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Thermodynamic systems as extremal hypersurfaces

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ABSTRACT

We apply variational principles in the context of geometrothermodynamics. The thermodynamic phase space $\mathcal{T}$ and the space of equilibrium states $\mathcal{E}$ turn out to be described by Riemannian metrics which are invariant with respect to Legendre transformations and satisfy the differential equations following from the variation of a Nambu–Goto-like action. This implies that the volume element of $\mathcal{E}$ is an extremal and that $\mathcal{E}$ and $\mathcal{T}$ are related by an embedding harmonic map. We explore the physical meaning of geodesic curves in $\mathcal{E}$ as describing quasi-static processes that connect different equilibrium states. We present a Legendre invariant metric which is flat (curved) in the case of an ideal (van der Waals) gas and satisfies Nambu–Goto equations. The method is used to derive some new solutions which could represent particular thermodynamic systems.

1. Introduction

The geometry of thermodynamics has been the subject of moderate research since the original works by Gibbs [1] and Caratheodory [2]. Results have been achieved in two different approaches. The first one consists in introducing metric structures on the space of thermodynamic equilibrium states $\mathcal{E}$, whereas the second group uses the contact structure of the thermodynamic phase space $\mathcal{T}$. Weinhold [3] introduced on $\mathcal{E}$ a metric defined as the Hessian of the thermodynamic potential. This approach has found applications also in the context of the renormalization group [4], the identification of states to a specific phase [5], the thermodynamic uncertainty relations [6], and black hole thermodynamics (see [7,8] and references cited there). The second approach, proposed by Hermann [9], uses the natural contact structure of the phase space $\mathcal{T}$. Extensive and intensive thermodynamic variables are taken together with the thermodynamic potential to constitute coordinates on $\mathcal{T}$. A special subspace of $\mathcal{T}$ is the space of equilibrium states $\mathcal{E}$.

Geometrothermodynamics (GTD) [10,11] was recently developed as a formalism that unifies the contact structure on $\mathcal{T}$ with the metric structure on $\mathcal{E}$ in a consistent manner, by considering only Legendre invariant metrics on $\mathcal{T}$. This last property is important to guarantee that the properties of a system do not depend on the thermodynamic potential used for its description. In [11], a simple metric was used in GTD in order to reproduce geometrically the noncritical behavior of the ideal gas and the critical behavior of the van der Waals gas (see, for instance, Ref. [12]), indicating that thermodynamic curvature can be used as a measure of thermodynamic interaction. This result has been corroborated in the case of black holes [13–15].

In the present work we explore an additional aspect of GTD. The thermodynamic metrics used so far in GTD have been derived by using only the Legendre invariance condition. Now we ask the question whether those metrics can be derived

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as solutions of a certain set of differential equations, as is usual in field theories. We will see that this task is realizable. In fact, it turns out that the map $\varphi : \mathcal{E} \to \mathcal{T}$ can be considered as a harmonic map, if the thermodynamic variables satisfy the differential equations which follow from the variation of a Polyakov-like action. This result confers thermodynamics a geometric structure that resembles that of the bosonic string theory. In fact, we will show that thermodynamic systems can be interpreted as "strings" embedded in a higher dimensional, curved phase space.

This paper is organized as follows. In Section 2 we review the fundamentals of GTD. In Section 3 we show that the embedding map φ can be considered as a harmonic map with a naturally induced Polyakov-like action from which a set of differential equations can be derived. Section 4 contains an analysis of the thermodynamic length, the variation of which leads to the geodesic equations for the metric of $\mathcal{E}$. In Section 5 we present the most general Legendre invariant metric we have found and use it to derive the geometric structure of thermodynamic systems with an arbitrary finite number of different species. As concrete examples we investigate the geometry of the ideal gas, the van der Waals gas, and derive a few new fundamental equations which are compatible with the geometric structures of GTD. Finally, Section 6 is devoted to a discussion of our results.

2. Geometrothermodynamics

Consider the $(2n+1)$-dimensional space $\mathcal{T}$ coordinatized by the set $Z^A = \{\Phi, E^a, I^a\}$, with the notation $A = 0, \ldots, 2n$ so that $\Phi = Z^0$, $E^a = Z^a$, $a = 1, \ldots, n$, and $I^a = Z^{n+a}$. Here Φ represents the thermodynamic potential, E^a are the extensive variables and I^a the intensive variables. Consider the Gibbs 1-form [9]

$$\Theta = \mathrm{d}\Phi - \delta_{ab} I^a \mathrm{d}E^b, \qquad \delta_{ab} = \mathrm{diag}(1, 1, \ldots, 1) \tag{1}$$

