mathcal{E}$). We also notice that Θ^U and Θ^S are two different geometric objects defined on $\mathcal{T}$ and that they are related according to

$$\Theta^S = -\frac{1}{T}\Theta^U\,. \tag{1.29}$$

From (1.29), we see immediately that the 1-forms Θ^U and Θ^S, corresponding to taking the energy or entropy representations, define the *same* contact structure (c.f. (1.15)) and they are related exactly according to (1.24) (with $E^{(i)} = S$ and $I_{(i)} = T$).

Another fundamental definition is that of a Legendre transformation.

Definition 7. *A* Legendre transformation (LT) *is a change of coordinates in the phase space $\mathcal{T}$ such as*

$$\begin{gathered}(\Phi, E^a, I_a) \to (\tilde{\Phi}, \tilde{E}^a, \tilde{I}_a)\,, \\ \Phi = \tilde{\Phi} - \tilde{E}^k \tilde{I}_k\ , \quad E^i = -\tilde{I}_i, \quad E^j = \tilde{E}^j, \quad I_i = \tilde{E}^i, \quad I_j = \tilde{I}_j\ ,\end{gathered} \tag{1.30}$$

where $i, k, l \in I$ and $j \in J$ and $I \cup J$ is any disjoint decomposition of the set of indices $\{1, \ldots, n\}$.

When $I = \{1, \ldots, n\}$ it is called a *total Legendre transformation* (TLT), while when $I \subset \{1, \ldots, n\}$ it is called a *partial Legendre transformation* (PLT). Note that Legendre transformations belong to the special class of contactomorphisms which leave the representative unchanged, i.e. $f^*(\Theta) = \Theta$, i.e. they are *strict* *contactomorphisms.*

In classical homogeneous thermodynamics, the physical properties of the system do not depend on the thermodynamic potential which one uses for the description [1]. We will show now how this property manifests as a symmetry of the contact structure. For instance, considering a system with two degrees of freedom, we can change the thermodynamic potential from the internal energy U with its natural variables $E^1 = S, E^2 = V, I_1 = T, I_2 = -P$, to the Gibbs free energy G with its natural variables $\tilde{E}^1 = T, \tilde{E}^2 = P, \tilde{I}_1 = S, \tilde{I}_2 = V$, using the total Legendre transformation

$$\begin{gathered}(U, S, V, T, -P) \to (G, T, P, S, V)\,, \\ \tilde{\Phi} = G = U - TS + PV\ , \quad \tilde{E}^1 = T, \ \ \tilde{E}^2 = P, \quad \tilde{I}_1 = S, \ \ \tilde{I}_2 = V\ ,\end{gathered} \tag{1.31}$$

and the two corresponding contact forms satisfy

$$\Theta^U = \mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V = \mathrm{d}G + S\mathrm{d}T - V\mathrm{d}P = \Theta^G\,. \tag{1.32}$$

Legendre submanifolds and the equilibrium space $\mathcal{E}$

Due to condition (1.16), the contact distribution is maximally non-integrable. Therefore the major role is played by its maximal dimensional integral submanifolds, i.e. the so-called *Legendre submanifolds*, which we will denote by $\mathcal{E}$. We list here some important properties of the Legendre submanifolds of the contact distribution, which lead us to identify them with the manifolds of equilibrium states of thermodynamic systems.

(i) First of all the name Legendre submanifolds is justified by the fact that they are invariant under Legendre transformations (1.30), i.e. a Legendre transformation maps a Legendre submanifold into itself (whenever the LT is well defined, see Chapter 2).

(ii) Furthermore, because the contact distribution is maximally non-integrable, the dimension of any Legendre submanifold of the $(2n+1)$-dimensional thermodynamic phase space, coincides with the number n of thermodynamic degrees of freedom.

(iii) Finally, we provide a well-known theorem whose proof can be found e.g. in [65]. Given a generating function $f(I_i, E^j)$ of n variables I_i, $i \in I$, and E^j, $j \in J$, with $I \cup J$ any partition of the set of indices $\{1, \ldots, n\}$, the $n+1$ equations

$$E^i = -\frac{\partial f}{\partial I_i}\,, \quad I_j = \frac{\partial f}{\partial E^j}\,, \quad \Phi = f - I_i\,\frac{\partial f}{\partial I_i} \tag{1.33}$$

define a Legendre submanifold $\mathcal{E}$ of $(\mathcal{T}, [\Theta])$. Conversely, every Legendre submanifold of $(\mathcal{T}, [\Theta])$ in a neighborhood of any point is defined by (1.33) for at least one of the 2^n possible choices of the subset I.

Keeping in mind the above facts about Legendre submanifolds, and assuming without loss of generality that the independent variables on $\mathcal{E}$ are the $\{E^a\}$, for $a = 1, \dots, n$, we give the following geometrical definition.

Definition 8. *The* equilibrium space *corresponding to a thermodynamic system whose phase space is given by $(\mathcal{T}, [\Theta])$ is the Legendre submanifold $\mathcal{E}$ satisfying the condition*

$$\varphi^*(\Theta) = \left(\frac{\partial}{\partial E^a} \Phi(E^b) - I_a \right) \mathrm{d}E^a = 0 \,, \tag{1.34}$$

equivalent to the first law of thermodynamics and the equations of state

$$\mathrm{d}\Phi(E^a) = I_a \mathrm{d}E^a, \quad \textit{and} \quad I_a = \frac{\partial}{\partial E^a} \Phi(E^b) \,. \tag{1.35}$$

Therefore $\Phi = f(E^a)$ corresponds to the thermodynamic potential and $\varphi : \mathcal{E} \to \mathcal{T}$ reads

$$\varphi(E^a) = \left(\Phi(E^a), E^a, I_a = \frac{\partial}{\partial E^a} \Phi(E^b) \right) . \tag{1.36}$$

1.2.3 Riemannian structures

Besides the global contact structure $(\mathcal{T}, [\Theta])$ of the phase manifold of thermodynamics defined in the previous section, one can introduce a Riemannian structure $(\mathcal{E}, g)$ in the equilibrium manifold $\mathcal{E}$ in several ways. The thermodynamic metrics that we are going to introduce here are defined as the Hessian of some potential. As such, they account for fluctuations in the ensemble related to the potential used and give a "measure" of the strength of the thermodynamic fluctuations by means of the curvature of such manifold. Therefore, one can get a local information about phase transitions and critical points.

Weinhold and Ruppeiner metrics on the equilibrium space $\mathcal{E}$

In a set of papers [12], F. Weinhold introduced in the seventies a scalar product on the tangent space of the equilibrium manifold $\mathcal{E}$ starting from considerations about equilibrium. Using a more geometric language, one can promote this scalar product to a Riemannian metric g defined in $\mathcal{E}$. In order for a system to be at equilibrium, the internal energy U with respect to the extensive variables has to be at a minimum (c.f. Sec. 1.1.3). This means that the first derivatives of U must vanish and the Hessian, i.e. the matrix of second derivatives, has to be a positive definite matrix. That is why Weinhold metric g^W is defined as the Hessian of the free energy U [12, 13]. For example, for a system with two degrees of freedom in the energy representation, i.e. with coordinates (S, V) on $\mathcal{E}$, Weinhold metric is naturally defined as

$$g^W = \frac{\partial^2 U}{\partial S^2}\, \mathrm{d}S \otimes \mathrm{d}S + 2\, \frac{\partial^2 U}{\partial S \partial V}\, \mathrm{d}S \otimes \mathrm{d}V + \frac{\partial^2 U}{\partial V^2}\, \mathrm{d}V \otimes \mathrm{d}V. \tag{1.37}$$

The physical meaning of Weinhold metric is thus clear from its definition, the metric being positive definite as long as the system is in an equilibrium configuration and degenerate or negative definite out of equilibrium. Thus a change from equilibrium to non-equilibrium is signaled by the vanishing of the determinant of Weinhold metric.

Some years later G. Ruppeiner [14], starting from statistical physics and more precisely from the Gaussian approximation to the probability density of fluctuations around a point of maximum entropy, proved that the Hessian of the entropy S (with a minus sign) gives the equilibrium space $\mathcal{E}$ a different Riemannian structure from that of Weinhold. Remarkably, Ruppeiner geometry was found to be conformally related to the one proposed by Weinhold, the relation being [60]

$$g^R = \frac{1}{T}\, g^W. \tag{1.38}$$

Moreover, Ruppeiner metric is intrinsically related to the underlying statistical properties. In fact the scalar curvature of the Riemannian manifold representing the system using Ruppeiner metric happens to diverge at the critical point with exactly the same critical exponent as the correlation volume for any ordinary systems (see e.g. [15] for a review).

Ruppeiner metric is thus defined as (minus) the Hessian of the entropy. As such, for a thermodynamic system with two degrees of freedom in the entropy representation, it is written in its natural variables (U, V) as

$$g^R = -\left(\frac{\partial^2 S}{\partial U^2}\, \mathrm{d}U \otimes \mathrm{d}U + 2\, \frac{\partial^2 S}{\partial U \partial V}\, \mathrm{d}U \otimes \mathrm{d}V + \frac{\partial^2 S}{\partial V^2}\, \mathrm{d}V \otimes \mathrm{d}V \right). \tag{1.39}$$

Weinhold and Ruppeiner thermodynamic geometries have been largely used in the literature to study ordinary systems and in particular Ruppeiner metric has been also used to study the thermodynamics of many black holes configurations (see [16] and references therein). This is because one can argue that, being Ruppeiner metric defined only from thermodynamic quantities and containing at the same time informations about the statistical model, then it can provide some hints towards the resolution of the long standing problem of understanding the microscopic properties of black holes (see e.g. [16]). Unfortunately, as we shall see in Chapter 5, some misleading and puzzling situations appear when treating black holes with the afore-mentioned methods without considering the peculiar features of black holes as thermodynamic systems (see the discussion in Chapter 5).

A metric by Mrugala on the phase space $\mathcal{T}$

Mrugala [10] was the first to introduce a metric structure on the phase space $\mathcal{T}$, which reproduces the thermodynamic metrics of Weinhold and Ruppeiner when projected onto the equilibrium space $\mathcal{E}$ [10, 11]. For a system with n degrees of freedom, the metric by Mrugala in the general contact coordinates of the phase space $\mathcal{T}$ reads

$$G^M \equiv \Theta \otimes \Theta + \mathrm{d}I_a \otimes \mathrm{d}E^b \,, \tag{1.40}$$

where $a, b = 1, \ldots, n$ and Θ is the contact form (1.19). It is easy to see that

$$\varphi^*(G^M)|_{\Phi=U} = g^W \quad \text{and} \quad \varphi^*(G^M)|_{\Phi=S} = -g^R \,, \tag{1.41}$$

where $\varphi : \mathcal{E} \to \mathcal{T}$ is the natural embedding of $\mathcal{E}$ onto $\mathcal{T}$ defined in (1.36) and g^W and g^R are defined in (1.37) and (1.39) respectively. We notice that Eq. (1.41) in particular means that G^M is not symmetric under a change of representation on $\mathcal{T}$ (c.f. equation (1.22)) and that using different representations one gets two different geometric objects. Moreover, it is easy to see (c.f. [24]) that G^M is neither symmetric with respect to Legendre transformations (1.30). Therefore, the Hessian metrics of Weinhold and Ruppeiner naturally arise from the different choice of the thermodynamic potential.

We comment that an analysis of the statistical origin of the metric (1.40) was addressed in [10] and the mathematical aspects of the corresponding contact Riemannian structure have been extensively studied in [11].

2 Legendre symmetry and first order phase transitions

In Section 1.1.6 we have discussed the occurrence of phase transitions in ordinary thermodynamics, pointing out that the presence of a first order phase transition demands an ensemble inequivalence and the introduction of a larger space, in which all the thermodynamic variables are present, thus recovering the full information about the system. That is to say, that while on the single phase of a system we can rule out some irrelevant thermodynamic degrees of freedom and work on the equilibrium space $\mathcal{E}$ by means of the pullback defined in Eq. (1.36), on the other side in the coexistence region between two or more different phases such pullback is not well defined and we need to work on the full thermodynamic phase space $\mathcal{T}$. In this chapter we formulate this observation more precisely.

Indeed we will get a characterization of first order phase transitions as equilibrium processes on the thermodynamic phase space for which the Legendre symmetry is broken. Furthermore, we consider generalized theories of thermodynamics, where the potential is a homogeneous function of any order β and we propose a (contact) Hamiltonian function that fully describes thermodynamic equilibrium. We show that such Hamiltonian is a conserved quantity related to the Legendre symmetry. That is, it is identically zero as long as the total Legendre transformation of the system is well defined, whereas it changes when the Legendre symmetry breaks, i.e. when the system separates into two phases. We will show that, whenever the thermodynamic potential is homogeneous of order one, such energy is zero also over the region of coexistence. Finally, in the end of the Chapter we use these results to infer that the description in equilibrium of first order phase transitions is possible only when the potential is a homogeneous function of order one, unless a generalized version of the zeroth law of thermodynamics is considered in order to allow for equilibrium at different values of the "intensive" quantities. We use all these results to derive a new zeroth law of thermodynamics that consistently applies to the case of generalized potentials of any order. In particular, we mention that this result can be useful in the context of black holes thermodynamics, as we shall investigate further in Chapter 5.

2.1 First order phase transitions

In the modern treatment of phase transitions it is common to associate the emerging of such phenomena with the breaking of some symmetry of the system. However, some of the most familiar phase transitions have not been settled yet within this framework, e.g. the liquid-vapor phase transition of water (see for instance the discussion in Section 4.1.3 in [55]). Moreover, in the recent years special interest has been devoted to the thermodynamics of systems with long-range interactions (including e.g. black holes [35], self-gravitating systems [36], cold atoms in an optical lattice [37], nanoscale materials [38] and so on), which cannot be treated in the context of standard thermodynamics and therefore require a generalization of the homogeneity condition of the thermodynamic potential.

In this section, we consider systems whose thermodynamic potential is a homogeneous function of any order and argue that all such systems have a common theoretical symmetry that breaks whenever a coexistence of two phases is present, i.e. the *Legendre symmetry*. In fact, according to the contact description of the phase space of thermodynamics introduced in Section 1.2.2, the equilibrium condition is given by integral submanifolds of the contact distribution. In particular, for a system with n degrees of freedom, the maximal integral submanifolds (the *Legendre submanifolds*) are of dimension n. This is representative of the fact that on such submanifolds the thermodynamic potential Φ and the intensive variables I_a can all be expressed as functions of the extensive variables E^a, where a runs from 1 to n, without any loss of information. At the same time, using the equations of state, one can perform a total Legendre transformation to change the thermodynamic potential and switch the independent variables to be the intensive ones. It is thus clear that the Legendre transformation on the phase space induces a diffeomorphism between the extensive and the intensive variables on each Legendre submanifold. We will show in the next section that this is always the case as long as the potential satisfies the convexity conditions, that is, the system is in a single phase [1]. However, many of the thermodynamic potentials undergo regions of instability. Therefore, the Legendre transformation is not defined in such regions. In standard thermodynamics, one can recover stability by means of the Maxwell equal area law, but the Legendre symmetry cannot be restored [1]. We show here how the breaking of the Legendre symmetry allows for intersections of Legendre submanifolds and hence for processes that quit one thermodynamic phase and go to the other. Such processes are the *coexistence processes*. In this way one is able to characterize the single phase region of any thermodynamic system as a Legendre submanifold (i.e. a *maximal* integral submanifold), and the region of coexistence as the region where the breaking of the Legendre symmetry leads to the coexistence of the corresponding Legendre submanifolds.

Furthermore, we will define a function on the phase space that vanishes whenever the system is in equilibrium. A natural candidate for such a function stems from Euler's identity for homogeneous systems, therefore let us call such function *the Euler's contact Hamiltonian* (ECH). The ECH provides the natural analogue in contact geometry of the Hamiltonian description of Mechanics. In fact, as conservative Hamiltonian dynamics is restricted to submanifolds of constant Hamiltonian, in the same way all thermodynamic processes are constrained to submanifolds where the ECH is zero. Moreover, calculating the differential of the ECH on each Legendre submanifold one can directly derive the generalized Gibbs-Duhem equation. We will discuss how this equation imposes constraints on the admissible thermodynamic processes and conclude that for "non-extensive" thermodynamic systems, equilibrium among the system's sub-parts requires a reformulation of the zeroth law. Finally, we will provide a new generalized zeroth law of thermodynamics for systems whose thermodynamic potential is a homogeneous function of order different from one, such definition being compatible with the Gibbs-Duhem equation. Moreover, we will discuss how our new definition of equilibrium is connected to a generalized version of the Tolman-Ehrenfest effect valid for systems with long-range interactions and we will provide arguments for a possible direct application in the thermodynamics of black holes.

2.2 Legendre symmetry and phase transitions

The description of an ordinary thermodynamic system can be performed using different potentials, which can be obtained one from the other by means of a Legendre transformation (c.f. Definition 7). Therefore, the question arises naturally if there is something special about Legendre transformations. To address this question, let us consider the contact description of the phase space of thermodynamics given in Section 1.2.2.

One clearly sees from the embedding (1.36) that in standard extensive thermodynamics $\Phi(E^a)$ is the thermodynamic potential, E^a are the extensive variables and I_a are the intensive ones. We remark here that the words *extensive* and *intensive* variables only apply in standard thermodynamics, whereas in the following we will work with generalized thermodynamics, where the potential and the variables E^a need not be extensive and the I_a do not necessarily need to be intensive, as we shall see. Nevertheless, in what follows we will continue to use this notation. In particular, we will always assume that Φ is a coordinate on the phase space $\mathcal{T}$, while $\Phi(E^a)$ is the corresponding potential on a Legendre submanifold $\mathcal{E}$ defined by φ, E^a will be the natural variables of $\Phi(E^a)$ and $I_a(E^b)$ the conjugate variables, obtained by means of the equations of state (c.f. Eq. (1.35)). Moreover, we will always take $\Phi(E^a)$ to be a homogeneous function of order β, although all the results can be straightforwardly generalized to the case of $\Phi(E^a)$ quasi-homogeneous (see [56] for a detailed discussion on quasi-homogeneous functions).

Let us now turn to describe briefly the process of coexistence (for a more detailed description see e.g. [1]). To do so, we refer to the $P-V$ and $P-T$ diagrams of the liquid-vapor coexistence for a Van der Waals fluid presented in Figs. 1.2 and 1.3. Above the critical temperature T_c, the isotherms on the $P-V$ diagram are decreasing functions of V and hence are stable. On the contrary, below the critical temperature, the isotherms have a region of instability, which is “cut-out” by means of the Maxwell construction, which consists in finding the equilibrium value for the pressure at which the two phases coexist at equilibrium. It turns out that such equilibrium value is given by requiring that the two areas indicated by I and II in the $P-V$ diagram be equal. It is crucial for our discussion to note that the way in which Maxwell construction operates to restore equilibrium is by requiring that the intensive quantities be equal between the two phases [1], which is the standard definition of equilibrium between two sub-parts of a system in ordinary thermodynamics.

Besides, it is also crucial to note that when a coexistence of two or more phases is present, the description in the variables E^a is *not equivalent* to that using the variables I_a. In fact, by looking at the two diagrams in Figs. 1.2 and 1.3, one immediately sees that in the $P-V$ coordinates the coexistence is given by a line, whereas in the $P-T$ coordinates it corresponds to the single point, indicated by q. This fact can be given a precise geometric interpretation that the change of coordinates in that region is not well defined. From a perspective similar to that of the Renormalization Group technique (see e.g. [54, 55] and references therein), this fact signals that in such region new parameters might be involved to account for the (now relevant) extra degrees of freedom, such parameters being in our case the full set of $2n+1$ thermodynamic variables in the phase space. Furthermore, the need for extra degrees of freedom hints at the breaking of some underlying symmetry. Indeed, we can prove the following result.

Proposition 1. *The descriptions using the “extensive” or the “intensive” coordinates are equivalent as long as the Legendre transform is well defined, i.e. when the convexity conditions are satisfied.*

Proof. In fact, the transformation from the thermodynamic potential $\Phi(E^a)$ to its total Legendre transform $\tilde{\Phi}(I_a)$ induces a diffeomorphism ψ on every Legendre submanifold $\mathcal{E}$ between the coordinates E^a and I_a given by the equations of state

$$I_a(E^b) = \frac{\partial}{\partial E^a}\Phi(E^b)\,. \tag{2.1}$$

It is easy to calculate the push-forward of such transformation, which is

$$\begin{aligned} \psi_* \,:\; T\mathcal{E} \quad &\longrightarrow \; T\mathcal{E} \\ \psi_*\left(X^a \partial_{E^a}\right) \equiv &\left(\frac{\partial^2 \Phi}{\partial E^a \partial E^b}\right) X^b \partial_{I_a}\,, \end{aligned} \tag{2.2}$$

where $X = X^a \partial_{E^a}$ is any vector field on $T\mathcal{E}$.

Therefore, the Legendre mapping between the two sets of coordinates is a diffeomorphism on $\mathcal{E}$ *as long as the Hessian of the potential* $\Phi(E^a)$ *is non-degenerate.* This ends the proof our statement. □

We notice that the same happens in Classical Mechanics with a Legendre transform mapping the Lagrange formulation into the Hamiltonian one, as long as the Lagrangian is non-degenerate. [1] Proposition 1 implies that at a given point p on $\mathcal{E}$ the total Legendre transformation from $\Phi(E^a)$ to $\tilde{\Phi}(I_a)$ is well defined if and only if the system satisfies the (strict) convexity conditions at that point p. An example of a system that globally satisfies the convexity conditions is the ideal gas. Hence the ideal gas has only one phase, which is represented in contact geometry by a single, smooth, Legendre submanifold. However, the majority of systems undergo instabilities and phase separation. Thus, let us analyze the consequences of the breaking of the Legendre symmetry over the coexistence region. First of all let us define in $\mathcal{T}$ the function

$$\tilde{\Phi} \equiv \Phi - E^a\, I_a\,, \tag{2.3}$$

where Einstein summation convention is being adopted. Note that $\tilde{\Phi} \neq \Phi$. In fact, $\tilde{\Phi}$ is the function on $\mathcal{T}$ that, when projected onto a Legendre submanifold $\mathcal{E}$, gives the thermodynamic potential $\tilde{\Phi}(I_a)$ corresponding to a total Legendre transformation of $\Phi(E^a)$.

Consider now a generic thermodynamic process γ on the phase space which lies in

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[1] Note also that in the case of ordinary thermodynamics (homogeneous systems of order one), the full Legendre transformation from the n extensive variables to the n intensive ones is always degenerate, due to the fact that the intensive variables are not independent (because of the Gibbs-Duhem relation). Therefore, one divides all the variables by means of a fixed one (e.g. the number of moles or the volume) reducing the number of variables by one and obtaining "densitisized" quantities, for which the total Legendre transform is well defined.

the single phase region, that is, in the region of a Legendre submanifold $\mathcal{E}$ where the Legendre transformation is well defined. Along such process the thermodynamic potential $\Phi(E^a)$ changes according to the first law

$$\mathrm{d}\Phi(\dot{\gamma}) = I_a(\gamma)\mathrm{d}E^a(\dot{\gamma})\,. \tag{2.4}$$

At the same time, the potential given by the total Legendre transform $\tilde{\Phi}(I_a)$ also changes according to the first law

$$\mathrm{d}\tilde{\Phi}(\dot{\gamma}) = -E^a(\gamma)\mathrm{d}I_a(\dot{\gamma})\,. \tag{2.5}$$

On the contrary, along the coexistence process γ_c the values of the intensive variables are fixed by the Maxwell requirement of equilibrium between the two phases, while the extensive variables change, so that $\Phi(E^a)$ changes normally, in agreement with the first law (2.4), while $\mathrm{d}\tilde{\Phi}(\dot{\gamma}_c) = 0$.