where summation over repeated indices is assumed. The pair $(\mathcal{T}, \Theta)$ is called a contact manifold [9], if $\mathcal{T}$ is differentiable and Θ satisfies the condition $\Theta \wedge (\mathrm{d}\Theta)^n \neq 0$. It can be shown [9] that if there exists a second differential form $\tilde{\Theta}$ which satisfies the condition $\tilde{\Theta} \wedge (\mathrm{d}\tilde{\Theta})^n \neq 0$ on $\mathcal{T}$, then Θ and $\tilde{\Theta}$ must be related by a Legendre transformation [16], $\{Z^A\} \to \{\widetilde{Z}^A\} = \{\tilde{\Phi}, \tilde{E}^a, \tilde{I}^a\}$,

$$\Phi = \tilde{\Phi} - \delta_{kl} \tilde{E}^k \tilde{I}^l, \qquad E^i = -\tilde{I}^i, \qquad E^j = \tilde{E}^j, \qquad I^i = \tilde{E}^i, \qquad I^j = \tilde{I}^j, \tag{2}$$

where $i \cup j$ is any disjoint decomposition of the set of indices $\{1, \ldots, n\}$, and $k, l = 1, \ldots, i$. This implies that the contact structure of $\mathcal{T}$ is invariant with respect to Legendre transformations. Consider, in addition, a nondegenerate metric G on $\mathcal{T}$. We define the *thermodynamic phase space* as the triplet $(\mathcal{T}, \Theta, G)$ such that Θ defines a contact structure on $\mathcal{T}$ and G is a Legendre invariant metric on $\mathcal{T}$. A straightforward computation shows that the flat Euclidean metric is not Legendre invariant. For simplicity, the phase space will be denoted by $\mathcal{T}$. The *space of equilibrium states* is an n-dimensional Riemannian manifold $(\mathcal{E}, g)$, where $\mathcal{E} \subset \mathcal{T}$ is defined by a smooth map $\varphi : \mathcal{E} \to \mathcal{T}$, satisfying the conditions $\varphi^*(\Theta) = 0$ and $g = \varphi^*(G)$, where φ^* is the pullback of φ. The smoothness of the map φ guarantees that g is a well-defined, nondegenerate metric on $\mathcal{E}$. For the sake of concreteness we choose E^a as the coordinates of $\mathcal{E}$. Then, $\varphi : \{E^a\} \mapsto \{\Phi(E^a), E^a, I^a(E^a)\}$, and the condition $\varphi^*(\Theta) = 0$ yields the first law of thermodynamics and the condition for thermodynamic equilibrium:

$$\mathrm{d}\Phi = \delta_{ab} I^a \mathrm{d}E^b = I_b \mathrm{d}E^b, \qquad \frac{\partial \Phi}{\partial E^a} = \delta_{ab} I^b = I_a. \tag{3}$$

The explicit form of φ implies that the function $\Phi(E^a)$ must be given. In thermodynamics $\Phi(E^a)$ is known as the fundamental equation from which all the equations of state of the system can be derived. It also satisfies the second law of thermodynamics which is equivalent to the condition [12]

$$\frac{\partial^2 \Phi}{\partial E^a \partial E^b} \geq 0. \tag{4}$$

In addition, the degree β of homogeneity of the thermodynamic potential, i.e., $\Phi(\lambda E^a) = \lambda^\beta \Phi(E^a)$, with constant λ and β, appears then in Euler's identity: [11]

$$\beta \Phi = E^a I_a = E^a \frac{\partial \Phi}{\partial E^a}. \tag{5}$$

The metric defined by $g = \varphi^*(G)$ represents the *thermodynamic metric* of $\mathcal{E}$ whose components are explicitly given as

$$g_{ab} = \frac{\partial Z^A}{\partial E^a} \frac{\partial Z^B}{\partial E^b} G_{AB} = Z^A_{,a} Z^B_{,b} G_{AB}. \tag{6}$$

It is worth noticing that the application of a Legendre transformation on G corresponds to a coordinate transformation of g. Indeed, if we denote by $\{\tilde{Z}^A\}$ the Legendre transformed coordinates in $\mathcal{T}$, then the transformed metric $\tilde{G}_{AB} = \frac{\partial Z^C}{\partial \tilde{Z}^A} \frac{\partial Z^D}{\partial \tilde{Z}^B} G_{CD}$ induces on $\mathcal{E}$ the metric $\tilde{g}_{ab} = \frac{\partial \tilde{Z}^A}{\partial \tilde{E}^a} \frac{\partial \tilde{Z}^B}{\partial \tilde{E}^b} \tilde{G}_{AB}$. It is then easy to see that these metrics are related by the transformation law

$$\tilde{g}_{ab} = \frac{\partial E^c}{\partial \tilde{E}^a} \frac{\partial E^d}{\partial \tilde{E}^b} g_{cd}. \tag{7}$$