The breaking of the correspondence between the changes in the two potentials is a motivation to define on the phase space the following function

Definition 9. *The* Euler's contact Hamiltonian (ECH) *is the function on the thermodynamic phase space $\mathcal{T}$ defined as*

$$\mathbb{E} \equiv (1-\beta)\Phi - \tilde{\Phi}\,, \tag{2.6}$$

where $\tilde{\Phi}$ is the function defined in (2.3).

Let us consider now a Legendre submanifold $\mathcal{E}$ given by the map (1.36). We can state the following result.

Proposition 2. *The Euler's contact Hamiltonian vanishes on each Legendre submanifold, i.e.*

$$\mathbb{E}|_{\mathcal{E}} = -\beta\Phi(E^a) + I_a\,E^a \equiv 0\,. \tag{2.7}$$

Proof. The proof directly follows from the definition (2.3) and the generalized Euler equation for homogeneous functions [24]. □

From Proposition 2 it follows that

Corollary 1. *All the leaves of the contact distribution are characterized as zeroth levels of the ECH.*

Proof. It can be shown that each leaf of the contact distribution is contained in a Legendre submanifold (see [68]). Therefore the corollary directly follows from Proposition 2. □

It is worth remarking that, contrary to what happens in symplectic mechanics, every contact hamiltonian function f on the thermodynamic phase space generates a flow that is tangent only to its level surfaces $f = 0$ [8, 9]. Therefore, the above result implies that the flow generated by the ECH is at every point tangent to the equilibrium submanifolds, i.e. it is a thermodynamic process. This suggests that *any* thermodynamic process can be characterized by the flow of the ECH plus some boundary conditions consistent with the laws of thermodynamics, a matter which will be the content of our future work [69].

Moreover, one can also use the pullback of φ to calculate the differential of $\mathbb{E}$ on each Legendre submanifold. It turns out that

Lemma 1. *The vanishing of* $\mathrm{d}\mathbb{E}$ *is equivalent to the generalized Gibbs-Duhem relation, i.e.*

$$\begin{aligned}\varphi^{*}(\mathrm{d}\mathbb{E})|_{\text{single phase}} &= (1-\beta)\varphi^{*}(\mathrm{d}\Phi) - \varphi^{*}(\mathrm{d}\tilde{\Phi}) = \\ &= (1-\beta)I_a \mathrm{d}E^a + E^a \mathrm{d}I_a = 0\,.\end{aligned} \tag{2.8}$$

Proof. The proof is straightforward and it follows from the definition of φ (equation (1.36)) and that of $\tilde{\Phi}$ (equation (2.3)). □

If instead one considers a process γ_c over the region of coexistence (which by the Gibbs phase rule [1] necessarily happens on a submanifold which is not maximal, i.e. it is not a Legendre submanifold), one has that $\tilde{\Phi}$ is constant, that is $\mathrm{d}\tilde{\Phi}(\dot{\gamma}_c) = 0$, as we have already discussed. Therefore, it results the following

Lemma 2. *Along a process of coexistence* γ_c *on* $\mathcal{T}$ *we have that*

$$\mathrm{d}\mathbb{E}(\dot{\gamma}_c) = (1-\beta)\,\mathrm{d}\Phi(\dot{\gamma}_c) = (1-\beta)\,I^c_a\,\mathrm{d}E^a(\dot{\gamma}_c)\,, \tag{2.9}$$

where the notation I^c_a *means that the values of the "intensive" quantities are fixed along the coexistence process* γ_c*.*

It is immediate to see that in the case $\beta = 1$ the relation (2.9) is identically zero, and therefore during the process of coexistence the two phases are in equilibrium (having the same values for the intensive quantities) and at the same time the Gibbs-Duhem equation is satisfied. Nevertheless, when $\beta \neq 1$, $\mathrm{d}\mathbb{E}$ along the coexistence is not zero, which means that the generalized Gibbs-Duhem relation *is not consistent with the usual definition of equilibrium.* However, since the Gibbs-Duhem relation (2.8) is obtained from the homogeneity of the potential by assuming that the first law and the equations of state are satisfied, one concludes that it is the definition of equilibrium between the two phases as having all the "intensive" quantities fixed to be equal which is too stringent in the case of potentials which are not homogeneous of order one. We can now state the following

Theorem 1. *The coexistence of two phases at equilibrium cannot happen when the thermodynamic potential is a homogeneous function of order different from one, unless one introduces a different notion of equilibrium for such systems, by relaxing the hypothesis that all the "intensive" quantities have to be the same in the two phases.*

Proof. From Lemma 1 it follows that the generalized Gibbs-Duhem equation must be satisfied for the system to be at equilibrium. However, phase separation and the usual zeroth law of thermodynamics imply that the coexistence process can happen only if the values of the "intensive" quantities are constant (Maxwell construction). Lemma 2 shows that the two conditions cannot happen at the same time, unless $\beta = 1$. ☐

Note that for thermodynamic systems subjected to a gravitational field, it is known that there can be thermal equilibrium (no heat exchange) even if the value of the temperature is not the same at all points. This is known as the Tolman-Ehrenfest effect [70]. Such result depends on the fact that heat, as any form of energy, has a weight. However, it can also be seen as due to a general property of the gravitational field, i.e. the fact that it is a long-range interaction. The consequence is that the usual Boltzmann-Gibbs-Shannon entropy is non-extensive and the thermodynamics has to be different from that of an extensive system. Generally speaking, all systems with long-range interactions have non-extensive properties and a generalized version of the Tolman-Ehrenfest effect for different types of such systems has been discussed in [39]. We remark that our investigation of equilibrium in homogeneous systems with order different from one independently hints at the need for a careful re-definition of equilibrium in the case of systems whose potential is not homogeneous of order one. In particular, in the next section we show how to adjust the zeroth law of thermodynamics for homogeneous systems of any degree in order to make it consistent with equation (2.8) when the system is split into parts, as e.g. over the region of coexistence.

2.3 Generalized zeroth law for homogeneous systems

In ordinary thermodynamics, the potential $\Phi(E^a)$ is required to be a homogeneous function of order one of the variables E^a. It turns out that the conjugated variables $I_a(E^b)$ are then homogeneous functions of order zero, that is, *intensive* quantities.

This fact has a fundamental consequence: the $I_a(E^b)$ are constant at equilibrium, which means that they take the same value on every subsystem. For example, a system at equilibrium must have a constant temperature among all its parts. It follows that if one divides the system into two parts, these parts must have the same value of the intensive quantities in order to be at equilibrium [1]. We remark that this physical property descends from the mathematical requirement of having the functions $I_a(E^b)$ that are homogeneous of order zero. In fact, writing the homogeneity relation

$$I_a(\lambda E^b) = \lambda^0 I_a(E^b)\,, \tag{2.10}$$

one can set λ equal to different fractions, that is, divide the original system into subsystems, and see that the values of the I_a stay the same.

Let us now move from this consideration in order to find a new simple definition of equilibrium which applies to homogeneous thermodynamic systems of any order, it is consistent with the generalized Gibbs-Duhem identity - equation (2.8) - and at the same time provides a natural generalization of the Tolman-Ehrenfest effect. As we have seen, the mathematical property that explains why the $I_a(E^b)$ are constant in ordinary thermodynamics is that they are homogeneous of order zero. Therefore, let us construct in the general case homogeneous quantities of order zero, that will play the role of intensities. Consider a thermodynamic potential $\Phi(E^a)$ which is homogeneous of order β in the variables E^a. By the properties of homogeneous functions [56], it follows that the corresponding conjugated functions $I_a(E^b)$ are homogeneous of order $\beta - 1$. Thus, we define

$$\tilde{I}_a(E^b) \equiv \frac{I_a(E^b)}{(E^a)^{\beta-1}} \qquad a = 1, \dots, n\,. \tag{2.11}$$

It is immediate to verify that the $\tilde{I}_a(E^b)$ are homogeneous functions of order zero.

Now let us introduce a generalized zeroth law for homogeneous systems.

Definition 10. (Generalized Zeroth Law) *We say that a homogeneous system of order β is* at equilibrium *between its parts if and only if the values of the $\tilde{I}_a(E^b)$ are constant.*

Furthermore, let us see now how the Gibbs-Duhem identity (2.8) is consistent with the new definition of equilibrium. To make the discussion concrete, we present the particular case of the region of coexistence of two different phases during a first order phase transition, although the result is valid in general for any splitting of the system into sub-parts at equilibrium. First let us recall that in the region where the system is in a single phase, equation (2.8) is an identity for any homogeneous function, no matter which definition of equilibrium is given. The problem with the use of non-intensive quantities for the definition of equilibrium only arises when the system is divided into sub-parts. Perhaps the most evident and the most important case is the one of coexistence, in which the system naturally separates into two phases. So let us start by rewriting equation (2.8) in terms of the $\tilde{I}_a(E^b)$ defined in (2.11), to obtain

$$(1-\beta)\tilde{I}_a\left(E^a\right)^{\beta-1}\mathrm{d}E^a + E^a\mathrm{d}\big(\tilde{I}_a\left(E^a\right)^{\beta-1}\big) = 0\,. \tag{2.12}$$

Now, considering a process of coexistence γ_c as in the preceding section, and rewriting equation (2.12) by expanding the second differential, we get

$$(1-\beta)\tilde{I}_a\left(E^a\right)^{\beta-1}\mathrm{d}E^a(\dot{\gamma}_c) + E^a\big[\left(E^a\right)^{\beta-1}\mathrm{d}\tilde{I}_a(\dot{\gamma}_c) + (\beta-1)\left(E^a\right)^{\beta-2}\tilde{I}_a\mathrm{d}E^a(\dot{\gamma}_c)\big] = 0\,. \tag{2.13}$$

Finally, imposing the condition that the coexistence process happens at equilibrium, which means, according to the Definition 10, that the values of the $\tilde{I}_a(E^b)(\gamma_c)$ must be constant, the first addend in the square brackets vanishes and therefore we recover an identity.

2.4 Conclusions

In sum, we have shown here how the breaking of the Legendre symmetry can be always associated to first order phase transitions in the case of ordinary thermodynamics. This signals that the region of the phase diagram in which the system is in a single phase can be seen as a disordered, symmetric phase with respect to this global symmetry of the general theory of thermodynamics, while in the region of coexistence this symmetry is broken, the system separates into two phases and hence new parameters are necessary to fully describe it. We have also argued that such parameters shall be the complete set of thermodynamic variables that constitute the thermodynamic phase space. Moreover, we have introduced a (contact) Hamiltonian energy for thermodynamics that defines all the possible equilibrium processes as orbits constrained to submanifolds of the thermodynamic phase space defined as zeroth levels of such energy. The construction has been given for homogeneous thermodynamic potentials of any order and therefore these results apply to any homogeneous generalization of standard extensive thermodynamics. An interesting byproduct of our Hamiltonian formulation of homogeneous thermodynamics is that a generalized zeroth law of thermodynamics shall be introduced in order to make the notion of equilibrium consistent with the generalized Gibbs-Duhem relation. In particular, this result reminds of the generalized Tolman-Ehrenfest effect proposed in [39] and it is of central interest in the study of the equilibrium properties of all the systems with long-range interactions. For example, recently the thermodynamics of many black holes in the AdS background has been shown to have similarities with the Van der Waals model and, based on the analytical form of the potentials, the presence of a first order phase transition has been inferred [40, 41, 44, 45, 46, 47]. We argue here that the analogy based on the equation of state and on the analytical form of the potentials might also be integrated with a consistent definition of equilibrium between the different phases. To this end, we have introduced here a new zeroth law of thermodynamics that is consistent with the Gibbs-Duhem relation for all systems with a homogeneous thermodynamic potential of any order. This definition can easily be extended to all quasi-homogeneous functions [56] and therefore can apply to all the thermodynamic systems for which some scaling laws are computable. It is also interesting to note that our definition of thermodynamic equilibrium for homogeneous systems has a direct similarity with the Tolman-Ehrenfest effect and also with the definition of equilibrium in Tsallis statistical mechanics (see e.g. [66, 67]). These topics are of much interest, since our investigation is based on a purely mathematical approach. Therefore we will investigate in more detail the relationship with the generalizations of the Tolman-Ehrenfest effect and with the equilibrium definition in statistical mechanics of non-extensive systems in our future efforts.

3 Symmetries and Geometrothermodynamics

3.1 Introduction to GTD

In this chapter we introduce in detail the theory of Geometrothermodynamics, as coined by H. Quevedo [24]. This theory aims at unifying the contact description of the phase space $\mathcal{T}$ with the Riemannian description of the equilibrium space $\mathcal{E}$. This is done by means of introducing a metric structure on $\mathcal{T}$ and requiring that it satisfies the Legendre symmetry, in order to make it compatible with the contact structure.

Legendre invariance of the Riemannian structure is motivated by the fact that Legendre transformations (1.30) only account for an interchange between conjugate pairs of thermodynamic variables once a representation has been chosen (e.g. the internal energy). This results in different but equivalent descriptions through the distinct thermodynamic potentials (i.e. the enthalpy and the Helmholtz and Gibbs free energies). Just as in General Relativity the physical reality cannot depend on a particular choice of coordinates, thermodynamics is independent of the potential one uses to describe a given system. Therefore, Legendre invariance should be an essential ingredient of any geometric construction of thermodynamics. Moreover, we have seen in Chapter 2 that the contact structure of the phase space of thermodynamics and its symmetry with respect to Legendre transformations play a major role in the realization of first order phase transitions and we have argued that they can provide a unique frame to describe all the phenomena of ensemble inequivalence in generalized homogeneous thermodynamics.

Therefore, the GTD programme aims to promote the contact geometry of the phase space into a Riemannian contact manifold such that the metric has the Legendre symmetry. This automatically translates into a Legendre invariant metric description in its maximal integral submanifolds, i.e. the equilibrium manifolds $\mathcal{E}$. In this sense GTD comes as a synthesis of the previous works on the contact geometry of the phase space and the intrinsic geometry of the equilibrium space that we have summarized in Section 1.2, with the additional ingredient of the Legendre symmetry for the Riemannian structure.

In addition, thermodynamics should also be independent of the representation one employs to describe a system, i.e. one should be able to work with the internal energy or entropy representations with no distinctions. This can be understood as an additional symmetry that should be incorporated in order to obtain a completely consistent geometric theory of thermodynamics. Such additional symmetry has never been addressed in the context of GTD and will be the matter of Section 3.3.

3.2 The Riemannian structure of the GTD programme

As we have seen in Section 1.2.2 , the contact 1-form Θ is invariant under Legendre transformations, whilst a change of representation corresponds to selecting a different 1-form in the class (1.17) defining the same contact structure. Therefore these symmetries all leave invariant both the contact structure $(\mathcal{T}, [\Theta])$ and the space of equilibrium states $\mathcal{E}$. In this sense, the intrinsic Riemannian structures introduced by Weinhold and Ruppeiner (see equations (1.37) and (1.39) respectively) on the equilibrium manifold $\mathcal{E}$ and the metric (1.40) on $\mathcal{T}$ found by Mrugala do not respect the underlying symmetries of the ambient manifolds. In fact, as we have seen in Sec. 1.2.3, selecting a different thermodynamic potential would change the geometric structure of the equilibrium manifold.

On the contrary, in addition to the geometric description of thermodynamics in terms of a contact structure, the GTD programme promotes the contact manifold $(\mathcal{T}, [\Theta])$ into a Riemannian contact manifold $(\mathcal{T}, [\Theta], G)$, where G is a metric sharing the symmetries of $[\Theta]$. We immediately comment that in the attempts to GTD done so far, the only symmetry considered to specify G was the invariance under LT. Hence in this section we will consider only this aspect, while we will address the discussion on the invariance under a change of representation in Section 3.3.

The class of metrics satisfying the requirement of Legendre invariance is vast and there is currently no general principle to select a particular one. The way to deal with this ambiguity has been to introduce some physical input from known systems and demanding that the curvature associated with the induced metric in the space of equilibrium states accounts for the expected phenomena, i.e. to be zero in the case of the ideal gas, or to diverge as one approaches a phase transition, taking us away from the local equilibrium hypothesis. Thus far, there are two independent families of metrics for $\mathcal{T}$ which can be classified according to their invariance properties [26], that is, those which are invariant under total Legendre transformations only, and those which are also invariant under the full set of partial Legendre transformations. Let us write them as

$$G_{\mathrm{T}} = \Theta \otimes \Theta + \Lambda(Z^A) \left(\xi^a{}_b E^b I_a\right) \left(\chi^c{}_d \, \mathrm{d}E^d \otimes \mathrm{d}I_c\right) \tag{3.1}$$

and

$$G_{\mathrm{P}} = \Theta \otimes \Theta + \Lambda\left(Z^A\right) \sum_{i=1}^{n} \left[\left(E^i I_i\right)^{2k+1} \mathrm{d}E^i \otimes \mathrm{d}I_i\right], \tag{3.2}$$

where $\Lambda(Z^A)$ is an arbitrary Legendre invariant function of the coordinates Z^A, k is an integer and $\xi^a{}_b$ and $\chi^a{}_b$ are diagonal constant matrices. Note that these matrices are not tensors. Their purpose is solely to indicate the form of the metrics. In previous works on GTD (see e.g. [25]), the specific form has been determined through the correct description of the relevant physical phenomena. On the one hand, the choice

$$\xi^a{}_b = \delta^a{}_b \quad \text{and} \quad \chi^a{}_b = \delta^a{}_b \tag{3.3}$$

has been used to describe ordinary systems both with first order and continuous phase transitions. On the other hand, second order phase transitions in black holes (the so-called *Davies phase transitions*) have been correctly described when

$$\xi^a{}_b = \delta^a{}_b \quad \text{and} \quad \chi^a{}_b = \eta^a{}_b\,, \tag{3.4}$$

where $\eta^a{}_b = \mathrm{diag}[-1, 1, \ldots, 1]$. The metrics (3.1) with the choices (3.3) and (3.4) are known in the GTD literature as G_I and G_{II}, respectively. Finally, we use the labels T and P to denote invariance under total and the full set of partial Legendre transformations.

Using the pullback of the mapping (1.36), we can naturally calculate the induced metrics in the space of equilibrium states, which are simply given by

$$g_{\mathrm{T}} = \varphi^*(G_{\mathrm{T}}) = \Lambda \left(\xi^a{}_b E^b \frac{\partial \Phi}{\partial E^a}\right) \chi^c{}_d \frac{\partial^2 \Phi}{\partial E^c \partial E^e} \, \mathrm{d}E^d \otimes \mathrm{d}E^e, \tag{3.5}$$

and

$$g_{\mathrm{P}} = \varphi^*(G_P) = \Lambda \sum_{i,j=1}^{n} \left[\left(E^i \frac{\partial \Phi}{\partial E^i}\right)^{2k+1} \frac{\partial^2 \Phi}{\partial E^i \partial E^j} \, \mathrm{d}E^i \otimes \mathrm{d}E^j\right]. \tag{3.6}$$

The core idea in the GTD programme is that the curvature associated with either (3.5) or (3.6) contains all the information about the "thermodynamic interaction" of a system specified by its fundamental relation $\Phi(E^a)$. For example, the lack of inter-particle interaction of the ideal gas is reflected by the vanishing of its associated curvature scalar. Similarly, this approach has proven to describe accurately continuous phase transitions as curvature singularities of the equilibrium manifold, i.e. configurations where the local equilibrium hypothesis is no longer valid [25]. At the same time, the idea that phase transitions can be represented as singularities of the equilibrium manifold has been extensively studied also in the case of black holes. In particular, in the literature of GTD, the phase structure of black holes is the one as first defined by Davies [35]. It turns out that, while ordinary thermodynamic systems are fully described by the metric G_I and its counterpart on the equilibrium space introduced above, in the case of Davies phase transitions in black holes one has to introduce a different geometric structure, the metric G_{II} and its pullback on $\mathcal{E}$. We will comment on the physical meaning of this necessity in Chapter 5.

Finally, the geometric structure of GTD has been used to infer new thermodynamic aspects in a wide variety of systems, from ordinary systems [24, 25, 26] to chemical reactions [27], form black holes [25, 28, 29, 30, 31, 32] to cosmological analysis [33], and also in economic models [34].

In the following section we derive a new metric structure in the GTD context that complies with all the symmetries of the underlying contact structure, as discussed in Section 1.2.2.

3.3 Change of representation and the natural metric in GTD

Having discussed the importance of the symmetry of the contact structure with respect to Legendre transformations in Chapter 2, in this chapter we present a thorough analysis of the symmetries of the metrics given in the GTD programme. We centre our attention on the invariance of the curvature of the space of equilibrium states under a change of representation. Assuming that the systems under consideration can be described by a fundamental relation which is a homogeneous function of a definite order, we demonstrate that such invariance is only compatible with total Legendre transformations in the present form of the programme. As a result, we give the explicit form of a new metric which is invariant under total Legendre transformations and whose induced metric produces a curvature which is independent of the fundamental representation.

Despite the fact that both families of metrics for $\mathcal{E}$, equations (3.5) and (3.6), are induced from the manifestly Legendre invariant metrics on $\mathcal{T}$, equations (3.1) and (3.2), in general, do not produce the same curvature for $\mathcal{E}$ when one changes from one fundamental representation to another (c.f. Section 1.2.2 above). The physical outcome of choosing a different member of the class $[\Theta]$ generating the contact structure of $\mathcal{T}$ should leave the geometric properties of $\mathcal{E}$ unchanged. Therefore, in what follows we will demand the change of representation (CR) symmetry of the programme through the isometry of the metrics on $\mathcal{E}$.

The symmetry under a change of representation has never been considered within the GTD formalism. The main aim of this chapter is to address this issue and arrive at the construction of a metric guided by its underlying symmetries. We show that the outcome of this process leads to a particular generalization of one of the previously known families of metrics in GTD. Thus, we obtain a consistent result from a different point of view. We consider the change of representation as described in Section 1.2.2 and we analyze how the induced metrics behave under such transformation. To this end, let us note the following points:

1. Our analysis will only consider systems which are described by homogeneous functions of a definite order.

2. If we have a homogeneous fundamental relation $\Phi(\lambda E^a) = \lambda^\beta \Phi(E^a)$, the new representation $E^{(i)} = E^{(i)}(\Phi, E^j)$ with $j \neq i$ is not a homogeneous function (one should extend the definition to quasi-homogeneous functions in order to have this property conserved. More details can be found in [56]).

3. The representation in which the system is described by a homogeneous function will be called the *canonical representation* and we will label it by Φ.

In this sense, the phase space metrics (3.1) and (3.2), together with their corresponding induced metrics (3.5) and (3.6), are written in the canonical representation.

Consider a slight generalization of the metric (3.1),

$$G^{\Phi} = \Theta \otimes \Theta + \left(\xi^a{}_b E^b I_a\right) \sum_{k,d} \Lambda_k(Z^A) \left(\chi^k{}_d \, \mathrm{d}E^d \otimes \mathrm{d}I_k\right), \tag{3.7}$$

where $\xi^a{}_b$ and $\chi^a{}_b$ are as in (3.1) and the functions $\Lambda_k(Z^A)$ can now be different for different values of k. Choosing the different representative $\Theta_{(i)}$ [c.f. equation (1.20)], we can rewrite G^Φ as

$$G^{E^{(i)}} = \Theta_{(i)} \otimes \Theta_{(i)} + \left(\xi^{a'}{}_{b'} E^{b'} I_{a'}\right) \sum_{k',d'} \Lambda_{k'}(Z^{A'}) \left(\chi^{k'}{}_{d'} \, \mathrm{d}E^{d'} \otimes \mathrm{d}I_{k'}\right), \tag{3.8}$$

which, using equations (1.22), can be related to the un-primed coordinates as

$$G^{E^{(i)}} = \frac{1}{{I_{(i)}}^2}\,\Theta\otimes\Theta + \left[\xi^{(i)}_{\ (i)}\frac{\Phi}{I_i} - \sum_{j\neq i}\xi^{j}_{\ j}\frac{E^j I_j}{I_{(i)}}\right]\left[\Lambda_{(i)}\chi^{(i)}_{\ (i)}\mathrm{d}\Phi\otimes\mathrm{d}\left(\frac{1}{I_{(i)}}\right) + \right.$$
$$\left. + \sum_{j\neq i}\Lambda_j\chi^{j}_{\ j}\mathrm{d}E^j\otimes\mathrm{d}\left(-\frac{I_j}{I_{(i)}}\right)\right]. \tag{3.9}$$

There is an implicit change in the Λ-functions under the prescribed coordinate transformation, namely

$$\Lambda_{(i)} = \Lambda_{(i)}\left[Z^{A'}\left(Z^A\right)\right] \quad \text{and} \quad \Lambda_j = \Lambda_j\left[Z^{A'}\left(Z^A\right)\right]. \tag{3.10}$$

Now we can state the following

Lemma 3. *If Λ_k is a Legendre invariant function for all k, then G^Φ is invariant under TLTs.*

Proof. It follows from the invariance of G_{T} provided each of the Λ_k is itself invariant. □

Proposition 3. *Let the fundamental relation $\Phi = \Phi(E^a)$ be a homogeneous function of order β. Then, the induced metrics $g^\Phi = \varphi^*(G^\Phi)$ and $g^{E^{(i)}} = \varphi^*(G^{E^{(i)}})$ are conformally related if and only if $\Lambda_{(i)} = \Lambda_j\ \chi^{j}_{\ j}\left(\chi^{(i)}_{\ (i)}\right)^{-1}$ (no sum over j) for all $j \neq i$.*

Proof. The induced metric $g^\Phi = \varphi^*(G^\Phi)$ can formally be written as

$$g^\Phi = (\xi^{a}_{\ b} I_a E^b)\ \sum_k \Lambda_k\,\chi^{k}_{\ c}\ \mathrm{d}I_k\otimes\mathrm{d}E^c, \tag{3.11}$$

where $I_a = \partial\Phi/\partial E^a$ and therefore

$$\mathrm{d}I_k = \frac{\partial^2\Phi}{\partial E^k\partial E^b}\ \mathrm{d}E^b\,. \tag{3.12}$$

Now, the induced metric in the $E^{(i)}$ representation, $g^{E^{(i)}} = \varphi^*(G^{E^{(i)}})$ is

$$g^{E^{(i)}} = \left[\xi^{(i)}_{\ (i)}\frac{\Phi}{I_{(i)}} - \sum_{j\neq i}\xi^{j}_{\ j}\frac{E^j I_j}{I_{(i)}}\right]\left[\Lambda_{(i)}\chi^{(i)}_{\ (i)}\left(\frac{\partial^2 E^{(i)}}{\partial\Phi^2}\mathrm{d}\Phi\otimes\mathrm{d}\Phi + \sum_{j\neq i}\frac{\partial^2 E^{(i)}}{\partial E^j\partial\Phi}\mathrm{d}E^j\otimes\mathrm{d}\Phi\right)\right.$$
$$\left. + \sum_{j\neq i}\Lambda_j\chi^{j}_{\ j}\left(\frac{\partial^2 E^{(i)}}{\partial\Phi\partial E^j}\mathrm{d}\Phi\otimes\mathrm{d}E^j + \sum_{k\neq i}\frac{\partial^2 E^{(i)}}{\partial E^j\partial E^k}\mathrm{d}E^j\otimes\mathrm{d}E^k\right)\right]. \tag{3.13}$$

In this representation we have the analogous relations to (3.12)

$$\mathrm{d}\left(\frac{1}{I_{(i)}}\right) = \frac{\partial^2 E^{(i)}}{\partial \Phi^2}\mathrm{d}\Phi + \sum_{k\neq i}\frac{\partial^2 E^{(i)}}{\partial E^k \partial \Phi}\mathrm{d}E^k, \tag{3.14}$$

$$\mathrm{d}\left(-\frac{I_j}{I_{(i)}}\right) = \frac{\partial^2 E^{(i)}}{\partial \Phi \partial E^j}\mathrm{d}\Phi + \sum_{k\neq i}\frac{\partial^2 E^{(i)}}{\partial E^k \partial E^j}\mathrm{d}E^k\,. \tag{3.15}$$

Since $\Phi(E^a)$ is a homogeneous function of order β, we have that

$$\beta\Phi = I_a E^a\,. \tag{3.16}$$

Using this result, together with equations (3.14), (3.15) and the first law of thermodynamics, equation (1.35), the expression for the induced metric (3.13) becomes

$$\begin{aligned} g^{E^{(i)}} = & -\frac{1}{\beta I_{(i)}}\left[\xi^{(i)}{}_{(i)}E^{(i)} + \sum_{j\neq i}\left(\xi^{(i)}{}_{(i)} - \xi^{j}{}_{j}\beta\right)\frac{I_j E^j}{I_{(i)}}\right] \\ & \times\left[-\Lambda_{(i)}\chi^{(i)}{}_{(i)}\frac{1}{I_{(i)}}\mathrm{d}E^{(i)}\otimes\mathrm{d}I_{(i)} - \Lambda_{(i)}\chi^{(i)}{}_{(i)}\sum_{j\neq i}\frac{I_j}{I_{(i)}^2}\mathrm{d}E^j\otimes\mathrm{d}I_{(i)}\right. \\ & \left. - \sum_{j\neq i}\Lambda_j\chi^{j}{}_{j}\frac{1}{I_{(i)}}\mathrm{d}E^j\otimes\mathrm{d}I_j + \sum_{j\neq i}\Lambda_j\chi^{j}{}_{j}\frac{I_j}{I_{(i)}^2}\mathrm{d}E^j\otimes\mathrm{d}I_{(i)}\right]\,, \end{aligned} \tag{3.17}$$

which can be factorized to

$$\begin{aligned} g^{E^{(i)}} = & -\frac{1}{\beta I_{(i)}}\left[\xi^{(i)}{}_{(i)}E^{(i)} + \sum_{j\neq i}\left(\xi^{(i)}{}_{(i)} - \xi^{j}{}_{j}\beta\right)\frac{I_j E^j}{I_{(i)}}\right] \\ & \times\left[\sum_{k}\Lambda_k\chi^{k}{}_{c}\mathrm{d}I_k\otimes\mathrm{d}E^c + \sum_{j\neq i}\left(\Lambda_j\chi^{j}{}_{j} - \Lambda_{(i)}\chi^{(i)}{}_{(i)}\right)\frac{I_j}{{I_{(i)}}^2}\mathrm{d}E^j\otimes\mathrm{d}I_{(i)}\right]\,. \end{aligned} \tag{3.18}$$

It follows that the two metrics are conformally related only when the condition

$$\Lambda_{(i)} = \Lambda_j\,\frac{\chi^{j}{}_{j}}{\chi^{(i)}{}_{(i)}} \quad \text{no sum over } j \quad \forall j\neq i, \tag{3.19}$$

is satisfied. In such case, and using (3.11), equation (3.18) reduces to

$$g^{E^{(i)}} = -\frac{1}{\beta I_{(i)}}\left[\xi^{(i)}{}_{(i)}E^{(i)} + \sum_{j\neq i}\left(\xi^{(i)}{}_{(i)} - \xi^{j}{}_{j}\beta\right)\frac{I_j E^j}{I_{(i)}}\right]\left[\xi^{a}{}_{b}E^b I_a\right]^{-1} g^{\Phi}. \tag{3.20}$$

Hence, the induced metrics in the two representations are conformally related. □

In the case of the GTD programme, condition (3.19) together with $\Lambda_{(i)} = \Lambda_j = \Lambda$, yield (a slight generalization of) the metric determined by ${\chi^a}_b = {\delta^a}_b$, namely G_I. Notice that the same condition rules out the choice ${\chi^a}_b = {\eta^a}_b$, that is, G_{II} does not lead to conformally related metrics in $\mathcal{E}$ for different representations.

Proposition 4. *The induced metric is invariant under change of representation if and only if the conformal factor is*

$$\Lambda(Z^A) = \frac{1}{{\xi^a}_b E^b I_a} \sum_{j \neq i} \frac{1}{E^j I_j} \, . \tag{3.21}$$

Proof. The metric G^Φ in (3.7) with the choice (3.21) gives,

$$G^\Phi = \Theta \otimes \Theta + \sum_{j \neq i} \frac{1}{E^j I_j} \sum_{k,d} \Lambda_k(Z^A) \left({\chi^k}_d \, \mathrm{d}E^d \otimes \mathrm{d}I_k \right) \, , \tag{3.22}$$

whilst

$$G^{E^{(i)}} = \frac{1}{{I_{(i)}}^2} \Theta \otimes \Theta + \sum_{j \neq i} \frac{-I_{(i)}}{E^j I_j} \left[\mathrm{d}\Phi \otimes \mathrm{d}\left(\frac{1}{I_{(i)}} \right) + \sum_{j \neq i} \mathrm{d}E^j \otimes \mathrm{d}\left(-\frac{I_j}{I_{(i)}} \right) \right] \, . \tag{3.23}$$

The pulled-back metrics are

$$g^\Phi = \sum_{j \neq i} \frac{1}{E^j I_j} \mathrm{d}E^a \otimes \mathrm{d}I_a \, , \tag{3.24}$$

and analogously to (3.18) we can factorize $\varphi^* \left(G^{E^{(i)}} \right)$ to obtain,

$$g^{E^{(i)}} = \sum_{j \neq i} \frac{-I_{(i)}}{E^j I_j} \left(-\frac{1}{I_{(i)}} \mathrm{d}E^a \otimes \mathrm{d}I_a \right) \, . \tag{3.25}$$

It follows immediately that

$$g^\Phi = g^{E^{(i)}} \, . \tag{3.26}$$

□

Note that the Λ-function is related to the primed coordinates through

$$\Lambda \left[Z^{A'} \left(Z^A \right) \right] = \frac{-\beta I_{(i)}}{\left[{\xi^{(i)}}_{(i)} E^{(i)} + \sum_{j \neq i} \left({\xi^{(i)}}_{(i)} - {\xi^j}_j \beta \right) \frac{I_j E^j}{I_{(i)}} \right]} \sum_{j \neq i} \frac{1}{E^j I_j} \, . \tag{3.27}$$

Corollary 2. $\Lambda(Z^A)$ *is invariant under total Legendre transformations.*

Proof. Using (1.30) in (3.21) for every pair of indexes we obtain

$$\tilde{\Lambda} = \frac{-1}{\xi^a{}_b\, \tilde{E}^b \tilde{I}_a} \sum_{j\neq i} \frac{-1}{\tilde{E}^j \tilde{I}_j} = \frac{1}{\xi^a{}_b(\tilde{E}^b \tilde{I}_a)} \sum_{j\neq i} \frac{1}{\tilde{E}^j \tilde{I}_j} = \frac{1}{\xi^a{}_b E^b I_a} \sum_{j\neq i} \frac{1}{E^j I_j} = \Lambda \,. \qquad (3.28)$$

□

Therefore, we have obtained a metric which is invariant under total Legendre transformations and whose associated curvature in the space of equilibrium states does not depend upon the chosen fundamental representation, provided one of the potentials is a homogeneous function. We call this metric the *natural metric* for GTD. In the canonical representation it is written as

$$G^{\natural} = \Theta \otimes \Theta + \sum_{j\neq i} \frac{1}{E^j I_j} \mathrm{d}E^a \otimes \mathrm{d}I_a \,. \qquad (3.29)$$

Now, let us show that invariance under change of representation is not compatible with G_{P}. To this end, let us write the metric (3.2) in the $E^{(i)}$ representation, that is

$$G_{\mathrm{P}}^{E^{(i)}} = \frac{1}{{I_{(i)}}^2} \Theta \otimes \Theta + \Lambda \left[\left(\frac{\Phi}{I_{(i)}} \right)^{2k+1} \mathrm{d}\Phi \otimes \mathrm{d} \left(\frac{1}{I_{(i)}} \right) + \right.$$
$$\left. + \sum_{j\neq i} \left(\frac{E^j I_j}{I_{(i)}} \right)^{2k+1} \mathrm{d}E^j \otimes \mathrm{d} \left(-\frac{I_j}{I_{(i)}} \right) \right] . \qquad (3.30)$$

Thus, we can prove the following

Proposition 5. *Let* $\Phi = \Phi(E^a)$ *be a homogeneous function of order* β*,* G_{P}^{Φ} *and* $G_{\mathrm{P}}^{E^{(i)}}$ *the metric* (3.2) *in the canonical and* $E^{(i)}$ *representations, respectively. Then, the induced metrics* $g_{\mathrm{P}}^{\Phi} = \varphi^* \left(G_{\mathrm{P}}^{\Phi} \right)$ *and* $g_{\mathrm{P}}^{E^{(i)}} = \varphi^* \left(G_{\mathrm{P}}^{E^{(i)}} \right)$ *cannot be conformally related.*

Proof. The induced metrics are

$$g_{\mathrm{P}}^{\Phi} = \Lambda \sum_{i=1}^{n} \left(E^i \frac{\partial \Phi}{\partial E^i} \right)^{2k+1} \mathrm{d}E^i \otimes \mathrm{d}I_i \quad \text{and} \qquad (3.31)$$

$$g_{\mathrm{P}}^{E^{(i)}} = \Lambda \left[\left(\frac{\Phi}{I_{(i)}} \right)^{2k+1} \mathrm{d}\Phi \otimes \mathrm{d} \left(\frac{1}{I_{(i)}} \right) + \sum_{j\neq i} \left(\frac{E^j I_j}{I_{(i)}} \right)^{2k+1} \mathrm{d}E^j \otimes \mathrm{d} \left(-\frac{I_j}{I_{(i)}} \right) \right] , \qquad (3.32)$$

where the differentials of the intensive variables are the same as in (3.12), (3.14) and (3.15).

Using the generalized Euler identity (3.16), we can rewrite (3.32) as

$$\begin{aligned} g_{\mathrm{P}}^{E^{(i)}} =& \Lambda \left[\frac{-1}{{I_{(i)}}^2} \left(\frac{E^a I_a}{\beta I_{(i)}} \right)^{2k+1} \mathrm{d}\Phi \otimes \mathrm{d}I_{(i)} + \right. \\ & \left. + \sum_{j \neq i} \left(\frac{E^j I_j}{I_{(i)}} \right)^{2k+1} \mathrm{d}E^j \otimes \left(-\frac{1}{I_{(i)}} \mathrm{d}I_j + \frac{I_j}{{I_{(i)}}^2} \mathrm{d}I_{(i)} \right) \right] , \end{aligned} \tag{3.33}$$

and substituting the first law (1.35), we can factorize the expression above to obtain

$$\begin{aligned} g_{\mathrm{P}}^{E^{(i)}} =& -\Lambda \left[\left(\frac{E^a I_a}{\beta I_{(i)}} \right)^{2k+1} \sum_{j \neq i} \frac{I_j}{{I_{(i)}}^2} \left[1 - \left(\beta \frac{E^j I_j}{E^a I_a} \right)^{2k+1} \right] \mathrm{d}E^j \otimes \mathrm{d}I_{(i)} \right. \\ & \left. + \frac{1}{I_{(i)}} \left(\frac{E^a I_a}{\beta I_{(i)}} \right)^{2k+1} \mathrm{d}E^{(i)} \otimes \mathrm{d}I_{(i)} + \frac{1}{I_{(i)}} \sum_{j \neq i} \left(\frac{E^j I_j}{I_{(i)}} \right)^{2k+1} \mathrm{d}E^j \otimes dI_j \right] . \end{aligned} \tag{3.34}$$

The only possibility of making (3.34) conformal to (3.31) is that $k = -1/2$, which is inconsistent with the partial Legendre invariance of G_{P} (k must be an integer). $\square$

3.4 Example: homogeneous systems with two degrees of freedom

In the simplest situation, when the fundamental relation is homogeneous of order one, i.e. when $\beta = 1$, and taking $\xi^{(i)}{}_{(i)} = \xi^j{}_j = 1$ for any $i \neq j$, the metric $g_{\mathrm{T}}^{E^{(i)}}$, equation (3.20), reduces to

$$g^{E^{(i)}} = - \left[I_{(i)}^{-1} E^{(i)} \frac{1}{I_a E^a} \right] g^{\Phi} . \tag{3.35}$$

Now, let us consider a system with two degrees of freedom. The two representations that are commonly used are those of the internal energy and entropy. Let us take $\Phi = U(S, V)$ and $E^{(i)} = S(U, V)$. In this case, the induced metrics are conformally related as

$$g^S = - \left[T^{-1} S \left(\frac{1}{ST - PV} \right) \right] g^U . \tag{3.36}$$

It is clear that these two conformally related metrics do not produce the same curvature. Thus, we will not obtain the same thermodynamic information whenever we make a change of representation.

Note that if we work instead with the metric (3.24)

$$g^{\natural} = \varphi^{*}\left(G^{\natural}\right) = \sum_{j\neq i} \frac{1}{E^{j} I_{j}} \mathrm{d}E^{a} \otimes \mathrm{d}I_{a}\,, \tag{3.37}$$

we obtain

$$g^{\natural}_{U} = -\frac{1}{PV}\left(\mathrm{d}S \otimes \mathrm{d}T - \mathrm{d}V \otimes \mathrm{d}P\right) = g^{\natural}_{S} \tag{3.38}$$

and, therefore, the curvature scalar is the same in both representations, i.e., the change of representation is a symmetry for such a metric.

Finally, let us consider the manifestly not Legendre invariant case of G_{P} with $\Lambda = 1$ and $k = -1/2$, whose pullback generates Hessian metrics for the equilibrium space. In this case, the metrics g^{U}_{P} and g^{S}_{P}, equations (3.31) and (3.34) respectively, are conformally related through [8, 9]

$$g^{S}_{\mathrm{P}} = -\frac{1}{T}\, g^{U}_{\mathrm{P}}\,. \tag{3.39}$$

This case corresponds to the Hessian metrics of the energy and entropy potential which have been introduced in Section 1.2.3.[1] This simple exercise shows that Hessian metrics not only fail to be symmetric with respect to Legendre transformations, but they also give different curvatures in each representation.

3.5 Conclusions

In this chapter, we have analyzed in detail the symmetries of the metric structure of the GTD programme. As it has been previously argued, the Legendre symmetry is paramount in preserving the notion that the physical reality should be independent of the thermodynamic potential used to describe it. Furthermore, we have pointed out in Chapter 2 the physical meaning of such symmetry and the relationship between the breaking of this conservation law and the appearence of ensemble inequivalence.

Within the GTD programme, analogously to field theories, curvature is the geometric object accounting for the physics of the system. The metrics G_{T} and G_{P} – equations (3.1) and (3.2), respectively – satisfy the desired invariance in the thermodynamic phase space $\mathcal{T}$ and, therefore, produce the same curvature for the space of equilibrium states $\mathcal{E}$ independently of the thermodynamic potential used. However, Legendre invariance alone is not sufficient to guarantee a unique description

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[1] Note that we are using here the metric in the entropy representation defined as the Hessian of S, without an overall minus sign. For this reason we get an extra minus sign with respect to Eq. (1.38).

of a thermodynamic system in terms of its curvature, i.e. we also need to demand invariance of the curvature under a change of fundamental representation. Such a problem has remained largely unanalyzed.

We have derived a new metric compatible with the symmetry under change of representation in the GTD programme. This has been found to be a slight generalization of G_{T} with Λ given by (3.21), that is $G^{\natural}$ [c.f. equation (3.29)]. The pullback of this metric on the equilibrium manifold, in turn, is conformal to the Hessian metrics of the energy and the entropy and therefore is the natural candidate to account for the introduction of fluctuations in the context of GTD. Consequently, the metric $G^{\natural}$ should be applied to all the ordinary systems with continuous phase transitions as a further ingredient to the equilibrium description provided by the contact structure represented by Θ. Indeed, the two objects show some sort of complementarity, the contact structure giving information about the first law and hence equilibrium states of the system, including the region of coexistence, while the metric structure corresponds to fluctuations and stability conditions derived from the second law. Both descriptions break down in the critical region of continuous phase transitions, represented by a divergence of the scalar curvature. We have also shown that symmetry with respect to partial Legendre transformations cannot be preserved if we demand symmetry for a change of representation for G_{P}, a result which deserves a more detailed investigation in the future.

All the metrics found so far in GTD, using only the Legendre invariance condition, contain the arbitrary conformal factor $\Lambda(Z^A)$. This is an additional degree of freedom that can be used to reach diverse objectives. For instance, in the study of the thermodynamics of black holes [32], one finds that the curvature singularities determine the Davies phase transition structure and, in addition, Λ can be chosen in such a way that the limiting case of extremal black holes corresponds to curvature singularities too. Here, we have found that Λ can also be used to reach representation invariance directly from the phase space. We believe that the conformal freedom that follows from the phase space still might have more applications at the level of the equilibrium space.

Finally, let us remark that the metric found here is expected to fail to represent the correct description whenever the Legendre symmetry of the system is broken, i.e. for systems showing ensemble inequivalence (see Chapter 5 for a more detailed discussion on this topic in the case of black holes thermodynamics).

4 Applications of the natural metric to ordinary systems

In this chapter we employ the metric structure (3.29) to study ordinary thermodynamic systems. The new feature of this metric is that, in addition to Legendre symmetry, it exhibits symmetry under a change of representation. Here, we present a thorough analysis for the ideal gas, the Van der Waals fluid, the one dimensional Ising model and some other systems of cosmological interest.