3. The harmonic map

In analytic geometry, a thermodynamic system is described by an equation of state $f(E^a, I^a) = 0$ which determines a surface in the space with coordinates $\{E^a, I^a\}$. Probably, one of the most important contributions of analytic geometry to the understanding of thermodynamics is the identification of points of phase transitions with extremal points of the surface $f(E^a, I^a) = 0$. More detailed descriptions of these contributions can be found in standard textbooks on thermodynamics (see, for instance, [12]). This approach, however, implies that the equation $f(E^a, I^a) = 0$ must be determined experimentally. Here we present an alternative approach in which a thermodynamic system is described by an extremal hypersurface, satisfying a system of differential equations. This alternative approach provides a solid mathematical structure to thermodynamics, and opens the possibility of finding extremal surfaces and investigating their thermodynamic properties by analyzing their geometric structure. In fact, we will use the method of harmonic maps, which has been extensively used in field theories and appears naturally in the context of GTD.

Consider the phase space with metric G and coordinates Z^A, and suppose that an arbitrary nondegenerate metric h is given in $\mathcal{E}$. The smooth map $\varphi : \mathcal{E} \to \mathcal{T}$, or in coordinates $\varphi : \{E^a\} \mapsto \{Z^A\}$, is called a *harmonic map*, if the coordinates Z^A satisfy the equations following from the variation of the action [17]

$$I_h = \int_{\mathcal{E}} \mathrm{d}^n E \sqrt{|h|} h^{ab} Z^A_{,a} Z^B_{,b} G_{AB}. \tag{8}$$

Here $|h| = |\det(h_{ab})|$. The variation of I_h with respect to Z^A leads to

$$\frac{\delta I_h}{\delta Z^A} = 0 \Leftrightarrow \mathcal{D}_h Z^A := \frac{1}{\sqrt{|h|}} \left(\sqrt{|h|} h^{ab} Z^A_{,a} \right)_{,b} + \Gamma^A_{BC} Z^B_{,b} Z^C_{,c} h^{bc} = 0 \tag{9}$$

where Γ^A_{BC} are the Christoffel symbols associated to the metric G_{AB}. For given metrics G and h, this is a set of $2n+1$ second-order, partial differential equations for the $2n+1$ thermodynamic variables Z^A. This set of equations must be treated together with the equation for the metric h, i.e.,

$$\frac{\delta I_h}{\delta h^{ab}} = 0 \Leftrightarrow T_{ab} := g_{ab} - \frac{1}{2} h_{ab} h^{cd} g_{cd} = 0, \tag{10}$$

where g_{ab} is the metric induced on $\mathcal{E}$ by the pullback φ^* according to (6). This is an algebraic constraint from which it is easy to derive the expression

$$h^{ab} g_{ab} = 2 \left(\frac{|g|}{|h|} \right)^{1/2}, \tag{11}$$

where $|g| = |\det(g_{ab})|$. This analysis is similar to the analysis performed in string theory for the bosonic string by using the Polyakov action. In fact, action (8) with $n = 2$ and a flat "background", $G_{AB} = \eta_{AB}$, is known as the Polyakov action [18]. By analogy with string theory, from the above description we can conclude that a thermodynamic system with n degrees of freedom can be interpreted as an n-dimensional "membrane" which "propagates" on a curved background metric G. The quotation marks emphasize the fact that at this level we have no explicit timelike parameter for the description of the membrane. Neither have we a timelike coordinate in the set Z^A so that the metric G could be interpreted as a background spacetime where the membrane propagates. Nevertheless, this analogy allows us to handle thermodynamics as a field theory where the thermodynamic variables satisfy a set of second-order differential equations. As in string theory, there is an equivalent description in terms of a Nambu–Goto-like action. Introducing the relationship (11) into the action (8) and using the expression (6) for the induced metric, we obtain the action $I_g = 2\int_{\mathcal{E}} \mathrm{d}^n E \sqrt{|g|}$ from which we derive the Nambu–Goto equations

$$\mathcal{D}_g Z^A = \frac{1}{\sqrt{|g|}} \left(\sqrt{|g|} g^{ab} Z^A_{,a} \right)_{,b} + \Gamma^A_{BC} Z^B_{,b} Z^C_{,c} g^{bc} = 0. \tag{12}$$

Since the action I_g is proportional to the volume element of the manifold $\mathcal{E}$, Eq. (12) can be interpreted as stating that the volume element induced in $\mathcal{E}$ must be an extremal. An equivalent interpretation is that the submanifold $\mathcal{E}$ can be represented as an extremal hypersurface contained in $\mathcal{T}$. The Nambu–Goto equations (12) can be investigated by using standard procedures of string theory.