Before starting, let us write the induced metric on the space of equilibrium states $\mathcal{E}$ in general coordinates, that is

$$g^{\natural} = \sum_{j\neq i} \left(E^j \frac{\partial \Phi}{\partial E^j} \right)^{-1} \frac{\partial^2 \Phi}{\partial E^b \partial E^a} \, \mathrm{d}E^a \otimes \mathrm{d}E^b. \tag{4.1}$$

4.1 The ideal gas

Let us begin with the simplest example, the ideal gas. In this case, the fundamental relation in the entropy representation is given by [1]

$$s(u,v) = \frac{3}{2} \ln u + \ln v \,, \tag{4.2}$$

where we use molar quantities, $R = \kappa_B = N_A = 1$ with κ_B the Boltzmann constant, N_A the Avogadro number and u and v represent the molar internal energy and the molar volume of the system, respectively. The natural metric, equation (4.1), for this representation reads

$$g_s^{\natural} = -\frac{3}{2}\frac{1}{u^2} \mathrm{d}u \otimes \mathrm{d}u - \frac{1}{v^2} \mathrm{d}v \otimes \mathrm{d}v \,, \tag{4.3}$$

and its associated scalar curvature vanishes, in agreement with the hypothesis that the curvature is a macroscopic measure of the inter-particle interaction.

Working in the energy representation we have

$$u(s,v) = \left(\frac{1}{v}\,e^{s}\right)^{\frac{2}{3}}\,, \tag{4.4}$$

and the corresponding metric takes the form

$$g^{\natural}_{u} = -\frac{2}{3}\mathrm{d}s \otimes \mathrm{d}s - \frac{5}{3v^2}\mathrm{d}v \otimes \mathrm{d}v + \frac{4}{3v}\mathrm{d}s \otimes \mathrm{d}v\,. \tag{4.5}$$

As expected its curvature scalar also vanishes. Using any of the fundamental relations, equations (4.2) or (4.4), it is straightforward to verify that the metrics (4.3) and (4.5) are the same geometric object. This can also be done for the Gibbs free energy $g(T,P) = u - Ts + Pv$ as it comes from the total Legendre transformation applied to u. In view of the above agreement, it is an interesting exercise to explore the geometric behavior if one attempts to work instead with a thermodynamic potential obtained from a partial Legendre transformation. For instance, in the Helmholtz free energy $F(T,v)$ representation

$$F(T,v) = u - Ts = \frac{1}{2}T\left[3 - 2\ln v - 3\ln\frac{3}{2}T\right]\,, \tag{4.6}$$

the metric (4.1) takes the explicit form

$$g^{\natural}_{F}(T,v) = \frac{3}{2T^2}\mathrm{d}T \otimes \mathrm{d}T - \frac{1}{v^2}\mathrm{d}v \otimes \mathrm{d}v + \frac{2}{Tv}\mathrm{d}T \otimes \mathrm{d}v\,. \tag{4.7}$$

If we write the expression above in terms of the coordinates $\{s,v\}$ it becomes

$$g^{\natural}_{F}(s,v) = \frac{2}{3}\mathrm{d}s \otimes \mathrm{d}s - \frac{5}{3v^2}\mathrm{d}v \otimes \mathrm{d}v\,. \tag{4.8}$$

Not surprisingly, it yields a different metric to (4.5), as $G^{\natural}$ is not symmetric under partial Legendre transformations. Nevertheless, an interesting feature is that the scalar curvature for this potential vanishes as well. It is easy to verify that for the enthalpy $H(s,P) = u + Pv$ the same situation is repeated. We will work out in the next section a more complicated case in which this feature is no longer reproduced, e.g. the Van der Waals fluid (see Section 1.1.5). In this case we will see that the geometric description is exactly the same for both representations s and u, and correctly signalizes both the first order and the continuous phase transition as curvature singularities, while for a potential related to u through a partial Legendre transformation (e.g. $F(T,v)$) we have that, being the natural metric a different object, the geometric description of the phase transition might not be correct.

4.2 The Van der Waals system

The fundamental equation for the Van der Waals fluid in the entropy representation is given by

$$s(u,v)=\frac{3}{2}\ln\left(u+\frac{a}{v}\right)+\ln\left(v-b\right). \tag{4.9}$$

The natural metric (4.1) is thus given by

$$\begin{aligned}g_s^{\natural}=&\frac{3v^2(v-b)}{(uv+a)\left[2uv^2-a(v-3b)\right]}\mathrm{d}u\otimes\mathrm{d}u+\frac{6a(v-b)}{(uv+a)\left[uv^2-a(v-3b)\right]}\mathrm{d}u\otimes\mathrm{d}v+\\&+\frac{2u^2v^4-(v^2-6bv+3b^2)(2auv+a^2)}{v^2(v-b)(uv+a)(2uv^2-av+3ab)}\mathrm{d}v\otimes\mathrm{d}v,\end{aligned} \tag{4.10}$$

and the scalar curvature obtained is

$$R_s^{\natural}=\frac{N_s^{\mathrm{vdW}}(u,v)}{4\left(3ab-av+2uv^2\right)\left(a\left(-3b^2+6bv-2v^2\right)+uv^3\right)^2} \tag{4.11}$$

where the numerator function is

$$\begin{aligned}N_s^{\mathrm{vdW}}(u,v)=\Big[&a^3\left(27b^5-243b^4v+504b^3v^2-378b^2v^3+113bv^4-11v^5\right)\\&+2a^2uv^2\left(-72b^4+174b^3v-111b^2v^2+16bv^3+v^4\right)\\&+4au^2v^4\left(-3b^3+12b^2v-11bv^2+v^3\right)-8bu^3v^7\Big].\end{aligned} \tag{4.12}$$

In the energy representation we have

$$u(s,v)=\frac{a(v-b)^{\frac{2}{3}}-ve^{\frac{2}{3}s}}{v(v-b)^{\frac{2}{3}}}. \tag{4.13}$$

In this case, the metric takes the form

$$\begin{aligned}g_u^{\natural}=&\frac{4e^{2s/3}v(v-b)}{9a(v-b)^{5/3}-6e^{2s/3}v^2}\mathrm{d}s\otimes\mathrm{d}s+\frac{8e^{2s/3}v}{6e^{2s/3}v^2-9a(v-b)^{5/3}}\mathrm{d}s\otimes\mathrm{d}v\\&+\frac{2(5e^{2s/3}v^3-9a(v-b)^{8/3})}{3v^2(v-b)(2e^{2s/3}v^2-3a(v-b)^{5/3})}\mathrm{d}v\otimes\mathrm{d}v.\end{aligned} \tag{4.14}$$

and the curvature is given by

$$R_u^{\natural}=\frac{N_u^{\mathrm{vdW}}(s,v)}{4(v-b)^{1/3}\left(2e^{2s/3}v^2-3a(v-b)^{5/3}\right)\left(e^{2s/3}v^3-3a(v-b)^{8/3}\right)^2} \tag{4.15}$$

where the numerator is now

$$\begin{aligned} N_u^{\mathrm{vdW}}(s,v) = \big[&-9a^3(v-b)^{16/3}\left(3b^2-2bv+v^2\right) \\ &- 6a^2e^{2s/3}v^2(v-b)^{11/3}\left(24b^2-14bv+v^2\right) \\ &+4ae^{4s/3}v^4\left(3b^4-15b^3v+17b^2v^2-6bv^3+v^4\right)-8be^{2s}v^7(v-b)^{1/3}\big] . \end{aligned} \tag{4.16}$$

It is a straightforward calculation to substitute the fundamental relation, equation (4.9), in the above equation to obtain the same scalar curvature we get form the entropy representation, equation (4.11).

In order to analyze the first order phase transition of the Van der Waals system we start from (4.11). Using the equations of state

$$\frac{1}{T}=\frac{\partial s}{\partial u} \quad \text{and} \quad \frac{P}{T}=\frac{\partial s}{\partial v} \tag{4.17}$$

we obtain

$$P=\frac{2uv^2-av+3ab}{3v^2(v-b)}\,, \tag{4.18}$$

which we can use to express the curvature scalar in the entropy representation, equation (4.11), as a function of the pressure and the volume, that is,

$$\begin{aligned} R^{\natural}(v,P)=&\frac{1}{3Pv^2(v-b)\left(2ab-av+Pv^3\right)^2}\Big[-a^2Pv^2\left(18b^3-5b^2v-4bv^2+v^3\right) \\ &-a^3(v-6b)(v-2b)^2-aP^2v^4\left(-3b^3+21b^2v-14bv^2+v^3\right)+3bP^3v^7(v-b)\Big]. \end{aligned} \tag{4.19}$$

It is immediate to see that the scalar curvature obtained from the natural metric (4.19) diverges at

$$2ab-av+Pv^3=0\,. \tag{4.20}$$

The denominator clearly vanishes at these points, while the numerator,

$$\mathrm{Num}\left[R^{\natural}(v_c,P_c)\right]=-\frac{1}{v_c^2}\left[a^3(v_c-2b)^2\left(-9b^3+21b^2v_c-13bv_c^2+v_c^3\right)\right], \tag{4.21}$$

remains finite. It is worth mentioning that the additional points where the denominator of the curvature scalar (4.19) vanishes lack of physical meaning, as one can observe from the fundamental equation (4.9).

The curve described by (4.20) is of special interest in thermodynamics, because it is the *spinodal curve*, i.e. the line where the *local* stability conditions fail. This means that it is the locus of points in the phase diagram where some of the second derivatives of the potential vanish and after which the system enters an unstable (thus non-thermodynamical) region. Hence, we see that the analysis with the curvature scalar of the thermodynamic metric following from the Van der Waals analytical equation gives two important indications about the information carried by the metric structure. The first information is that *the intrinsic Riemannian structure takes account of the local stability.* In fact, for the Van der Waals system, the *global* stability conditions, i.e. the global convexity of the thermodynamic potential (together with the additivity of the system), imply phase separation and Maxwell construction to happen before reaching the spinodal curve (see Sec. 1.1.3). For example, looking at Figure 1.2 one sees that the Maxwell curve of coexistence on a generic unstable isotherm begins much before the point of change of concavity is reached. Therefore, the diverging of the curvature in this region signals that there is a changing in the stability of the system and forbids to enter the non-thermodynamical region of the phase diagram. However, the complete GTD analysis, considering also the global contact structure of the phase space is telling us that this region cannot be reached, because of the Maxwell process described in Chapter 2. We note that this is the same as in ordinary thermodynamics, where one “cuts away” the metastable as well as the unstable region by means of the Maxwell law, based on the global analysis of the convexity of the potential, rather than on local conditions.

The second feature about the geometric analysis by means of the curvature is that, being the metric (4.1) conformal to the Hessian of the potential, the curvature divergences correctly signal the points where the local stability fails. In other words, provided we are to analyze a system where the global stability requirement does not necessarily hold, or a non-extensive system (as in the case of black holes), where phase separation cannot help to forbid the access to the metastable region, therefore such analysis would be much useful to indicate where the potential loses its concavity and where the ensemble inequivalence and the instabilities appear (c.f. Chapter 2).

Besides, Ruppeiner showed (see [15]) that the scalar curvature of metrics based on the Hessian of the potential diverges at the critical point of a continuous phase transition exactly in the same way as the correlation volume. It is easy to check that the curvature (4.19) diverges at

$$v_{\rm cr} = 3\,b\,, \qquad P_{\rm cr} = \frac{a}{27\,b^2}\,, \tag{4.22}$$

which is the location of the Van der Waals critical point in our notation. Moreover, repeating the same argument provided by Ruppeiner, that is, the scaling assumption of the free energy in the critical region [15], one can show that the divergence of the scalar curvature of the metric (4.1) at a continuous phase transition is always the same as that of the correlation volume. Therefore, the macroscopic function of state $R^{\natural}(v,P)$ gives information about the microscopic nature of the system, at least inside the critical region, where the two concepts of microscopic and macroscopic seem to merge, due to the divergence of spatial correlations among microscopic states.

Now we show explicitly that $G^{\natural}$ does not carry the same information in the case of the Van der Waals system if one attempts to derive it starting with the Helmholtz free energy $F(T,v)$ as the potential. This is easily understood by noting that $F(T,v)$ cannot be considered the canonical representation nor its related (inverse) representation, given that it depends on T which is not an extensive parameter evading the notion of homogeneity. The Helmholtz free energy is

$$F(T,v)=\frac{1}{2\,v}\left[3\left(T\,v-\ln\frac{3\,T}{2}\right)-2\left(a+T\,v\,\ln(v-b)\right)\right]. \qquad (4.23)$$

In this case, the natural metric is

$$\begin{aligned}g^{\natural}_F=\frac{3\,v\,(v-b)}{2\,T\left[a(v-b)-Tv^2\right]}\,\mathrm{d}T\otimes\mathrm{d}T+\frac{2\,v}{T\,v^2-a\,(v-b)}\,\mathrm{d}T\otimes\mathrm{d}v\\+\frac{TV^3-2a(v-b)^2}{v^2(v-b)\left[a(v-b)-Tv^2\right]}\,\mathrm{d}v\otimes\mathrm{d}v\,,\end{aligned} \qquad (4.24)$$

and its associated curvature scalar is written as

$$R^{\natural}_F(T,v)=\frac{N^{\natural}_F(T,v)}{\left[T\,v^2-a\,(v-b)\right]\left[6\,a\,(v-b)^2-5\,T\,v^3\right]^2}\,, \qquad (4.25)$$

where

$$\begin{aligned}N^{\natural}_F(T,v)&=-15\,b\,T^3\,v^7-3\,a^2\,T\,(v-b)^2\,v^2\left(v^2-14\,b\,v+24\,b^2\right)+\\&-3\,a^3\,(v-b)^3\left(v^2-2\,b\,v+3\,b^2\right)+a\,T^2\,v^4\left(5\,v^3-25\,b\,v^2+54\,b^2\,v-9\,b^3\right).\end{aligned} \qquad (4.26)$$

Using the equations of state one can express this curvature in terms of the pressure and the volume to obtain

$$\begin{aligned}R^{\natural}_F(v,P)=\frac{-1}{Pv^2(v-b)(5Pv^3-av+6ab)^2}\Big[a^3(v-2b)(v-6b)^2-15bP^3v^7(v-b)\\-aP^2v^4(5v^3-70bv^2+99b^2v-9b^3)-aPv^2(7v^3-50bv^2+39b^2v+54b^3)\Big].\end{aligned} \qquad (4.27)$$

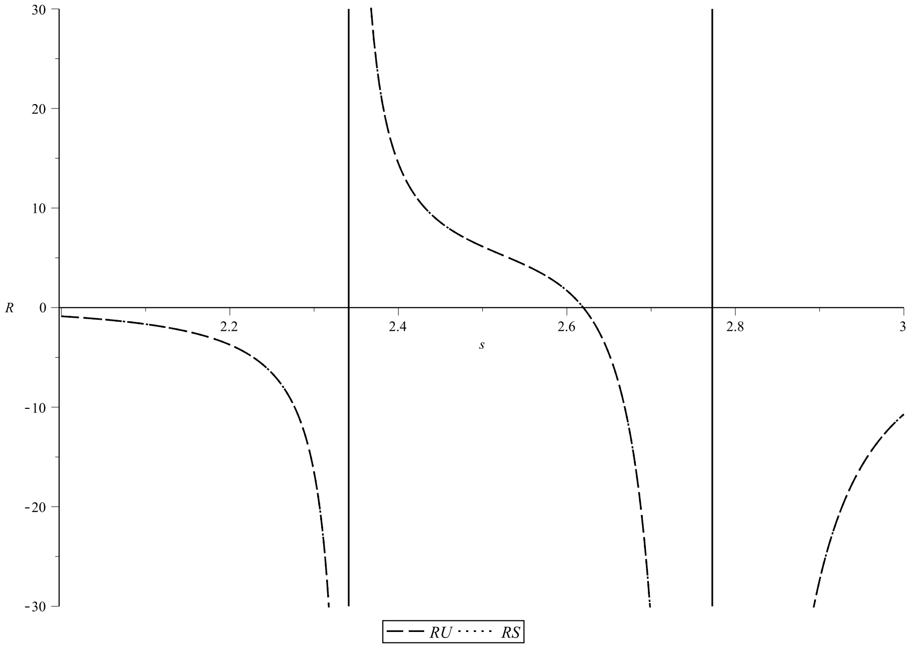

Figure 4.1: This figure shows the curvature scalar for the Van der Waals system in both, energy and entropy representations. As expected, they are superimposed and show divergences at the points of the spinodal curve. Here, we are using reduced variables.

Evidently, this curvature scalar does not coincide with the one obtained from the canonical representations, equation (4.19), nor its description of the spinodal curve and continuous phase transition is accurate. This is a consequence of the fact that the natural metric is not symmetric under partial Legendre transformations.

4.3 The one-dimensional Ising model

A slightly more complicated example is that of the one-dimensional Ising model. It is well known that there are no phase transitions for this system, albeit the statistical origin of its fundamental relation presents non-trivial interaction (see [53] for a particularly simple explanation of the reason why one-dimensional systems cannot have phase transitions). In this case, the free energy obtained from the partition function is written as

$$f(\beta, H) = -T \ln\left[\cosh\left(\frac{H}{T}\right) + \sqrt{\sinh^2\left(\frac{H}{T}\right) + \exp\left(-\frac{4J}{T}\right)}\right], \tag{4.28}$$

where H is the magnetic field, β is the inverse of the temperature T and J is the coupling constant, measuring the intensity of the interaction between the spins.

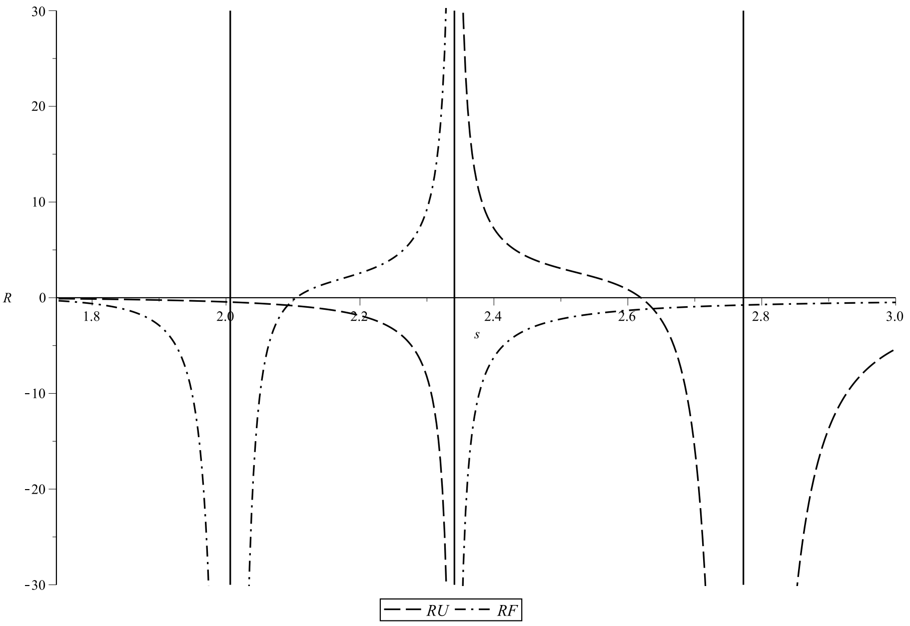

Figure 4.2: This figure shows the curvature scalar for the Van der Waals system in both, energy and Helmholtz free-energy, representations. Here we observe that the curvatures do not coincide. Moreover, the scalar curvature $R^\natural_F$ diverges at different points.

Note that both, T and H are *intensive* parameters, thus the free-energy (4.28) corresponds to the total Legendre transformation of the internal energy U. Therefore, using the invariance of the natural metric under such a transformation, we can freely use this potential instead of the internal energy.

In this case, the scalar curvature has the form

$$R^\natural = \frac{N(T,H)}{HT}\,\frac{\left[\cosh\left(\frac{H}{T}\right)+\sqrt{\cosh^2\left(\frac{H}{T}\right)-1+\exp\left(-\frac{4J}{T}\right)}\right]^{-3}}{\sinh\left(\frac{H}{T}\right)\exp\left(\frac{8J}{T}\right)}\,, \tag{4.29}$$

where $N(T,H)$ corresponds to the numerator of $R^\natural$, whose explicit expression is not very illuminating for our argument.

According to our analysis, should we find that $R^\natural$ becomes singular this would indicate an instability and a consequent phase transition. However, it is easy to show that this only happens in the limit when T goes to zero. In Figure 4.3 we show a numeric analysis of the curvature scalar (4.29) where we observe that, indeed, the only divergence occurs at $T = 0$. Moreover, the curvature becomes asymptotically constant for larger values of T. Thus, as we knew, the one-dimensional Ising model corresponds to an interacting system from the thermodynamic point of view, but without phase transitions.

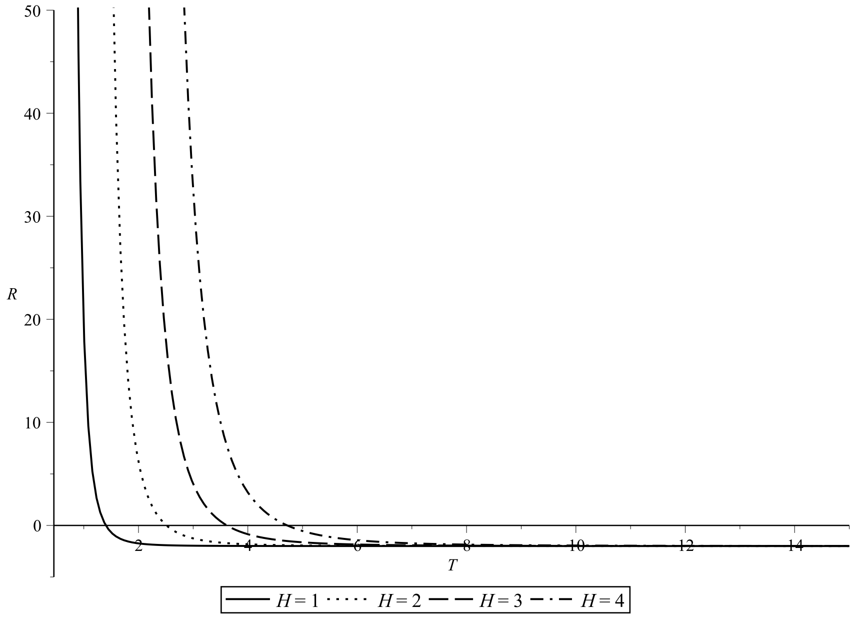

Figure 4.3: This figure shows various plots of the curvature scalar with respect to the temperature for distinct intensities of the magnetic field. The one-dimensional Ising model does not present a curvature singularity other than at $T = 0$, which is excluded by the third law of thermodynamics. For large T the curvature becomes asymptotically constant.

4.4 Generalized Chaplygin gas and the dark fluid equation

Recently, within the realm of cosmological applications of GTD [33], it has been proposed a fundamental relation depending on a pair of parameters which encloses the cases of the generalized Chaplygin gas and a dark fluid which can mimic the phenomenology of the ΛCDM model. The fundamental equation in the entropy representation is

$$s(u,v) = s_0 \left(\ln u^{1+\alpha} + C \ln v^{1+\beta}\right), \tag{4.30}$$

where α and β are real constants that determine the type of fluid we are dealing with.

In this case, the expression for the metric is not very illuminating. However, it is interesting to note that the expression for the metric determinant,

$$\det(g^{\natural}_S) = \frac{\left[C\,(\alpha-\beta)\,v^{1+\beta} + \beta\, e^s\right] e^s}{C\,(1+\alpha)(1+\beta)\,v^{3+\beta}\,(-e^s + C\,v^{\alpha+\beta})}, \tag{4.31}$$

identically vanishes in the case $\alpha = \beta = 0$ and thus the metric is degenerate.

Interestingly, this corresponds exactly to the ΛCDM model.

The curvature scalar in the entropy representation is given by

$$R^{\natural}_{s} = -\frac{(\beta+1)^2\left(C^2\,\alpha\,v^{2\beta+2} + 2\,C\,\alpha\,u^{\alpha+1}\,v^{\beta+1} + \beta\,u^{2\alpha+2}\right)}{2\left(C\alpha v^{\beta+1} + \beta\,u^{\alpha+1}\right)^2}\,, \tag{4.32}$$

whereas in the energy representation one obtains

$$R^{\natural}_{u} = -\frac{(\beta+1)^2\left(-2\,C\,e^{\frac{s}{s_0}}\,v^{\beta+1}(\beta-\alpha) + \beta\,e^{\frac{2s}{s_0}} + C^2\,v^{2\beta+2}(\beta-\alpha)\right)}{2\left(\beta\,e^{\frac{s}{s_0}} - C\,v^{\beta+1}(\beta-\alpha)\right)^2}\,. \tag{4.33}$$

It is an easy task to verify that the curvature is the same in both representations.

An interesting feature of this is that, in the case when $\alpha = \beta$, the curvature scalar is constant,

$$R^{\natural}_{\alpha=\beta} = -\frac{(1+\alpha)^2}{2\,\alpha}\,. \tag{4.34}$$

Spaces of constant curvature are important and interesting in physics. A full analysis of them lies beyond the present work. However, it is worth mentioning that the case of constant curvature with $0 \leq \alpha \leq 1$ reproduces the equations of state for the generalized Chaplygin gas, while $\alpha = \beta = 1$ corresponds to the dubbed variable Chaplygin model. Moreover, when $\alpha = \beta \leq 0$ one obtains generic equations of state for various polytropic fluids. We take this as an indication that dark energy models might show some peculiar properties from the point of view of the geometry of thermodynamics, from which we could get some insights about the physical nature of the constituents of dark energy. It would be interesting to focus on this characterization in the future.

4.5 Conclusions

In this chapter we have worked out some applications of the natural metric derived in Chapter 3, which is symmetric under total Legendre transformations and change of the fundamental representation [c.f. equations (3.29) and (4.1)].

We have shown that the thermodynamic curvature of (4.1) correctly accounts for the thermodynamic interaction and phase transition structure of a number of physical systems. In particular, we analyzed the thermodynamic geometry of the ideal gas, the Van der Waals fluid, the one-dimensional Ising model and a fundamental relation with recent application in cosmology describing the generalized Chaplygin gas or a dark fluid [33] from a completely invariant point of view.

The case of the Van der Waals gas, as usual, is very illustrative. On the one hand it helped us to show the local nature of the intrinsic metric description on the equilibrium manifold and compare it with the global one examined in Chapter 2. This also served us in order to discuss the possibility to use the local description for systems in which the global condition on the convexity of the potential fails, i.e. systems with long-range interactions, as we will further discuss in the next chapter referring to the case of black holes. For such systems, due to the inequivalence of the various statistical ensembles, it will be interesting to analyze the local description in each potential, whenever possible. On the other hand, with the example of the Van der Waals model, we have seen the importance of working in the canonical representation of the metric (4.1), that is, using the internal energy or the entropy or their total Legendre transform as the potential. In fact, as expected, the metric gives a different thermodynamic information if instead one uses the Helmholtz free energy $F = F(T, v)$, which is the result of applying a partial Legendre transformation to the canonical representation $u = u(s, v)$. In this case, the singularities of the curvature signal the occurrence of different instabilities which are in disagreement with the known results [1], whereas working in the canonical representation we recover the correct phase transition structure. This is clearly understood if one recalls how the natural metric was constructed.

The situation with the one-dimensional Ising model was a bit more subtle. The fundamental relation (4.28) is a function of the magnetic field intensity and the temperature, both intensive variables. Here we used the fact that $G^\natural$ is symmetric with respect to total Legendre transformations to infer that the curvature associated with the metric using the Gibbs free energy as the potential would correctly account for the thermodynamic interaction as if an expression for the internal energy were available.

Finally, the case of the generalized Chaplygin gas opened the possibility of analyzing the class of thermodynamic potentials producing a space of equilibrium states of constant curvature and also to understand the thermodynamic properties of cosmological fluids modeling dark energy. Such analysis will be carried out elsewhere.

In the next chapter we will work out more in detail the discussion about the physical significance of the local description given by the Riemannian geometry of the equilibrium space in the case of systems with long-range interactions. In particular, we will consider the phase transition structure in the case of black holes.

5 Black holes thermodynamics and phase transitions

One of the fields where the ideas presented in this work can have the largest applications is in black holes thermodynamics. This is because for systems where one has a detailed microscopic description at hand, then one in principle has already all the tools to understand the physics of the system. However, for black holes this is not the case. Having a microscopic description for black holes thermodynamics would mean having a microscopic description of the gravitational degrees of freedom, i.e. a microscopic description of gravity, which is dubbed to be far from being achieved. Therefore, our geometric framework, which permits to infer microscopic properties from the knowledge of the macroscopic functions of state, can provide to be quite useful in this area. However, black holes must be handled with special care, because they are not ordinary thermodynamic systems, as we will shortly see.

In particular in this chapter we address the concept of phase transitions in black holes thermodynamics from a very general perspective. To do so, we will first review the different definitions of phase transitions that have been given in the context of black holes, since, as we shall see, they lead to different results. Having clarified the definitions, we will make clear that continuous phase transitions can be described in the case of black holes by the same means as for ordinary systems. On the other side, we will give a general argument to show that a different tool from the GTD description can be used to understand the so-called Davies phase transitions.

5.1 Phase transitions in black holes

After the seminal work of Davies [35], much attention has been devoted to phase transitions in black holes thermodynamics (see e.g. [71, 72, 73, 74, 75, 76] for some interesting early works on the topic). This is a peculiar and very active topic in modern research on physics. Indeed, in the current approach to phase transitions in black holes, we have (at least) five different definitions of phase transitions. Let us quickly review these definitions here.

The first definition is that of Davies [35], to which we refer here as Davies Phase Transitions (DPT). According to Davies approach, second order phase transitions happen in black holes whenever there is a change of sign in one of the heat capacities, typically through a divergency. This is the most basic and at the same time the most discussed definition of second order phase transitions in black holes. In fact, Davies points of phase transitions are not exactly what one generally uses to define phase transitions in ordinary thermodynamics (c.f. Section 1.1.6). In fact, as we will discuss in the next section, from the point of view of ordinary thermodynamics, they are more related to the change of stability of the system in the region dominated by fluctuations in some of the thermodynamic variables. As such, they may better account for stability with respect to different possible ensembles.

A second possibility is the Extremal Limit Transition (ELT), which has been regarded by a number of authors as the only point where a phase transition can occur in black holes, due to the change in the topological structure and symmetry of the hole which happens at that limit [71, 73, 76]. However, it is not really clear what the two different phases would be in that case, because on the one side one has a black hole, but on the other side one would have a naked singularity, and naked singularities are supposed to be forbidden in nature, according to the cosmic censorship conjecture.

Moreover, in the recent years various authors have discovered an analogy between black holes and ordinary thermodynamic systems, such as e.g. the Van der Waals fluid, especially in the case of AdS background [42, 43, 44, 45, 46, 47]. Thence, we are given a third type of phase transitions in black holes, i.e. the usual first order and continuous phase transitions taking place in the Van der Waals phase diagram. Such hypothesis has a special appeal, due to the fact that it is connected with the AdS/CFT correspondence [77] and moreover because it permits to reconcile standard definitions from thermodynamics in the case of black holes. However, as we argued in Chapter 2, such coexistence *à la VdW* should be also implemented with a consistent re-definition of the zeroth law (c.f. Section 2.3).

Furthermore, for black holes in dimensions higher than four, the uniqueness theorem does not apply and explicit solutions that can have different topologies of the horizon for the same values of the parameters have been found recently [78]. Therefore, phase transitions are also possible related to a change in the topology at points other than the extremal limit, as for instance in the case of the conjectured black hole/black ring phase transition in five dimensions [79].

Finally, another type of black phase transitions has been studied in the literature, the so-called glassy type (see e.g. [80, 81]). Glassy phase transitions are found in nature in liquids that are supercooled and solidify without crystallization, for example silicate glasses. Although glassy systems are not well understood form the physical point of view [53, 82], nevertheless they allow for a mathematical treatment, and the same treatment is also possible in some black holes cases.

In this work, we give a brief account of Davies approach and we focus on the debate about the physical meaning of DPT. In particular, we will compare DPT to continuous phase transitions in the case of ordinary thermodynamics. Moreover, we introduce tools from thermodynamic geometry that can distinguish between a continuous phase transition and a DPT.

5.2 Davies phase transitions

When thinking about black holes, one should keep in mind that they are systems in which the gravitational interaction is extremely strong. From the thermodynamic point of view, the consequence is that the long-range interactions of the gravitational field cannot be ignored. Therefore, we understand that black holes cannot be considered as ordinary thermodynamic systems. Mathematically, this can be seen for example from Bekenstein's entropy area law [20], which in particular implies that the entropy of a black hole is not an additive quantity. Moreover, the mass as a thermodynamic potential (given by the Smarr formula [35]) is not a homogeneous function of order one. Thus, one can try to deal with black holes thermodynamics by means of the tools of ordinary thermodynamics and thermodynamic geometry, but most likely some strange and inconsistent properties would come out, such as e.g. negative or infinite heat capacities, ensemble inequivalence and thermodynamic instabilities. In addition, from the point of view of phase transitions, one could expect to find phase transitions that appear in one ensemble and that are invisible in a different one (see [49] for a detailed classification of phase transitions in systems that show ensemble inequivalence). Indeed, we argue here that it is perfectly normal to find new types of phase transitions in black holes thermodynamics. In particular, it is not surprising to find phase transitions that are accessible in one ensemble only. When considered from the point of view of ordinary thermodynamics, such transitions would be forbidden and the change from a stable to an unstable phase in one of the ensembles would be prevented by phase separation as in the VdW case (c.f. Chapter 2). However, in black holes thermodynamics the occurrence of ensemble inequivalence and different phase transitions is perfectly possible, because of the loss of the additivity property of the potential, which means that the system cannot simply separate into phases and follow the Maxwell (straight line) construction. Davies [35] was the first to discover such type of transitions by investigating the Kerr-Newmann family of black holes. Davies phase transitions are defined in general as the curves of divergence of one of the second order response functions which define the local stability conditions of the system. As such, they belong to a region of the thermodynamic diagram of metastability, a region in which the Legendre transformation is ill-defined and the thermodynamic description using different potentials gives different results (see the discussion in Chapter 2 for the same situation in a first order phase transition and [49] for a general approach in statistical mechanics).

Therefore, we argue here that one cannot expect to recover the correct results for black holes thermodynamics (as for any thermodynamic systems with long-range interactions) by means of the tools of thermodynamic geometry that apply to ordinary systems. This can possibly explain the puzzling results obtained when comparing Weinhold or Ruppeiner metrics with Davies curves of phase transitions for black holes [16, 50, 51, 52]. For this reason, we propose here that a different thermodynamic geometry from the GTD programme, one which has been shown in the literature to apply to the case of black holes [28, 29, 31, 32], could be the correct one to deal with transitions that emerge in the case of "non-extensive" systems, whose thermodynamics is ensemble dependent.

Let us investigate Davies phase transitions more in detail and compare them with continuous phase transitions at the critical point of e.g. the Van der Waals phase diagram. Davies analyzes black holes phase transitions for the Kerr-Newman family by looking at divergences of heat capacities at some fixed (extensive) quantity. In particular, he writes that there is a second order phase transition for the Reissner-Nordström black hole when C_Q diverges and for the Kerr black hole when C_J diverges.

However, such transitions do not happen at a point, but along a line, i.e. for the case of the Reissner-Nordström black hole whenever $\phi = 1/\sqrt{3}$ (ϕ being the "electric field") and for the Kerr black hole whenever $J = 0.68\,M$ (J being the angular momentum). Davies himself writes that *"The phenomenon which occurs at the critical values of α and β may be then classified as a second order phase transition. Such a transition is characterized by continuity of G and its first derivatives, but a discontinuity in the second derivatives, e.g. heat capacity".*

Such approach resembles Ehrenfest classification, which, however is not the standard definition in the modern treatments of thermodynamics [1, 55]. In fact, points where heat capacities diverge (or change sign through a zero) are essentially points where the thermodynamic potential changes the concavity and the local conditions of equilibrium fail. Such points form a locus known in the literature as the *spinodal curve*. Again, Davies underlies this fact by speaking of a *stable phase* contrary to an unstable one: *"Above the transition values the specific heat is positive, permitting isothermal equilibrium with a surrounding heat bath"*. That is, below the critical curve the heat capacity is negative and no equilibrium is possible with respect to thermal fluctuations.

In fact, a real thermodynamic treatment (using ordinary thermodynamics) in such region is therefore to be excluded, due to the fact that the system in the region of the spinodal curve is unstable to fluctuations in the values of the thermodynamical functions of state. To be more precise, in ordinary thermodynamics such curve is of great interest because it signals the presence of unstable isotherms and the need to literally "cut" them to reconstruct thermodynamic stability, following the Maxwell equal area law, as discussed in Section 1.1.6. However, after cutting the unstable region and restoring thermodynamic stability, such a region comprising the spinodal curve is excluded from the domain of thermodynamic investigation and does not play any role in the phase transitions phenomena. For example, in the Van der Waals case, the spinodal curve is given by the equation $(\partial_V P)_T = 0$, which indicates that the pressure reaches a minimum along the isothermal, and thence after such value the pressure will begin to increase as one increases the volume, a typical sign of instability. Equivalently, we can rewrite such condition as $\partial_V^2 F = 0$, where $F(T, V)$ is the Helmoltz free energy, or also as $\kappa_T \to \infty$, with κ_T being the isothermal compressibility [1]. Moreover, looking at Figure 1.2, it is easy to see that, due to the *global* condition of convexity of the potential, the Maxwell construction operates long before the region in which the *local* stability conditions are broken (see also Figure 1.4, where the points at which the global stability condition fails are indicated as 2 and 5, while the ones where the local conditions break are indicated as 3 and 4). Therefore, as we see, in the case of the VdW fluid, phase separation of the system happens long before we reach the region where a second derivative of the potential changes sign, thus preventing such types of local and ensemble inequivalent phase transitions.

On the other side, continuous phase transitions, or critical points, are encountered as *points* in the phase diagram where a line of coexistence ends (see Figure 1.3). This is the case for example of the VdW gas or of the Ising model in two dimensions [1, 55]. For instance, in the VdW case, such point is at the end of the liquid-vapor phase coexistence and is mathematically defined by adding another equation, e.g. $(\partial_V^2 P)_T = 0$ to the one defining the spinodal curve. That is, the critical point lies at the extremum of the spinodal curve. Therefore one obtains just one value for the temperature, one for the pressure and only one for the volume, i.e. only one point in the phase diagram, instead of having the full spinodal. In addition, typically a continuous phase transition is associated with a change in the internal symmetries of the system, a process which has not been motivated yet for black holes, neither at Davies points nor at critical points like the Van der Waals-like. On this regard, the only physical change which represents a true change in the black hole structure for black holes in the Einstein theory in four dimensions is the extremal limit transition, but the problem in that case is the definition of the thermodynamic “phase” which corresponds to a naked singularity. On the other hand, when General Relativity is extended to higher dimensions, changes in the topology and hence in the symmetry of black holes are possible for critical values of the thermodynamic functions, as has been clearly pointed out e.g. in [79].

Therefore, based on all the preceding heuristic observations, we conclude that Davies lines (in fact they are lines and not points) are in general better understood from the thermodynamic perspective as spinodal curves, and they represent points where the system passes from a stable (viz. thermodynamical) phase to an unstable (viz. un-thermodynamical) one. This is perfectly in agreement with the changing of the heat capacity from being positive to negative (with an infinite discontinuity in the case of the KN family of black holes). However, being the heat capacity the only diverging response function at this line, we see that this phenomenon is due to the local aspects typical of non-extensive systems, and for this reason it strongly depends on the choice of the ensemble.

In addition, we note that the interpretation given here of the diverging of only one of the response functions as describing a change from a stable phase to an unstable one perfectly matches with the Poincaré method to analyze stability by means of turning points in conjugacy diagrams (see e.g. [79]).

Finally, we remark that such interpretation also immediately and very simply explains the dependence of Davies points on the chosen ensemble. That is, for an ordinary system the critical point representing a continuous phase transition is independent of the chosen thermodynamic potential and/or representation, since all the thermodynamic response functions diverge at such point. On the contrary, Davies curves are lines of divergence of only one of the response functions, and moreover in a region where the Legendre symmetry is broken. Therefore, it is an obvious consequence that in general they are linked to the thermodynamic ensemble in which the corresponding response function is directly defined.

In the next section we will see these topics in the context of thermodynamic geometry.

5.3 Thermodynamic geometries

5.3.1 Weinhold and Ruppeiner geometries

For black holes systems with two thermodynamic degrees of freedom, we can write Weinhold metric (1.37) in terms of the mass M as follows

$$g^W = \frac{\partial^2 M}{\partial S^2}\,\mathrm{d}S \otimes \mathrm{d}S + 2\,\frac{\partial^2 M}{\partial S \partial X}\,\mathrm{d}S \otimes \mathrm{d}X + \frac{\partial^2 M}{\partial X^2}\,\mathrm{d}X \otimes \mathrm{d}X\,, \tag{5.1}$$

where X is an “extensive” variable depending on what are the parameters of the black hole, e.g. charge $X = Q$ or angular momentum $X = J$, for the Reissner-Nordström black hole and the Kerr spacetime, respectively.

First we observe that one can express Weinhold metric in a more physical fashion, using the heat capacity at constant X, the generalized adiabatic compressibility and the coefficient of expansion. In fact, the heat capacity and the adiabatic compresibility are defined as [1]

$$C_X = \left(\frac{\partial M}{\partial S}\right)_X \left(\frac{\partial^2 M}{\partial S^2}\right)^{-1} = T\left(\frac{\partial^2 M}{\partial S^2}\right)_X^{-1}, \tag{5.2}$$

$$\kappa_S = -\frac{1}{X}\left(\frac{\partial X}{\partial P}\right)_S = \frac{1}{X}\left(\frac{\partial^2 M}{\partial X^2}\right)_S^{-1}, \tag{5.3}$$

whereas the coefficient of expansion is

$$\alpha_S = \frac{1}{X}\left(\frac{\partial X}{\partial T}\right)_S = \frac{1}{X}\left(\frac{\partial^2 M}{\partial X \partial S}\right)^{-1}. \tag{5.4}$$

Hence Weinhold metric can be rewritten as

$$g^W = \frac{T}{C_X}\,\mathrm{d}S \otimes \mathrm{d}S + \frac{2}{X\alpha_S}\,\mathrm{d}S \otimes \mathrm{d}X + \frac{1}{V\kappa_S}\,\mathrm{d}X \otimes \mathrm{d}X\,. \tag{5.5}$$

Although Weinhold never introduced a real metric structure and was not interested himself to calculate the scalar curvature of such structure, nevertheless several authors have used this Riemannian geometry, especially to study Davies phase transitions for black holes. The results are quite puzzling. In fact, there are some examples in which the scalar curvature of Weinhold metric (5.5) diverges at points that are different from those where C_X is singular. Two relevant cases (which we will use here as models, like the VdW fluid for ordinary thermodynamics) are those of the Kerr black hole, for which the Weinhold scalar curvature vanishes and the Reissner-Nordström black hole, for which the thermodynamic curvature is different from zero, but does not diverge along the curve $\phi = 1/\sqrt{3}$ (see. e.g. [50, 51, 52]), which is the line found by Davies, where the heat capacity becomes singular [35].

These simple examples immediately show that Weinhold geometry cannot in general reproduce the singularities in the heat capacity, hence under this criterion it is not a satisfactory choice, since it may yield to misleading results when seeking Davies phase transitions for black holes. In any case, it might happen that for some particular systems the curvature diverges at the phase transition point, but this seems to be more a coincidence, rather than a general fact.

Let us now analyze Ruppeiner metric (1.39). Using the relation (1.38) and the definitions (5.2)-(5.4), it turns out that one can rewrite this metric as

$$g^R = \frac{1}{T}\left(\frac{T}{C_X}\, dS \otimes dS + \frac{2}{X\,\alpha_S}\, dS \otimes dX + \frac{1}{X\,\kappa_S}\, dX \otimes dX\right) . \qquad (5.6)$$

As we have argued in Section 1.2.3, it has been shown that for ordinary thermodynamic systems the scalar curvature of Ruppeiner geometry gives information about the underlying statistical model [14, 15, 16]. In particular, it has the same behavior of the correlation volume near the critical point representing a continuous phase transition and since the correlation volume diverges at critical points, then the divergences of the curvature scalar of Ruppeiner metric always contain information about the continuous phase transitions of the system.[1] Therefore, it is tempting to investigate the phase structure of black holes using Ruppeiner metric, and from this infer information about the underlying statistical model corresponding to black holes thermodynamics [16, 17].

However, it is important to consider that black holes are not ordinary thermodynamic systems, that is, their entropy is not an additive quantity and in most of the cases the fundamental equation is not even homogeneous, so that their phase structure depends on the considered ensemble or fundamental relation. Indeed, we see again from the model examples that Ruppeiner geometry cannot reproduce the full variety of phase transitions occurring in black holes. For example, on the one hand in the case of the Reissner-Nordström black hole the corresponding Ruppeiner geometry is flat, which should be interpreted as the absence of thermodynamic fluctuations. On the other hand the analysis of Davies [35] shows the presence of curves of phase transitions. Furthermore, for the Kerr black hole, the thermodynamic manifold with the Ruppeiner metric is curved, but shows no divergences at the curves found by Davies. Notwithstanding, it shows a divergence at the extremal limit (see e.g. [50, 51]).

We give here a simple interpretation of such puzzling results. Since the deter-

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[1] Note that the same can be said about the natural metric for GTD presented in Section 3.3

minant of Ruppeiner metric is, by definition, proportional to the determinant of the Hessian of the entropy, Ruppeiner thermodynamic curvature diverges at all points where the local stability conditions for the entropy fail, i.e. all points where thermodynamic instabilities develop in the microcanonical ensemble. Moreover, it is clear from expression (5.6) that if C_X diverges, then not necessarily the determinant is zero, i.e. not necessarily the scalar curvature diverges. It is therefore interesting to note that Ruppeiner thermodynamic curvature diverges in a number of cases on Davies line for black holes, but not in all the cases. This further supports the interpretation of Davies lines as curves where a new type of phase transition is occurring, a type which is typical of systems with long-range interactions and that can possibly occur only in one ensemble. Therefore, according to this interpretation given here, the different behavior of Ruppeiner thermodynamic curvature might be depending on whether Davies phase transitions are visible or not in the microcanonical ensemble where Ruppeiner geometry is defined [49].