4. Geodesics in the space of equilibrium states

In the space of equilibrium states $\mathcal{E}$ the line element $\mathrm{d}s^2 = g_{ab} \mathrm{d}E^a \mathrm{d}E^b$ can be considered as a measure for the distance between two points t_1 and t_2 with coordinates E^a and $E^a + \mathrm{d}E^a$, respectively. Let us assume that the points t_1 and t_2 belong to the curve $\gamma(\tau)$. Then, we define the *thermodynamic length* L as

$$L = \int_{t_1}^{t_2} \mathrm{d}s = \int_{t_1}^{t_2} \left(g_{ab} \mathrm{d}E^a \mathrm{d}E^b \right)^{1/2} = \int_{t_1}^{t_2} \left(g_{ab} \dot{E}^a \dot{E}^b \right)^{1/2} \mathrm{d}\tau, \tag{13}$$

where the dot represents differentiation with respect to τ. The condition that the thermodynamic length be an extremal $\delta L = \delta \int_{t_1}^{t_2} \mathrm{d}s = 0$ leads to the equations

$$\frac{\mathrm{d}^2 E^a}{\mathrm{d}\tau^2} + \Gamma^a_{bc} \frac{\mathrm{d}E^b}{\mathrm{d}\tau}\frac{\mathrm{d}E^c}{\mathrm{d}\tau} = 0, \tag{14}$$

where Γ^a_{bc} are the Christoffel symbols of the thermodynamic metric g_{ab}. These are the geodesic equations in the space $\mathcal{E}$ with affine parameter τ. The solutions to the geodesic equations depend on the explicit form of the thermodynamic metric g which, in turn, depends on the fundamental equation $\Phi = \Phi(E^a)$. Therefore, a particular thermodynamic system leads to a specific set of geodesic equations whose solutions depend on the properties of the system. Not all the solutions need to be physically realistic since, in principle, there could be geodesics that connect equilibrium states that are not compatible with the laws of thermodynamics. Those geodesics which connect physically meaningful states will represent quasi-static thermodynamic processes. Therefore, a quasi-static process can be seen as a dense succession of equilibrium states. This is in agreement with the standard interpretation of quasi-static processes in ordinary thermodynamics [12]. The affine parameter τ can be used to label each of the equilibrium states which are part of a geodesic. Because of its intrinsic freedom, the affine parameter can be chosen in such a way that it increases as the entropy of a quasi-static process increases. This opens the possibility of interpreting the affine parameter as a "time" parameter with a specific direction which coincides with the direction of entropy increase.

5. Applications

To solve the differential equations of GTD (12) one must specify *a priori* a Legendre invariant metric G for the phase space [11]. The metric

$$G = \left(\mathrm{d}\Phi - I_a \mathrm{d}E^a\right)^2 + \Lambda (E_a I_a)^{2k+1} \mathrm{d}E^a \mathrm{d}I^a, \tag{15}$$

with k being an integer and Λ an arbitrary Legendre invariant function, is the most general metric we have found that is invariant with respect to arbitrary Legendre transformations. To determine the metric structure of $\mathcal{E} \subset \mathcal{T}$ we choose the map $\varphi : \{E^a\} \mapsto \{\Phi(E^a), E^a, I^a(E^a)\}$ so that the condition $g = \varphi^*(G)$ for (15) yields

$$g = \Lambda \left(E_a \frac{\partial \Phi}{\partial E^a}\right)^{2k+1} \frac{\partial^2 \Phi}{\partial E^b \partial E^c} \delta^{ab} \mathrm{d}E^a \mathrm{d}E^c, \tag{16}$$

where we have used the first law of thermodynamics and the equilibrium conditions as given in Eqs. (3). In ordinary thermodynamics, the most used representation is based upon the internal energy U. The extensive variables are chosen as the entropy S, volume V, and the particle number of each species N_m. For simplicity we fix the maximum number of species as $n-2$ so that $m = 1, \ldots, n-2$. The dual variables are denoted as temperature T, pressure $-P$, and chemical potentials μ_m. The coordinates of $\mathcal{T}$ are then $Z^A = \{U, S, V, N_m, T, -P, \mu_m\}$, and the fundamental Gibbs 1-form becomes $\Theta = \mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V - \sum_m \mu_m \mathrm{d}N_m$. As for the Riemannian structure of $\mathcal{T}$, the most general Legendre invariant metric (15) becomes

$$G = \left(\mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V - \sum_{m=1}^{n-2} \mu_m \mathrm{d}N_m\right)^2 + \Lambda\left[(ST)^{2k+1}\mathrm{d}S\mathrm{d}T + (VP)^{2k+1}\mathrm{d}V\mathrm{d}P + \sum_{m=1}^{n-2}(N_m\mu_m)^{2k+1}\mathrm{d}N_m\mathrm{d}\mu_m\right]. \tag{17}$$