5.3.2 The thermodynamic metric g^{II}

Another argument that supports our interpretation of Davies phase transitions in black holes comes from a different choice of the thermodynamic metric. In the context of GTD, it has been argued that there is a metric which is dubbed to reproduce Davies phase transitions for black holes [25]. The expression for this metric in the equilibrium space in general coordinates is

$$g^{II} = \left(E^c \frac{\partial \Phi}{\partial E^c}\right) \left(\eta_{ab}\, \delta^{bf} \frac{\partial^2 \Phi}{\partial E^f \partial E^d}\, dE^a \otimes dE^d\right), \tag{5.7}$$

which corresponds to the choice (3.4) discussed in Chapter 3.

Due to the fact that this geometric structure is not symmetric with respect to change in the representation (c.f. Chapter 3), we now write its expression in the M representation for black holes, which reads

$$g^{II}_M = \left(S\,\frac{\partial M}{\partial S} + X\,\frac{\partial M}{\partial X}\right) \left(-\frac{\partial^2 M}{\partial S^2}\, dS \otimes dS + \frac{\partial^2 M}{\partial X^2}\, dX \otimes dX\right). \tag{5.8}$$

Using (5.8) and the equations of state $\partial_S M = T$, $\partial_X M = Y$, with Y the conjugated variable corresponding to X (e.g. $X = J$ and $Y = \Omega$ for the Kerr black hole), we can rewrite this metric in terms of the heat capacity at constant X and the isentropic compressibility κ_S, obtaining

$$g^{II}_M = (TS + XY) \left(-\frac{T}{C_X}\, dS \otimes dS + \frac{1}{X\kappa_S}\, dX \otimes dX\right). \tag{5.9}$$

From this expression, we immediately notice that, being the determinant of such metric proportional to the diagonal elements of the Hessian of the potential M, i.e. to the inverse of the heat capacity at constant extensive variable and to the inverse of the isentropic compressibility, it is obvious that the determinant vanishes when (one of) these response functions diverge. Therefore at such points the scalar curvature of this metric always diverges.

Thus, without the need of any complicated calculations, we have shown (somehow heuristically but completely generally) that the metric (5.8) always diverges along Davies curves for black holes phase transitions. Moreover, it can be easily verified that the metric (5.8) does not diverge at the critical point for a VdW system (see equation (4.22)), an explicit example of the fact that the two diverging phenomena happening at a continuous phase transition or at Davies curves have indeed a different nature.

5.4 Conclusions

Many authors have investigated phase transitions in black holes. In particular, it has been suggested that the use of thermodynamic geometry in this field can give important insights, overcoming in part the lack of a microscopic description.

In this work, we have speculated that there exist different kinds of phase transitions in black holes, corresponding to different thermodynamical and geometrical definitions. In particular, we have argued that Davies curves of phase transitions are a peculiar effect that emerges in systems with long-range interactions. In particular, we can explain from this perspective why they depend on the chosen ensemble and why the usual tools of thermodynamic geometry that apply to ordinary systems are expected to fail when applied to Davies phase transitions. To make clear our statements, we have provided examples of black holes for which the thermodynamic curvatures derived from the Hessian of the internal energy and of the entropy fail to reproduce the correct phase structure (the Reissner-Nordström and Kerr black holes) and we have also given general arguments about the reasons why one should include different geometric structures to represent such transitions. Finally, we presented a geometric structure from GTD that has always been found in agreement with Davies phase transitions structure and we have shown why from our perspective this geometry is the correct one to account for these new thermodynamic features characterizing not only black holes but in general all systems with long-range interactions.

In this chapter we hope to have clarified the description of the different types of possible phase transitions occurring in black holes, getting insights from both the thermodynamical and thermodynamic geometric points of view.

In the next chapter we will further investigate Davies phase transitions using the thermodynamic geometry (5.7) in the model examples of the Reissner-Nordström and Kerr black holes in any spacetime dimensions and then also in the case of the Myers-Perry black holes in five dimensions for different values of the angular momenta, which will give us the chance to study a relatively simple black hole system with three thermodynamic degrees of freedom.

6 Reissner-Nordström, Kerr and Myers-Perry black holes

In this chapter we study the thermodynamics and Geometrothermodynamics of different black hole configurations in more than four spacetime dimensions. In the first two sections we find the conditions under which Davies phase transitions occur in higher-dimensional static Reissner-Nordström and stationary Kerr black holes. Our results indicate that the equilibrium manifold of all these black hole configurations is in general curved and that curvature singularities appear exactly at those curves where Davies phase transitions occur. Then in the third section we consider the Myers-Perry black holes in five dimensions for three different cases, depending on the values of the angular momenta. Again, we find a non-trivial thermodynamic structure in all cases, which is fully reproduced by the analysis performed with the techniques of Geometrothermodynamics. Moreover, we observe that in the cases when only one angular momentum is present or the two angular momenta are fixed to be equal, i.e. when the thermodynamic system depends on two degrees of freedom only, there is a complete agreement between the divergences of the generalized susceptibilities and the singularities of the equilibrium manifold, whereas when the two angular momenta are fully independent, that is, when the thermodynamic system is three dimensional, additional singularities in the curvature appear. However, we prove that such singularities are due to the changing from a stable phase to an unstable one.

6.1 Reissner-Nordström black hole in any dimension

The solution for the charged black hole with no angular momentum (Reissner-Nordström black hole) can be extended to any dimension. The corresponding line element in d spacetime dimensions reads [51]

$$ds^2 = -V\,\mathrm{d}t^2 + V^{-1}\,\mathrm{d}r^2 + r^2\,\mathrm{d}\Omega^2_{(d-2)}\,, \tag{6.1}$$

where $d\Omega^2_{(d-2)}$ is the line element on the $(d-2)$-dimensional unit sphere, $\Omega_{(d-2)} = 2\pi^{\frac{d-1}{2}}/\Gamma(\frac{d-1}{2})$, and V is defined as

$$V = 1 - \frac{16\pi G M}{(d-2)\Omega_{(d-2)}} \frac{1}{r^{d-3}} + \frac{8\pi G}{(d-2)(d-3)} \frac{Q^2}{r^{2(d-3)}} \,. \tag{6.2}$$

Solving the equation $V = 0$, one can find the event horizon in any dimensions and thus derive the area and the corresponding entropy.

6.1.1 Thermodynamics

The fundamental equation for the entropy reads [51]

$$S(M,Q) = \left(M + M\sqrt{1 - \frac{d-2}{2(d-3)}\frac{Q^2}{M^2}} \right)^{\frac{d-2}{d-3}} \,. \tag{6.3}$$

Inverting (6.3), one obtains the mass function

$$M(S,Q) = \frac{S^{\frac{d-3}{d-2}}}{2} + \frac{d-2}{4(d-3)}\frac{Q^2}{S^{\frac{d-3}{d-2}}} \,, \tag{6.4}$$

that satisfies the first law of thermodynamics $dM = TdS + \phi dQ$, where ϕ is usually interpreted as an electric potential. Then, the temperature and the electric potential are

$$T(S,Q) = \frac{2(d-3)\, S^{\frac{2(d-3)}{d-2}} - (d-2)\, Q^2}{4\,(d-2)\, S^{\frac{2d-5}{d-2}}} \;, \quad \phi(S,Q) = \frac{(d-2)\, Q}{2\,(d-3)\, S^{\frac{d-2}{d-3}}} \,. \tag{6.5}$$

In the extremal limit,

$$\left.\frac{Q^2}{M^2}\right|_{\text{extremal}} = \frac{2(d-3)}{d-2} \quad \text{i.e.} \quad \left.\frac{Q^2}{S^{\frac{2(d-3)}{d-2}}}\right|_{\text{extremal}} = \frac{2(d-3)}{d-2} \,, \tag{6.6}$$

the temperature of the black hole vanishes and the electric potential is constant. Incidentally, in the extremal case, one gets $M^2 = \phi^2 Q^2$. Note that this limit exists in any dimension. We will see in the next section that the situation is different for the Kerr black hole, for which there is an extremal limit only up to dimension five [51].

We now calculate the response functions (5.2)-(5.4) corresponding to the potential M for the RN black hole to see what are the points where Davies phase transitions take place. The heat capacity at constant Q reads

$$C_Q = \frac{M_S}{M_{SS}} = -\frac{(d-2)S\left((d-2)\,Q^2 - 2(d-3)\,S^{\frac{2(d-3)}{d-2}}\right)}{(d-2)(2d-5)\,Q^2 - 2(d-3)\,S^{\frac{2(d-3)}{d-2}}}\,, \tag{6.7}$$

where $M_S = \partial M/\partial S$, etc. The other two response functions that can be directly defined in this ensemble are the isentropic compressibility

$$\kappa_S = \frac{M_{QQ}^{-1}}{Q} = \frac{2\,(d-3)\,S^{\frac{d-3}{d-2}}}{(d-2)\,Q}\,, \tag{6.8}$$

and the isentropic expansion

$$\alpha_S = \frac{M_{SQ}^{-1}}{Q} = -\frac{2\,S^{\frac{2d-5}{d-2}}}{Q^2}\,. \tag{6.9}$$

We note that the only possible divergence is that of the heat capacity, which takes place when the denominator of (6.7) is zero, i.e. whenever

$$\left.\frac{Q^2}{S^{\frac{2(d-3)}{d-2}}}\right|_{\text{phase transition}} = \frac{2(d-3)}{(2d-5)(d-2)}\,. \tag{6.10}$$

One can prove that this value is in the black hole region, i.e. that the condition

$$\frac{Q^2}{M^2} \leq \frac{2(d-3)}{d-2} \tag{6.11}$$

is satisfied. By using Eq. (6.3), we can rewrite Eq. (6.10) to be

$$\frac{Q^2}{M^2} = \frac{4d^2 - 22d + 30}{(d-2)^3}\,, \tag{6.12}$$

which is easily proven to be inside the black hole region for any value of $d > 3$.

It is also immediate to note in this model how Davies phase transitions depend on the chosen ensemble. For instance, if we use the ensemble corresponding to the "enthalpy", $H(S,\phi) = M - \phi Q$, we get

$$H(S,\phi) = -S^{\frac{d-3}{d-2}}\,\frac{2\phi^2\,(d-3) - d + 2}{2\,(d-2)}\,, \tag{6.13}$$

from which we can calculate

$$C_\phi = \frac{H_S}{H_{SS}} = -(d-2)\,S\,. \tag{6.14}$$

We observe that the heat capacity at constant ϕ has no singularities. Thus we expect no phase transitions from the thermodynamic analysis in this ensemble.

6.1.2 Geometrothermodynamics

Given the fundamental Eqs. (6.3) and (6.4) and the general metric (5.7), we can calculate the particular metric and the scalar curvature for the RN black hole both in the entropy and in the energy representations. The metric with $\Phi = S$ and $E^a = \{M, Q\}$ reads

$$\begin{aligned} g_S^{II} = &- \frac{\left[\frac{1}{2}M(2+\mathcal{E}(M,Q))\right]^{\frac{2(d-2)}{d-3}}}{\mathcal{D}(M,Q)} \Bigg\{ 4(d-2)^2(d-3) \times \\ &\times \Bigg[\left[(d-2)^2Q^2 - 4(d-3)M^2\right]\mathcal{E}(M,Q) + \\ &+ 2(d-1)(d-2)Q^2 - 8(d-3)M^2 \Bigg] \mathrm{d}M \otimes \mathrm{d}M + \\ &+ 2(d-2)^3 \Bigg[\left[(d-2)Q^2 - 2(d-3)^2M^2\right]\mathcal{E}(M,Q) - 4(d-3)^2M^2 \Bigg] \mathrm{d}J \otimes \mathrm{d}J \Bigg\} , \end{aligned} \tag{6.15}$$

where

$$\mathcal{D}(M,Q) = M^2(d-3)^4\Big((d-2)Q^2 - 2(d-3)M^2\Big)\mathcal{E}(M,Q)\Big(2+\mathcal{E}(M,Q)\Big)^2 \tag{6.16}$$

and

$$\mathcal{E}(M,Q) = \sqrt{4 - 2\frac{(d-2)}{d-3}\frac{Q^2}{M^2}} \, . \tag{6.17}$$

The scalar curvature is

$$R_S^{II} = \frac{\mathcal{N}_1(M,Q)}{\mathcal{A}_1(M,Q)^2\mathcal{B}_1(M,Q)^2} \, , \tag{6.18}$$

where

$$\begin{aligned} \mathcal{A}_1(M,Q) = &\Big[d^2Q^2 - 4d(M^2+Q^2) + 12M^2 + 4Q^2\Big]\mathcal{E}(M,Q) + \\ &+ 2d^2Q^2 - 2d(4M^2+3Q^2) + 24M^2 + 4Q^2 \end{aligned} \tag{6.19}$$

and

$$\mathcal{B}_1(M,Q) = \Big[-2d^2M^2 + d(12M^2+Q^2) - 18M^2 - 2Q^2\Big]\mathcal{E}(M,Q) - 4(d-3)^2M^2 \, . \tag{6.20}$$

Using a software for algebraic manipulations, we find that the only real root of the denominator of the curvature scalar (6.18) is given by

$$\left.\frac{Q^2}{S^{\frac{2(d-3)}{d-2}}}\right|_{\text{singularity}} = \frac{2(d-3)}{(2d-5)(d-2)}\,. \tag{6.21}$$

Furthermore, it can be proven that $\mathcal{N}_1(M,Q)$ is never zero where $\mathcal{A}_1(M,Q)$ and $\mathcal{B}_1(M,Q)$ are. From Eqs. (6.10) and (6.21), we can conclude that in fact the curvature singularities are located exactly at those points where phase transitions occur.

It is interesting to note that, although the thermodynamic metric (5.7) is not symmetric with respect to change in representation (see Chapter 3), nevertheless for this model we get the same results for the divergences of the scalar curvature using the thermodynamic potential $\Phi = M$ with independent variables $E^a = \{S,Q\}$, satisfying the fundamental equation (6.4). In fact, from the general thermodynamic metric (5.7), we obtain the metric

$$\begin{aligned} g^{II}_M =& \frac{1}{16(d-3)(d-2)^3S^2}\Bigg\{4(d-3)^3S^{\frac{2(d-3)}{d-2}} + \\ & - (d-2)^2Q^2\left[(d-1)(2d-5)Q^2S^{-\frac{2(d-3)}{d-2}} + 4(d-3)(d-4)\right]\Bigg\}\,\mathrm{d}S\otimes\mathrm{d}S + \\ & + \frac{1}{8(d-3)^2}\left\{(d-1)(d-2)Q^2S^{-\frac{2(d-3)}{d-2}} + 2(d-3)^2\right\}\mathrm{d}Q\otimes\mathrm{d}Q\,, \end{aligned} \tag{6.22}$$

from which we compute the curvature scalar

$$R^{II}_M = \frac{\mathcal{N}_2(S,Q)}{\mathcal{A}_2(S,Q)^4\mathcal{B}_2(S,Q)^3}\,, \tag{6.23}$$

where

$$\mathcal{A}_2(S,Q) = 2(d-3)^2S^{\frac{2(d-3)}{d-2}} + (d-1)(d-2)Q^2 \tag{6.24}$$

and

$$\begin{aligned} \mathcal{B}_2(S,Q) =& -4(d-3)^3S^{\frac{4(d-3)}{d-2}} + 4(d-2)^2(d-3)(d-4)Q^2S^{\frac{2(d-3)}{d-2}} + \\ & + (d-1)(d-2)^2(2d-5)Q^4\,. \end{aligned} \tag{6.25}$$

One can verify that the only points of divergence of R^{II}_M are given by the equation (6.21) which coincides with the condition for the phase transitions (6.10). Once more we see a concrete relationship between the curvature of the metric (5.7) and the phase structure of black holes defined by Davies.

To consider the behavior of the GTD analysis with respect to different ensembles, we turn now to the metric (5.7) and write it with the fundamental equation (6.13) so that $\Phi = H$ and $E^a = \{S, \phi\}$. The resulting metric reads

$$\begin{aligned} g_H^{II} &= \frac{(d-3)^2(6\phi^2 d - 14\phi^2 - d + 2)}{4(d-2)^3} \times \\ &\quad \times \left\{ \frac{2\phi^2 d - 6\phi^2 - d + 2}{S^{\frac{2}{d-2}}(d-2)^2} \mathrm{d}S \otimes \mathrm{d}S + 4S^{2\frac{d-3}{d-2}} \mathrm{d}\phi \otimes \mathrm{d}\phi \right\}. \end{aligned} \tag{6.26}$$

Consequently, the scalar curvature reads

$$R_H^{II} = \frac{\mathcal{N}_3(S,\phi)}{\mathcal{A}_3(S,\phi)^3 \mathcal{B}_3(S,\phi)^2}, \tag{6.27}$$

where

$$\mathcal{A}_3(S,\phi) = 6\phi^2 d - 14\phi^2 - d + 2, \tag{6.28}$$

i.e. the conformal factor in the metric (6.26) and

$$\mathcal{B}_3(S,\phi) = 2\phi^2(d-3) - d + 2. \tag{6.29}$$

Hence the first factor in the denominator, being the conformal factor in the metric (6.26), is equal to $SH_S + \phi H_\phi$, which, in turn, according to the generalized Euler identity, is proportional to H. Thus, the first term in the denominator of the scalar curvature is zero if and only if the thermodynamic potential vanishes, $H = 0$. Considering the equation of state $\phi = (\partial M/\partial Q)_S$, the second factor turns out to be zero for $S^2 = [Q^2(d-2)/2(d-3)]^{(d-2)/(d-3)}$, which corresponds exactly to the extremal black hole limit (6.6) with zero temperature. This is due to the fact that in this case the metric g_H^{II} becomes degenerate in the extremal limit. Thus, the only singularities arise from the limits of applicability of the thermodynamic approach to black holes, where we also expect the GTD approach to break down. We conclude that the scalar curvature in this ensemble has no true singularities, signaling the absence of phase transitions, in agreement with the results obtained from the study of the corresponding heat capacity (6.14).

As a final remark, we point out that the Hessian metric (5.1) with $X = Q$ (Weinhold's metric) for this case is curved, but the analysis of its scalar curvature gives no special information about the phase transition points. Moreover, for $\Phi = S$ (Ruppeiner's metric) the equilibrium manifold is flat [51].

6.2 Kerr black hole in any dimension

The solution for the Kerr black hole in arbitrary dimension corresponds to taking a Myers-Perry black hole with only one angular momentum different from zero. The line element is [83]

$$\begin{aligned} ds^2 = & -\mathrm{d}t^2 + \frac{\mu}{r^{d-5}\rho^2}\left(\mathrm{d}t + a\sin^2\theta\,\mathrm{d}\varphi\right)^2 + \frac{\rho^2}{\Delta}\,\mathrm{d}r^2 + \rho^2\,\mathrm{d}\theta^2 + (r^2+a^2)\sin^2\theta\,\mathrm{d}\varphi^2 \\ & + r^2\cos^2\theta\,\mathrm{d}\Omega^2_{(d-4)}\,, \end{aligned} \tag{6.30}$$

where

$$\rho^2 = r^2 + a^2\cos^2\theta\,, \qquad \Delta = r^2 + a^2 - \frac{\mu}{r^{d-5}} \tag{6.31}$$

and the physical mass M and angular momentum J are related to μ and a by

$$M = \frac{(d-2)\partial\Omega_{d-2}}{16\pi G}\,\mu\,, \qquad J = \frac{2}{d-2}\,M\,a\,, \tag{6.32}$$

where $\partial\Omega_{d-2}$ is the area of the $(d-2)$-dimensional unit sphere.

6.2.1 Thermodynamics

Following the notation of [51], the fundamental equation for the mass is

$$M(S,J) = \frac{d-2}{4}S^{\frac{d-3}{d-2}}\left(1+\frac{4J^2}{S^2}\right)^{\frac{1}{d-2}} \tag{6.33}$$

In the general case, it is not possible to invert to this equation, therefore we will work with the mass representation only. From (6.33) it follows that the temperature $T = (\partial M/\partial S)_J$ and the angular velocity at the horizon $\Omega = (\partial M/\partial J)_S$ are

$$T(S,J) = \frac{(d-3)\left(1+4\frac{d-5}{d-3}\frac{J^2}{S^2}\right)}{4S^{\frac{1}{d-2}}\left(1+4\frac{J^2}{S^2}\right)^{\frac{d-3}{d-2}}}\,, \quad \Omega(S,J) = \frac{2J}{S^{\frac{d-1}{d-2}}\left(1+4\frac{J^2}{S^2}\right)^{\frac{d-3}{d-2}}}\,, \tag{6.34}$$

from which it can be easily seen that an extremal limit for the Kerr black hole only exists only for $d \leq 5$. When $d = 4$ the limit is the usual Kerr bound $J/M^2 = 1$ and for $d = 5$ it is the Myers-Perry black hole bound $J^2/M^3 = 16/27$ (see e.g. [51]).

To investigate Davies phase transition structure of this black hole, we calculate the heat capacity at constant angular momentum J, to obtain

$$C_J = \frac{M_J}{M_{JJ}} = -\frac{(d-2)S(S^2+4J^2)\left[(d-3)S^2+4(d-5)J^2\right]}{48(d-5)J^4-24S^2J^2+(d-3)S^4} \tag{6.35}$$

Moreover, in this ensemble we can also define the isentropic compressibility

$$\kappa_S = \frac{M_{JJ}^{-1}}{J} = -\frac{S^{-\frac{d-5}{d-2}}(d-2)\left(S^2+4J^2\right)^{\frac{2d-5}{d-2}}}{2J\left[4(d-4)J^2-(d-2)S^2\right]} \tag{6.36}$$

and the isentropic expansion

$$\alpha_S = \frac{M_{SJ}^{-1}}{J} = \frac{S^{\frac{3}{d-2}}(d-2)\left(S^2+4J^2\right)^{\frac{2d-5}{d-2}}}{2J^2\left[4(d-5)J^2-(d-1)S^2\right]}\,. \tag{6.37}$$

We note that in this case there can be divergences from all of these quantities. First of all let us focus on the heat capacity. The divergences of the heat capacity are situated at the points which satisfy the relation

$$\left.\frac{J^2}{S^2}\right|_{\text{phase transition}} = \frac{d-3}{4\left(3+\sqrt{-3d^2+24d-36}\right)}\,. \tag{6.38}$$

The r.h.s. of eq. (6.38) is real only if $d = 4, 5, 6$, so that we can have a divergence in the heat capacity (a phase transition *à la Davies*) only for $d = 4, 5, 6$. Furthermore, investigating the other two response functions, we see that they diverge respectively when

$$\left.\frac{J^2}{S^2}\right|_{\text{phase transition}} = \frac{d-2}{4(d-4)}\,, \tag{6.39}$$

and

$$\left.\frac{J^2}{S^2}\right|_{\text{phase transition}} = \frac{d-1}{4(d-5)}\,, \tag{6.40}$$

which exist in any dimension $d > 4$ and $d > 5$, respectively.

For $d = 4, 5$, we have to check that the singularities of the heat capacity and the compressibility are in the black hole region. Indeed it is easily checked that they are. For example, for $d = 4$, we can obtain S from Eq. (6.38) and evalute J/M^2 at this critical value for S. Since the result is $J/M^2|_{S critical} = \sqrt{3+2\sqrt{3}}/(2+\sqrt{3})$, which is less than the extremal limit $J/M^2 = 1$, we can affirm that these points belong to the black hole region. Repeating the same steps for $d = 5$ and for the critical value for S from eq. (6.39), one can check that indeed all the singularities of the response functions are in the black hole region.

6.2.2 Geometrothermodynamics

Given the fundamental equation (6.33) and the general metric (5.7), we can calculate the particular metric and the thermodynamic curvature for the Kerr black hole only in the mass representation, which reads

$$\begin{aligned} g_M^{II} = & \frac{(d-3)}{16(d-2)\left(S^2+4J^2\right)^{\frac{2(d-3)}{d-2}}}\left\{\frac{48(d-5)J^4-24S^2J^2+(d-3)S^4}{S^{\frac{6}{d-2}}}\,\mathrm{d}S\otimes\mathrm{d}S\right. \\ & \left. -\,8\,S^{\frac{2(d-5)}{d-2}}\left[4(d-4)J^2-(d-2)S^2\right]\mathrm{d}J\otimes\mathrm{d}J\right\}. \end{aligned} \tag{6.41}$$

The scalar curvature can then be calculated. It turns out to be

$$R_M^{II} = \frac{\mathcal{N}_4(S,J)}{(d-3)\mathcal{A}_4(S,J)^2\mathcal{B}_4(S,J)^2}\,, \tag{6.42}$$

where

$$\mathcal{A}_4(S,J) = 48(d-5)J^4-24J^2S^2+(d-3)S^4 \tag{6.43}$$

and

$$\mathcal{B}_4(S,J) = 4(d-4)J^2-(d-2)S^2\,. \tag{6.44}$$

It is immediate to see that $\mathcal{A}_4(S,J)$ is exactly the denominator of the heat capacity (6.35) and $\mathcal{B}_4(S,J)$ is the denominator of the compressibility (6.36). Since both of them are in the denominator of R_M^{II} and since the numerator does not vanish at the points of singularity, we conclude that again we have a concrete relationship between the singularities of the curvature of the metric (5.7) and Davies phase transition structure.

6.3 Myers-Perry black hole in five dimensions

The Kerr black hole can be generalized to the case of arbitrary spacetime dimensions and arbitrary number of spins. It turns out that, provided d is the number of spacetime dimensions, then the maximum number of possible independent spins is $(d-1)/2$ if d is odd and $(d-2)/2$ if d is even [84]. Such general configurations are called Myers-Perry black holes. They deserve a special interest because they are the natural generalization of the well-known Kerr black hole to higher number of spins and because they are shown to coexist with the Emparan-Reall black ring solution [78] for some values of the parameters, thus providing the first explicit example of a violation in dimension higher than four of the uniqueness theorem (see e.g.

[85] for more details). The line element of the Myers-Perry black hole with an arbitrary number of independent angular momenta in Boyer-Lindquist coordinates for $d = 2\,n + 1$ (i.e. odd d) reads [84]

$$ds^2 = -\,\mathrm{d}t^2 + \frac{\mu\, r^2}{\Pi\, F}\left(\mathrm{d}t + \sum_{i=1}^{n} a_i\, \mu_i^2\, \mathrm{d}\phi_i\right)^2 + \frac{\Pi\, F}{\Pi - \mu r^2}\,\mathrm{d}r^2 + \\ + \sum_{i=1}^{n}(r^2 + a_i^2)\left(\mathrm{d}\mu_i^2 + \mu_i^2\,\mathrm{d}\phi_i{}^2\right) , \qquad (6.45)$$

with

$$F \;\equiv\; 1 - \sum_{i=1}^{n} \frac{a_i^2\,\mu_i^2}{r^2 + a_i^2}\,, \qquad \Pi \equiv \prod_{i=1}^{n}(r^2 + a_i^2)\,, \qquad (6.46)$$

and

$$\mu \equiv \frac{16\,\pi\, G\, M}{(d-2)\,\Omega_{(d-2)}}\,, \qquad a_i \equiv \frac{(d-2)}{2}\,\frac{J_i}{M}\,, \qquad (6.47)$$

where $\Omega_{(d-2)} = \frac{2\,\pi^n}{\Gamma(n)}$, M is the mass of the black hole, $J_i = J_1, \ldots, J_n$ are the $(d-1)/2$ independent angular momenta and the constraint $\sum_{i=1}^{n}\mu_i^2 = 1$ holds. Solving the equation $g^{rr} = 1/g_{rr} = 0$, one finds the radius of the event horizon (in any dimensions) and thus derives the area and the corresponding entropy, using Bekenstein's area law [51].

In particular, here we are interested in the five dimensional case, i.e. when $d = 5$. Myers-Perry black holes in five dimensions can have up to two independent angular momenta and the general equation for the area reads [51]

$$A = \frac{2\pi^2}{r_+}(r_+^2 + a_1^2)(r_+^2 + a_2^2)\,, \qquad (6.48)$$

where r_+ is the radius of the event horizon. From the above expression the entropy can be calculated, being

$$S = \frac{k_B\, A}{4\, G} = \frac{1}{r_+}\,(r_+^2 + a_1^2)(r_+^2 + a_2^2)\,, \qquad (6.49)$$

where we choose k_B and G such that S simplifies as in the second equality in (6.49).

Since it is rather complicated to calculate explicitly the above expression for the entropy, we will use the M representation. This is possible since the mass can be written in terms of S, J_1 and J_2 as [51]

$$M(S,J_1,J_2) = \frac{3}{4}\,S^{\frac{2}{3}}\left(1+4\frac{J_1^2}{S^2}\right)^{\frac{1}{3}}\left(1+4\frac{J_2^2}{S^2}\right)^{\frac{1}{3}} . \tag{6.50}$$

Eq. (6.50) thus represents the fundamental equation for the Myers-Perry black hole in five dimensions as a thermodynamic system. Starting from Eq. (6.50), we can analyze both the thermodynamic properties and their geometrothermodynamic counterparts. We will split the work in order to consider the three most interesting cases, i.e. when one of the two angular momenta is zero, when they are both non-zero but equal and finally when they are both non-zero and different among each other.

6.3.1 The case $J_2 = 0$

If either $J_1 = 0$ or $J_2 = 0$, we obtain the Kerr black hole in 5 dimensions, which has been analyzed in Section 6.2 (see the calculations and comments there for this case).

Moreover, since the thermodynamics of black holes can depend on the chosen ensemble (see e.g. [40] and [41]), we now proceed to calculate the Gibbsian response functions for this case, which can possibly give new information about the phase structure. Using the relations between thermodynamic derivatives (see [1]), we find out that the expressions for such response functions in the coordinates (S, J_1) used here are

$$C_{\Omega_1} = -\frac{S(3S^2-4J_1^2)}{S^2+4J_1^2}\,, \quad \kappa_T = -\frac{S^2-12J_1^2}{2J_1(S^2+4J_1^2)^{\frac{1}{3}}}\,, \quad \alpha_{\Omega_1} = -\frac{8\,S}{(S^2+4J_1^2)^{\frac{1}{3}}}\,. \tag{6.51}$$

It is immediate to see that C_{Ω_1} never diverges and it vanishes exactly at the same points where κ_S diverges. On the other side, κ_T is never divergent and it vanishes exactly where C_{J_1} diverges, while α_{Ω_1} is always finite. It follows that the Gibbsian response functions do not add any information to the knowledge of the phase structure of this configuration, as they change sign exactly at the points that we have already analyzed. Therefore, we conclude that the divergences of the scalar curvature of the metric (5.7) match exactly the points of Davies phase transitions.

In the next section we extend the analysis presented here and in Section 6.2 and show that when one adds a second spin there is still a concrete relation between the geometric description performed with (5.7) and the thermodynamic properties. To do so, we first focus on the special case of equation (6.50) in which $J_1 = J_2 = J$, and afterwards we will consider the completely general case, i.e. with J_1 and J_2 both different from zero and from each other. In that case, we will get a 3-dimensional thermodynamic manifold labelled by $(E^1 = S, E^2 = J_1, E^3 = J_2)$ and hence we will consider the 3-dimensional version of the metric (5.7).

6.3.2 The case $J_1 = J_2 \equiv J$

Another special case in Eq. (6.50) which is of interest is the case in which the two angular momenta are fixed to be equal, i.e. $J_1 = J_2 \equiv J$. This is interesting from the mathematical and physical point of view since it is the only case in which the angular momenta are both different from zero and at the same time the thermodynamic manifold is 2-dimensional. In fact, the mass fundamental equation (6.50) in this case is given by

$$M(S,J) = \frac{3}{4}\,S^{\frac{2}{3}}\left(1 + 4\frac{J^2}{S^2}\right)^{\frac{2}{3}} , \tag{6.52}$$

and the response functions can then be accordingly calculated, to give

$$\begin{gathered} C_J = -\frac{3S(S^4 - 16J^4)}{S^4 - 32J^2S^2 - 80J^4} , \quad \kappa_S = \frac{3S^{\frac{2}{3}}(S^2 + 4J^2)^{\frac{4}{3}}}{4J(3S^2 + 4J^2)} , \\ \alpha_S = -\frac{3}{16}\,\frac{S^{\frac{5}{3}}(S^2 + 4J^2)^{\frac{4}{3}}}{J^2(S^2 + 2J^2)} . \end{gathered} \tag{6.53}$$

From (6.53), it follows that in this case κ_S and α_S do not show any singularity, while C_J diverges at the roots of the denominator $\mathcal{D}_C = S^4 - 32J^2S^2 - 80J^4$. We also observe that the temperature of this black hole is given by

$$T \equiv \left(\frac{\partial M}{\partial S}\right)_J = \frac{S^2 - 4J^2}{2\,S^{5/3}(S^2 + 4J^2)^{1/3}} , \tag{6.54}$$

therefore the extremal limit $T = 0$ is reached when $\frac{J^2}{S^2} = \frac{1}{4}$.

Solving the Eq. $\mathcal{D}_C = 0$, we find that the singularities of the heat capacity are situated at a value S_{critical} for the entropy such that

$$\left.\frac{J^2}{S^2}\right|_{S=S_{\text{critical}}} = \frac{\sqrt{21} - 4}{20} , \tag{6.55}$$

which is less than the extremal limit. Therefore Davies points of phase transition belong to the black hole region and we shall investigate them.

It is convenient also in this case to write the full set of thermodynamic response functions, including the Gibbsian ones. Again, making use of the relations between thermodynamic derivatives, we find out that they read

$$C_\Omega = -\frac{S\,(S^2-4J^2)(3S^2+4J^2)}{(S^2+4J^2)^2}\,, \quad \kappa_T = -\frac{S^{2/3}}{4\,J}\frac{\mathcal{D}_C}{(S^2+4J^2)^{5/3}}\,,$$
$$\alpha_\Omega = 8\,S^{5/3}\,\frac{S^2+2J^2}{(S^2+4J^2)^{5/3}}\,. \tag{6.56}$$

In this case we observe that the only divergence of the response functions in (6.53), i.e. the divergence of C_J, is again controlled by the vanishing of κ_T. Furthermore, both C_J and C_Ω vanish at the extremal limit, but this does not correspond to any divergence of κ_S, hence we expect the curvature of the thermodynamic metric to diverge only at the points where $\mathcal{D}_C = 0$.

From the point of view of Geometrothermodynamics, given the fundamental equation (6.52) and the general metric (5.7), we can calculate the particular metric and the scalar curvature for the equilibrium manifold of the MP black hole with two equal angular momenta, both in the mass and in the entropy representations.

The metric in the M representation reads

$$g^{II}_M = \frac{1}{S^{4/3}(S^2+4J^2)^{2/3}}\left\{\frac{\mathcal{D}_C}{12\,S^2}\,\mathrm{d}S\otimes\mathrm{d}S + \frac{2(3S^2+4J^2)}{3}\,\mathrm{d}J\otimes\mathrm{d}J\right\}\,, \tag{6.57}$$

therefore its scalar curvature is

$$R_M = \frac{24S^{10/3}(S^2+4J^2)^{2/3}(5\,S^6+48\,J^2\,S^4-368\,J^4\,S^2-896\,J^6)}{\mathcal{D}_C^2(3S^2+4J^2)^2}\,. \tag{6.58}$$

The numerator is a not very illuminating function that never vanishes when the denominator is zero and $\mathcal{D}_C$ is exactly the denominator of the heat capacity C_J. Therefore, the singularities of R_M correspond exactly to those of C_J (resp. to the vanishing of κ_T). We remark that the factor $3S^2+4J^2$ in the denominator of R_M, though being always different from zero (thus not indicating any phase transition in this case), is exactly the denominator of the compressibility κ_S (resp. a factor in the numerator of C_Ω).

To continue with the analysis, in Chapter 3 it was presented a general relation (see Eq. (3.18) therein) to express g^{II} with $\Phi = S$ (i.e. in the S representation) in the coordinates of the M representation (i.e. $\{E^a\} = (S, J)$). Such relation in the present case reads

$$g_S^{II} = \frac{M - J\,\Omega}{T^3}\Bigg[T\,M_{SS}\,\mathrm{d}S \otimes \mathrm{d}S + 2\,\Omega\,M_{SS}\,\mathrm{d}S \otimes \mathrm{d}J + \\ + (2\,\Omega\,M_{SJ} - T\,M_{JJ})\,\mathrm{d}J \otimes \mathrm{d}J\Bigg]\,, \tag{6.59}$$

where $T \equiv (\partial M/\partial S)_J$ is the temperature, $\Omega \equiv (\partial M/\partial J)_S$ is the angular velocity at the horizon and $M_{E^aE^b} \equiv \frac{\partial^2 M}{\partial E^a \partial E^b}$, for $E^i = S, J$. Using Eq. (6.59) and Eq. (6.52) for the mass in terms of S and J, we can calculate the expression for metric g_S^{II} in the coordinates (S, J), which reads

$$\begin{aligned} g_S^{II} = & \frac{1}{3(S^2+4J^2)(S+2J)^2(S-2J)^2}\Bigg\{-\frac{3S^2-4J^2}{2}\mathcal{D}_C\,\mathrm{d}S\otimes\mathrm{d}S + \\ & + 8\,S\,J\,\frac{(3S^2-4J^2)}{(S+2J)(S-2J)}\,\mathcal{D}_C\,\mathrm{d}S\otimes\mathrm{d}J + \\ & - 4\,S^2\,\frac{9\,S^6+156\,S^4\,J^2+112\,S^2\,J^4-448\,J^6}{(S+2J)(S-2J)}\,\mathrm{d}J\otimes\mathrm{d}J\Bigg\}\,. \end{aligned} \tag{6.60}$$

Consequently, the scalar curvature is

$$R_S = \frac{\mathcal{N}_S}{(3S^2-4J^2)^3(S^2+4J^2)^2\,\mathcal{D}_C^2}\,, \tag{6.61}$$

where $\mathcal{N}_S$ is again a function which never vanishes at the points where the denominator is zero. From Eq. (6.61), we see that the denominator of C_J is present in the denominator of R_S. Furthermore, the factor S^2+4J^2 is never zero, hence it does not give any additional singularity. On the other hand, the factor $3S^2-4J^2$ is clearly vanishing when $\frac{J^2}{S^2} = \frac{3}{4}$, which is readily greater than the extremal limit $\frac{J^2}{S^2} = \frac{1}{4}$ and hence it has no physical relevance in our analysis.

We thus conclude that also in this case the GTD geometry g^{II} exactly reproduces the Davies phase transition structure of the Myers-Perry black holes both in the mass and in the entropy representation. We comment that in the entropy representation there is an additional singularity which does not correspond to any singularity of the response functions. However, such singularity is situated out of the black hole region and thus it is not to be considered here. We also remark that Ruppeiner curvature in this case reads

$$R = -\frac{S\,(S^2+12J^2)}{S^4-16J^4} \tag{6.62}$$

and hence it diverges only in the extremal limit, while Weinhold metric is flat.

In the next section we will analyze the general case of the Myers-Perry black hole in five dimensions, i.e. when the two angular momenta are allowed to vary freely.

6.3.3 The general case in which $J_1 \neq J_2 \neq 0$

Perhaps the most interesting case is the most general one, in which the two angular momenta are allowed to vary freely. In this case the thermodynamic manifold is 3-dimensional and the mass fundamental equation is given by (6.50).

The generalized susceptibilities can then be accordingly calculated. The heat capacity at constant angular momenta J_1 and J_2 reads

$$C_{J_1,J_2} = \frac{M_S}{M_{SS}} = -\frac{3\,S\,(S^2+4J_1^2)(S^2+4J_2^2)(S^4-16J_1^2J_2^2)}{\mathcal{D}_C}\,, \tag{6.63}$$

where

$$\mathcal{D}_C = S^8 - 12(J_1^2+J_2^2)S^6 - 320J_1^2J_2^2S^4 - 576J_1^2J_2^2(J_1^2+J_2^2)S^2 - 1280J_1^4J_2^4\,. \tag{6.64}$$

Furthermore, one can define the 3 analogues of the adiabatic compressibility as $(\kappa_S)_{ij} \equiv (\partial J_i/\partial\Omega_j)_S$. Therefore, we obtain

$$(\kappa_S)_{11} = \frac{3S^{\frac{2}{3}}(S^2+4J_1^2)^{\frac{5}{3}}}{2(S^2+4J_2^2)^{\frac{1}{3}}(3S^2-4J_1^2)}\,,\quad (\kappa_S)_{22} = \frac{3S^{\frac{2}{3}}(S^2+4J_2^2)^{\frac{5}{3}}}{2(S^2+4J_1^2)^{\frac{1}{3}}(3S^2-4J_2^2)}\,,$$
$$(\kappa_S)_{12} = \frac{3}{16}\,S^{2/3}\,\frac{(S^2+4\,J_1^2)^{2/3}(S^2+4\,J_2^2)^{2/3}}{J_1\,J_2}\,. \tag{6.65}$$

Finally, the analogues of the expansion are given by

$$\alpha_{S,J_2} \equiv \left(\frac{\partial J_1}{\partial T}\right)_S = -\frac{3}{8}\frac{S^{\frac{5}{3}}(S^2+4J_1^2)^{\frac{5}{3}}(S^2+4J_2^2)^{\frac{2}{3}}}{J_1(S^4+6S^2J_2^2+8J_1^2J_2^2)}\,,$$
$$\alpha_{S,J_1} \equiv \left(\frac{\partial J_2}{\partial T}\right)_S = -\frac{3}{8}\frac{S^{\frac{5}{3}}(S^2+4J_2^2)^{\frac{5}{3}}(S^2+4J_1^2)^{\frac{2}{3}}}{J_2(S^4+6S^2J_1^2+8J_1^2J_2^2)}\,. \tag{6.66}$$

In this case neither $(\kappa_S)_{12}$ nor the expansions show any singularity, while C_{J_1,J_2} diverges when $\mathcal{D}_C = 0$ and the compressibilities $(\kappa_S)_{11}$ and $(\kappa_S)_{22}$ diverge when $3S^2 - 4J_1^2 = 0$ and $3S^2 - 4J_2^2 = 0$ respectively. Furthermore, the temperature reads

$$T = \frac{S^4 - 16J_1^2J_2^2}{2S^{5/3}\,(S^2+4J_1^2)^{2/3}(S^2+4J_2^2)^{2/3}}\,, \tag{6.67}$$

hence the extremal limit is reached for $\frac{J_1J_2}{S^2} = \frac{1}{4}$. The heat capacity diverges when $\mathcal{D}_C = 0$, which is an algebraic equation of degree 8 in S. We can solve numerically such equation and obtain the critical value S = Scritical in terms of J_1 and J_2. Taking only the roots which are real and positive, we can compare them with the extremal limit by doing

$$\left.\frac{J_1J_2}{S^2}\right|_{S=\text{Sextremal}} - \left.\frac{J_1J_2}{S^2}\right|_{S=\text{Scritical}} = \frac{1}{4} - \left.\frac{J_1J_2}{S^2}\right|_{S=\text{Scritical}} . \tag{6.68}$$

The plot of the result is given in Fig. 6.1 for some values of J_1 and J_2. As we can see from Fig. 6.1, the difference in Eq. (6.68) is always positive, hence the points of phase transition signaled by the divergence of the heat capacity are always in the black hole region.

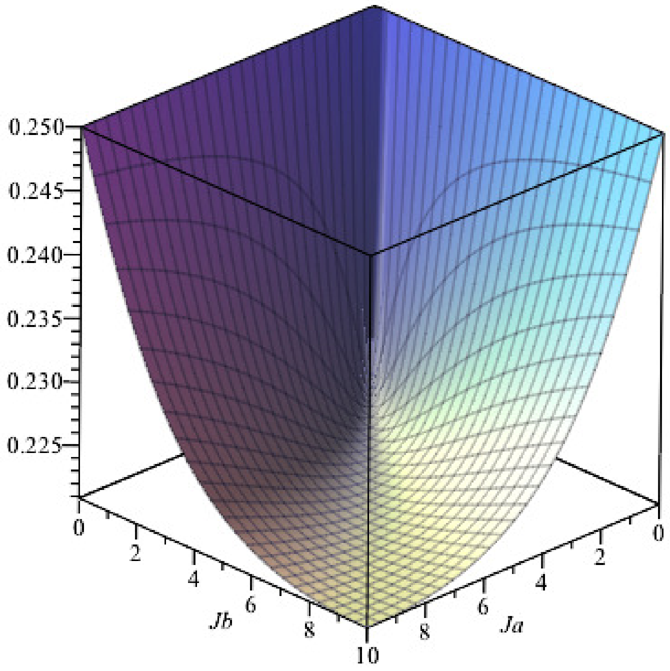

Figure 6.1: The difference between the extremal limit ($\frac{J_1J_2}{S^2} = \frac{1}{4}$) and the value of $\frac{J_1J_2}{S^2}$ at the critical point of the heat capacity, plotted for values of J_1 and J_2 in the interval $[0, 10]$.

In the same way, we can solve $3S^2 - 4J_1^2 = 0$ and see whether the divergence of $(\kappa_S)_{11}$ lies in the black hole region or not. It turns out that the denominator of $(\kappa_S)_{11}$ vanishes for values of S such that $\frac{J_1^2}{S^2} = \frac{3}{4}$, which means that $\frac{J_1J_2}{S^2} = \frac{3}{4}\frac{J_2}{J_1}$. Therefore, we have that $\frac{1}{4} - \frac{3}{4}\frac{J_2}{J_1}$ is positive provided $J_1 > 3J_2$ for $J_1 > 0$ or $J_1 < 3J_2$ for $J_1 < 0$. In sum, the divergences of $(\kappa_S)_{11}$ can be in the black hole region for appropriate values of J_1 and J_2. Analogously, the divergences of $(\kappa_S)_{22}$ can also be in the black hole region.

As in the preceding sections, we will now focus on the Gibbsian response functions, in order to make the analysis complete. The heat capacity at constant angular velocities can be defined as usual as $C_{\Omega_1,\Omega_2} \equiv T\left(\partial S/\partial T\right)_{\Omega_1,\Omega_2}$ and it reads

$$C_{\Omega_1,\Omega_2} = \frac{-3\,S(S^4-16J_1^2J_2^2)(3S^2-4J_1^2)(3S^2-4J_2^2)(S^2+4J_1^2)(S^2+4J_2^2)}{\mathcal{D}(S,J_1,J_2)}\,, \tag{6.69}$$

where the denominator is given by

$$\begin{aligned}\mathcal{D}(S,J_1,J_2) =\ & 9S^{12}+72(J_1^2+J_2^2)S^{10}+16(9J_1^4+95J_1^2J_2^2+9J_2^4)S^8+\\ & +5376J_1^2J_2^2(J_1^2+J_2^2)S^6-256J_1^2J_2^2(9J_1^4-101J_1^2J_2^2+9J_2^4)S^4+\\ & -6144J_1^4J_2^4(J_1^2+J_2^2)S^2-53248J_1^6J_2^6\,. \end{aligned}\tag{6.70}$$

Furthermore, one can define three generalized susceptibilities, analogous to the isothermal compressibility, as $(\kappa_T)_{ij} \equiv (\partial J_i/\partial \Omega_j)_T$.

For the Myers-Perry black hole they can be written as

$$(\kappa_T)_{11} = -\,\frac{S^{2/3}\mathcal{D}_C}{2}\,\frac{(S^2+4J_1^2)^{-\frac{1}{3}}(S^2+4J_2^2)^{-\frac{1}{3}}}{(S^6-12J_2^2S^4+48J_1^2J_2^2S^2+192J_1^2J_2^4)}\,, \tag{6.71}$$

$$(\kappa_T)_{22} = -\,\frac{S^{2/3}\mathcal{D}_C}{2}\,\frac{(S^2+4J_1^2)^{-1/3}(S^2+4J_2^2)^{-1/3}}{(S^6-12J_1^2S^4+48J_1^2J_2^2S^2+192J_2^2J_1^4)}\,, \tag{6.72}$$

while $(\kappa_T)_{12}$ has a more cumbersome expression and we will not write it here, since it has the same properties of $(\kappa_T)_{11}$ and $(\kappa_T)_{22}$ for as regards our analysis, i.e. it is proportional to the denominator of C_{J_1,J_2} defined in (6.64) and it has a non-trivial denominator (one can also introduce the two analogues of the thermal expansion, but for the sake of simplicity we are not going to write them here, since they do not show any singularities and hence they do not play any role in our analysis).

Therefore, from the thermodynamic point of view, we remark that the divergences of C_{J_1,J_2} are matched by the vanishing of the three quantities $(\kappa_T)_{ij}$, while the divergences of $(\kappa_S)_{11}$ and $(\kappa_S)_{22}$ are reproduced as zeroes of the heat capacity C_{Ω_1,Ω_2}. This behavior is in agreement with the analysis of the preceding sections. Furthermore, in this case the heat capacity C_{Ω_1,Ω_2} and the generalized compressibilities $(\kappa_T)_{ij}$ possibly show additional phase transitions, which is a further indication of the fact that black holes exhibit different thermodynamic behavior in different ensembles.

Now let us turn to the GTD analysis. Given the fundamental equation (6.50) and the general metric (5.7), we can calculate the particular metric and the scalar curvature for the MP black hole with two free angular momenta, both in the mass and in the entropy representations. The metric in the M representation reads

$$\begin{aligned} g_M^{II} = {}& \frac{(S^2+4J_1^2)^{-1/3}(S^2+4J_2^2)^{-1/3}}{3S^{4/3}} \left\{ \frac{-\mathcal{D}_{\mathcal{C}}}{4S^2(S^2+4J_1^2)(S^2+4J_2^2)}\,\mathrm{d}S\otimes\mathrm{d}S + \right. \\ & + \frac{(3S^2-4J_1^2)(S^2+4J_2^2)}{S^2+4J_1^2}\,\mathrm{d}J_1\otimes\mathrm{d}J_1 + \frac{(3S^2-4J_2^2)(S^2+4J_1^2)}{S^2+4J_2^2}\,\mathrm{d}J_2\otimes\mathrm{d}J_2 + \\ & \left. + 16J_1J_2\,\mathrm{d}J_1\otimes\mathrm{d}J_2 \right\}, \end{aligned} \tag{6.73}$$

hence its scalar curvature is

$$R_M = \frac{\mathcal{N}_M}{\mathcal{D}_C^2\left[3S^4-4S^2(J_1^2+J_2^2)-16J_1^2J_2^2\right]^2(S^2+4J_1^2)^{2/3}(S^2+4J_2^2)^{2/3}}\,, \tag{6.74}$$

where $\mathcal{D}_C$ is as usual the denominator of C_{J_1,J_2} defined in Eq. (6.64). Since there is no term in the numerator $\mathcal{N}_M$ which cancels out the divergences that happen when $\mathcal{D}_C = 0$, we can conclude that every phase transition related to the heat capacity C_{J_1,J_2} is properly reproduced by the scalar curvature R_M. In addition, in this case the factor $3S^4-4S^2(J_1^2+J_2^2)-16J_1^2J_2^2$ can also vanish, possibly giving an additional singularity which does not correspond to the ones shown by the response functions. It is easy to calculate that $3S^4-4S^2(J_1^2+J_2^2)-16J_1^2J_2^2 = 0$ for values of S such that

$$\frac{J_1J_2}{S^2} = -\frac{J_1^2+J_2^2-\sqrt{J_1^4+14J_1^2J_2^2+J_2^4}}{8\,J_1\,J_2}\,. \tag{6.75}$$

We can thus calculate the difference between the extremal limit $\frac{J_1J_2}{S^2}=\frac{1}{4}$ and the critical value (6.75). The result is

$$\begin{aligned} & \frac{1}{4} + \frac{J_1^2+J_2^2-\sqrt{J_1^4+14J_1^2J_2^2+J_2^4}}{8\,J_1\,J_2} = \\ & = -\frac{\left(J_1^2+J_2^2-6J_1J_2+\sqrt{J_1^4+14J_1^2J_2^2+J_2^4}\right)\left(J_1^2+J_2^2-\sqrt{J_1^4+14J_1^2J_2^2+J_2^4}\right)}{48\,J_1^2\,J_2^2}\,, \end{aligned} \tag{6.76}$$

which can be positive for appropriate values of J_1 and J_2. Therefore such points of divergence of R_M are in the black hole region for some values of the parameters. Hence we conclude that the behavior of R_M perfectly matches the behavior of C_{J_1,J_2}, but in this case it does not reproduce the possible additional phase transitions indicated by the singularities of the compressibilities $(\kappa_S)_{11}$ and $(\kappa_S)_{22}$ and possibly shows some additional unexpected singularities.

However, we can give a precise physical meaning to such additional singularities. In fact, if we evaluate the determinant of the Hessian of the mass with respect to the angular momenta J_1 and J_2 only, we get

$$\det(\,\mathrm{Hess}(M)_{J_1J_2}) = \frac{4\,(3S^4 - 4S^2(J_1^2+J_2^2) - 16J_1^2J_2^2)}{3\,S^{4/3}(S^2+4J_1^2)^{4/3}(S^2+4J_2^2)^{4/3}}\,, \tag{6.77}$$

from which we can see that the numerator is exactly the factor in the denominator of R_M whose roots give the additional singularities. Since the Hessians of the energy are related to the stability conditions, we suggest that the physical meaning of such additional divergences of R_M is to be found in a change of stability of the system, e.g. from a stable phase to an unstable one, as it is usual for the case of Davies phase transitions.

On the other side, using the relation (6.59) between the metrics g^{II} in the M and in the S representations, naturally extended to the 3-dimensional case with coordinates (S, J_1, J_2), i.e.

$$\begin{aligned} g_S^{II} &= \frac{M - J_1\,\Omega_1 - J_2\Omega_2}{T^3}\Big[T\,M_{SS}\,\mathrm{d}S\otimes\mathrm{d}S + 2\,\Omega_1\,M_{SS}\,\mathrm{d}S\otimes\mathrm{d}J_1 + \\ &+ 2\,\Omega_2\,M_{SS}\,\mathrm{d}S\otimes\mathrm{d}J_2 + (2\,\Omega_1\,M_{SJ_1} - T\,M_{J_1J_1})\,\mathrm{d}J_1\otimes\mathrm{d}J_1 + \\ &+ (2\,\Omega_2\,M_{SJ_2} - T\,M_{J_2J_2})\,\mathrm{d}J_2\otimes\mathrm{d}J_2 + \\ &- 2\,(T\,M_{J_1J_2} - \Omega_1\,M_{SJ_2} - \Omega_2\,M_{SJ_1})\,\mathrm{d}J_1\otimes\mathrm{d}J_2\Big]\,, \end{aligned} \tag{6.78}$$

we can now calculate the metric in the S representation, which reads

$$\begin{aligned} g_S^{II} = {} & \frac{[3S^4+4S^2(J_1^2+J_2^2)-16J_1^2J_2^2]\,\mathcal{D}_C}{3(S^2+4J_1^2)(S^2+4J_2^2)(S^2-4J_1J_2)^2(S^2+4J_1J_2)^2}\Bigg\{\frac{1}{2}\,\mathrm{d}S\otimes\mathrm{d}S + \\ & + \frac{4\,SJ_1(S^2+4J_2^2)}{(S^2-4J_1J_2)(S^2+4J_1J_2)}\mathrm{d}S\otimes\mathrm{d}J_1 + \frac{4\,SJ_2(S^2+4J_1^2)}{(S^2-4J_1J_2)(S^2+4J_1J_2)}\mathrm{d}S\otimes\mathrm{d}J_2 + \\ & - \frac{2\,S^2(S^2+4J_2^2)^2\,[3S^6+26S^4J_1^2+144S^2J_1^2J_2^2+320J_1^4J_2^2]}{\mathcal{D}_C(S^2-4J_1J_2)(S^2+4J_1J_2)}\mathrm{d}J_1\otimes\mathrm{d}J_1 + \\ & - \frac{2\,S^2(S^2+4J_1^2)^2\,[3S^6+26S^4J_2^2+144S^2J_1^2J_2^2+320J_2^4J_1^2]}{\mathcal{D}_C(S^2-4J_1J_2)(S^2+4J_1J_2)}\mathrm{d}J_2\otimes\mathrm{d}J_2 + \\ & - \frac{32\,S^2J_1J_2(S^2+4J_1^2)(S^2+4J_2^2)\,[5S^4+12S^2(J_1^2+J_2^2)+16J_1^2J_2^2]}{\mathcal{D}_C(S^2-4J_1J_2)(S^2+4J_1J_2)}\mathrm{d}J_1\otimes\mathrm{d}J_2\Bigg\}\,. \end{aligned} \tag{6.79}$$

The scalar curvature can thus be calculated to obtain

$$R_S = \frac{\mathcal{N}_S}{\mathcal{D}_C^2\,[3S^4+4S^2(J_1^2+J_2^2)-16J_1^2J_2^2]^3\,S^2(S^2+4J_1^2)(S^2+4J_2^2)}\,. \tag{6.80}$$

In this case we see again that the denominator of the heat capacity $\mathcal{D}_C$ is present in the denominator of R_S. Furthermore, the second factor, which is slightly different from the factor in the denominator of R_M, vanishes for values of S such that

$$\frac{J_1 J_2}{S^2} = \frac{J_1^2 + J_2^2 + \sqrt{J_1^4 + 14 J_1^2 J_2^2 + J_2^4}}{8\, J_1\, J_2} \,. \tag{6.81}$$

The above discussion for the additional singularity of R_M does not apply in this case, since one can easily show that the points described by (6.81) do not belong to the black hole region for any values of J_1 and J_2 and therefore they have no physical meaning. However, we comment in passing that such additional singularities are still related to the vanishing of the determinant of the Hessian of the entropy S with respect to the angular momenta J_1 and J_2. Therefore they still indicate the points where the Hessian vanishes, although they are not situated in the black hole region in this case. We infer from these results that the physical meaning of the divergences of the scalar curvature of the metric g^{II} for such a 3-dimensional equilibrium manifold is related to the divergences of the heat capacity at constant angular momenta and to the zeroes of the Hessian of the potential with respect to those momenta, both in the mass and in the entropy representation. On the other side, from the full analysis of the divergences of the generalized response functions, we see that there are other possible points of phase transitions, related to divergences of the compressibilities, which appear to be not enclosed by the analysis given with the metric g^{II}. We also comment that we could have used the potential $\Phi = G \equiv M - T\,S - J_1\,\Omega_1 - J_2\,\Omega_2$ in writing the metric (5.7) to study the GTD analysis in the G representation, but such investigation would have lead to exactly the same results, since the metric (5.7) is symmetric with respect to total Legendre transformations.

To conclude, we observe that in [51] the case of the full Myers-Perry black hole thermodynamics has been investigated using Weinhold and Ruppeiner thermodynamic geometries. The authors proved that both Weinhold and Ruppeiner scalar curvatures only diverge in the extremal limit.

6.4 Conclusions

In this chapter we have analyzed the geometric structure of the equilibrium manifold (5.7) for different black holes configurations in dimension higher than four.

We analyzed two of the most interesting higher dimensional black hole configurations, namely, the Reissner-Nordström and the Kerr black holes, which we consider because of their importance as model systems, like the Van der Waals and the Ising models in ordinary thermodynamics. First of all, we have derived all the Davies phase transitions, that follow from the analysis of the divergences of the thermodynamic response functions. In the case of the Reissner-Nordström black hole, we found that if we use the ensemble associated with the mass of the black hole, there exists only one curve of phase transition. On the other hand, if we use the ensemble associated with the enthalpy, no phase transitions exist. This is in perfect accordance with the interpretation given in Chapter 5 that Davies phase transitions are a special type of phase transitions that is characteristic of systems with long-range interactions and as such they depend on the ensemble. We have then explored the geometric properties of the corresponding equilibrium space by using GTD, with the mass as the thermodynamic potential, and found that a curvature singularity appears exactly along the curve where the phase transition occurs. If, instead, we use the enthalpy as thermodynamic potential, GTD provides a singularity-free equilibrium manifold. Thus, GTD reproduces the Davies phase transition structure of the Reissner-Norström black hole.

In the case of the higher dimensional Kerr black hole, the response functions predict more phase transitions than in the Reissner-Nordström case. It is not possible to compute explicitly other thermodynamic potentials, and so we perform all the calculations in the mass and representations. Again, we found true curvature singularities at the same points where phase transitions take place.

Finally, we have analyzed the thermodynamics and thermodynamic geometry of different Myers-Perry black holes configurations in five dimensions, classifying them according to the values of the two possible independent angular momenta. Our results indicate that the Myers-Perry black holes in five dimensions have a non-trivial phase structure in the sense of Davies. In particular, the analysis of the response functions indicate that both the heat capacities and the compressibilities defined in the M potential diverge at some points, which is usually interpreted as the hallmark of a phase transition. Interestingly, such a behavior is matched by the vanishing of the corresponding Gibbsian response functions in all the cases studied here. Moreover, in the most general case when the two angular momenta vary freely, we have shown that the Gibbsian response functions provide some additional singularities, indicating that the analysis in the M potential is different from that performed in the G potential, as expected.

In all the cases studied in this chapter, the phase transitions are well reproduced by the GTD analysis, while they are not reproduced by the thermodynamic geometries of Weinhold and Ruppeiner, whose analysis has been observed to correspond to other approaches (see e.g. [79]). We have also found that the scalar curvature of the metric g^{II} shows a very similar behavior in the M representation to that of the S representation. In particular, for the cases in which we have only two degrees of freedom we argue that no physical difference has been detected and we have shown that not only the phase transitions indicated by C_J are reproduced, but also the ones indicated by divergences of κ_S. Moreover, a detailed analysis of the Gibbsian response functions showed that such divergences correspond to points where κ_T and C_Ω vanish and change their character. We therefore conclude that for such cases the divergences of the scalar curvature of g^{II} reproduce the full set of Davies phase transitions considered here.

However, it seems that analyzing the general case in which both angular momenta are switched on, i.e. a thermodynamic system with three degrees of freedom, some differences might appear. In fact, the phase transitions signaled by C_{J_1,J_2} are still obtained as curvature singularities in both representations. Nevertheless, the scalar curvature has some additional divergences, which for the case of the M representation can be in the black hole region for appropriate values of the angular momenta and that apparently are not directly related to the response functions of the system. Nevertheless, we claim that such additional divergences are linked to the vanishing of the Hessian determinant of the potential M with respect to the two angular momenta, therefore they mark the presence of a transition from a stable phase to an unstable one, as it is always the case for Davies transitions. In our opinion this means that in the case of black holes that depend on three degrees of freedom one should enlarge the spectrum of possible phase transitions *à la Davies*, including also questions of stability related to thermodynamically relevant combinations of the response functions, i.e. (sub-)determinants of the Hessian of the potential. This is also supported by the analysis of the scalar curvature in the S representation, which again shows singularities exactly at those points where the Hessian of the entropy with respect to the two angular momenta vanishes, so from the mathematical point of view the situation is basically the same. It is interesting however to note that in the S representation such points are not in the black hole region, another direct evidence of the fact that black hole thermodynamics strictly depends on the potential being used. Moreover, in the completely general case, some additional divergences appear when considering the Gibbsian response functions, which are not present in the thermodynamic analysis in the M potential, nor are indicated as curvature singularities of g^{II}. The study of such additional singularities goes beyond the scope of this work and may be the matter of further investigation.

7 Conclusions and future directions

7.1 Summary of new results

In this work we have obtained some new results both in the context of the mathematical formulation of the contact and Riemannian structures of thermodynamics and in its applications to the physics of ordinary systems and generalized homogeneous thermodynamics, among which black holes.

First of all, we have started with the distinction between the global contact structure of the phase space, taking account of all the equilibrium processes related to the first law, including first order phase transitions, and the local metric structure, both of the phase space and of the equilibrium space, which takes account of the fluctuations from equilibrium and of the failure of the equilibrium hypothesis, i.e. continuous phase transitions.

Moving from these ideas, we have shown that first order phase transitions in generalized homogeneous thermodynamics are equilibrium processes on the phase space of thermodynamics for which the Legendre symmetry is broken. This study has also lead us to introduce a contact hamiltonian energy (which we named *Euler's contact Hamiltonian*) that fully characterizes equilibrium processes on the phase space of thermodynamics.

Moreover, such novel formulation has then been employed in this thesis in two ways. First, we have used Euler's contact Hamiltonian to derive a new zeroth law of thermodynamics that is completely consistent with the Gibbs-Duhem relation in the case of homogeneous thermodynamic potentials of any order. In this context, we have outlined the profound differences between ordinary systems and the ones with long-range interactions, in particular black holes. Second, the importance of the breaking of the Legendre symmetry in all the systems showing ensemble inequivalence has been repeatedly outlined, since this comes has a special motivation for the introduction of metric structures both on the phase space and on the equilibrium manifold that share this symmetry of the underlying contact structure. Motivated by this symmetry property and by the other relevant symmetry of the contact structure, i.e. the symmetry under change of representation, we have thus introduced a new Riemannian thermodynamic metric and argued that this structure is the natural metric to be used in the formalism of GTD. It turned out that this metric in the equilibrium manifold is conformally equivalent to the ones introduced by Weinhold and Ruppeiner, that is, it is conformal to an Hessian metric. As such, it has been assumed to be the natural structure to introduce fluctuations in the geometric formalism of GTD. Such assumption has been also tested here with standard examples from ordinary thermodynamics.

Besides, we have seen that black holes are very particular thermodynamic systems, since they are governed by long-range interactions and therefore they cannot be homogeneous of order one. This implies that one should abandon the usual form of the zeroth law of thermodynamics and perhaps generalize it in the way we have proposed here. Moreover, from the thermodynamic geometric point of view, it turns out that the geometric structures that give the complete description of the critical behavior for ordinary systems, i.e. Hessian metrics and their conformal equivalents, do not account for all the new possible phase transitions that emerge in the case of black holes. This problem is known in the literature and several attempts to find an explication have been given. We have given here the simplest explication for such peculiar behavior. Indeed, regarding black holes as systems governed by long-range interactions, we have claimed that their thermodynamics should be strictly non-extensive. One of the implications of this deduction is that they show ensemble inequivalence, negative specific heats and possibly phase transitions defined in only one of the ensembles, as it is often the case in phase transitions *à la Davies*. We also commented that this has some implications in the geometric description of black holes thermodynamics. In particular, one cannot expect that the same structure that governs ordinary extensive systems can be also comprehensive of all the new features about black holes (and in general systems with long-range interactions). From this point of view, we have investigated a metric structure in the GTD context that seems to be the exact counterpart of Davies transitions for black holes. The results here confirm this expectation, both in the particular cases examined and on a more general footing.

7.2 Open questions

Several questions about this work remain open so far and eventually will be addressed in further efforts. In particular, having derived here a contact hamiltonian formulation for generalized homogeneous thermodynamics, we expect that this can be naturally generalized to the case of quasi-homogeneous thermodynamic potentials [56]. It will be interesting to work out this further generalization and also express the new zeroth law derived here in such context. Moreover, we would like to fully analyze black holes thermodynamics from the general point of view of thermodynamics of systems with long-range interactions and generalized quasi-homogeneous functions. We think that also a feedback can be gained from these examples for as regards the geometric structure to be used in "non-extensive" thermodynamics, as for the case of the GTD metric g^{II} used here. To this regard, it would be interesting to adapt the formalism developed here making use of both the contact structure of the phase space and the Riemannian structure of the equilibrium manifold also to the general case of non-extensive systems. In fact, in the statistical mechanics of systems with long-range interactions various generalizations of the standard additive Boltzmann-Gibbs-Shannon entropy have been proposed quite recently, e.g. the so-called Tsallis entropy [86], and also the zeroth law of thermodynamics has been changed accordingly. We believe that there is a profound connection with the results found here from the macroscopic point of view and the ones encountered in "non-extensive" statistical mechanics. In this sense the fields of applicability are numerous, from self-gravitating systems in astrophysics to condensed matter, from black holes to high energy theories, up to the AdS-CFT correspondence and so forth.

Another fascinating topic is the investigation of systems with ensembles inequivalence with respect to the Renormalization Group techniques. As we have seen in this work, a very simple example of ensemble inequivalence is represented by first order phase transitions. We have also seen that this implies that the geometric space in which one is working has to be extended to the full phase space in order to recover the full information and we have speculated that this is similar to the description of Renormalization Group, where one rules out irrelevant degrees of freedom by using repeated iterations of the procedure. We believe that this parallelism between the RG techniques and the construction of phase spaces in thermodynamics that contain all the necessary information is more than a mere analogy.

Furthermore, regarding the natural metric structure introduced here to study ordinary thermodynamic systems, it has to be clarified what is exactly the physical meaning of the symmetry under a change of representation. We believe that, as the equilibrium contact hamiltonian is the conserved quantity related to symmetry under Legendre transformations, it is also possible to find a conserved quantity in the phase space of thermodynamics related to the symmetry under a change of representation. In this context, also the role of partial Legendre transformations should be clarified.

Finally, having built up a powerful geometric framework for generalized thermodynamics, it follows that we are in the position to use geometric tools such as distances, curvature, embedding and extremal principles to figure out relations among the thermodynamic laws and even new thermodynamic equations of state based on special geometric properties, a matter which can have applications e.g. in cosmology.

In sum, we hope that this will not be the conclusion of our investigation, but the starting point towards a deeper mathematical and physical understanding of various thermodynamic aspects of Nature.

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