For the space of equilibrium states $\mathcal{E}$ we choose the extensive variables $E^a = \{S, V, N_m\}$ with the embedding map $\varphi : \{E^a\} \mapsto \{Z^A\}$. Then, the condition $\varphi^*(\Theta) = 0$ generates the first law of thermodynamics and the equilibrium conditions

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{m=1}^{n-2} \mu_m \mathrm{d}N_m, \tag{18}$$

$$T = \frac{\partial U}{\partial S}, \qquad P = -\frac{\partial U}{\partial V}, \qquad \mu_m = \frac{\partial U}{\partial N_m}, \tag{19}$$

respectively. Furthermore, the metric of $\mathcal{E}$ is determined by (16) that becomes

$$\begin{aligned} g = \Lambda \Bigg\{ & \left(S\frac{\partial U}{\partial S}\right)^{\tilde{k}} \frac{\partial^2 U}{\partial S^2}\mathrm{d}S^2 + \left(V\frac{\partial U}{\partial V}\right)^{\tilde{k}} \frac{\partial^2 U}{\partial V^2}\mathrm{d}V^2 + \sum_{m=1}^{n-2}\left(N_m\frac{\partial U}{\partial N_m}\right)^{\tilde{k}} \frac{\partial^2 U}{\partial N_m^2}\mathrm{d}N_m^2 \\ & + \left[\left(S\frac{\partial U}{\partial S}\right)^{\tilde{k}} + \left(V\frac{\partial U}{\partial V}\right)^{\tilde{k}}\right]\frac{\partial^2 U}{\partial S\partial V}\mathrm{d}S\mathrm{d}V + \left[\left(S\frac{\partial U}{\partial S}\right)^{\tilde{k}} + \sum_{m=1}^{n-2}\left(N_m\frac{\partial U}{\partial N_m}\right)^{\tilde{k}}\right]\frac{\partial^2 U}{\partial S\partial N_m}\mathrm{d}S\mathrm{d}N_m \\ & + \left[\left(V\frac{\partial U}{\partial V}\right)^{\tilde{k}} + \sum_{m=1}^{n-2}\left(N_m\frac{\partial U}{\partial N_m}\right)^{\tilde{k}}\right]\frac{\partial^2 U}{\partial V\partial N_m}\mathrm{d}V\mathrm{d}N_m \Bigg\}, \end{aligned} \tag{20}$$

where $\tilde{k} = 2k + 1$. This is the most general metric corresponding to a multicomponent system with $n - 2$ different species. This metric turns out to be useful to describe chemical reactions which can then be classified in accordance to the geometric properties of the manifold $(\mathcal{E}, g)$. This result will be presented elsewhere.

5.1. The ideal gas

Consider a monocomponent ideal gas characterized by two degrees of freedom ($n = 2$) and the fundamental equation $U(S, V) = [\exp(S/\kappa)/V]^{2/3}$, where $\kappa = \text{const.}$ [12]. It is convenient to use the entropy representation in which the first law reads $\mathrm{d}S = (1/T)\mathrm{d}U + (P/T)\mathrm{d}V$, and the equilibrium conditions are $1/T = \partial S/\partial U$ and $P/T = \partial S/\partial V$. Consequently, for the phase space we can use the coordinates $Z^A = \{S, U, V, 1/T, P/T\}$ and the metric (15) takes the form

$$G = \left(\mathrm{d}S - \frac{1}{T}\mathrm{d}U - \frac{P}{T}\mathrm{d}V\right)^2 + \Lambda\left[\left(\frac{U}{T}\right)^{2k+1}\mathrm{d}U\mathrm{d}\left(\frac{1}{T}\right) + \left(\frac{VP}{T}\right)^{2k+1}\mathrm{d}V\mathrm{d}\left(\frac{P}{T}\right)\right]. \quad (21)$$

Moreover, the metric for the space of equilibrium can be derived from Eq. (16):

$$g = \Lambda\left\{\left(U\frac{\partial S}{\partial U}\right)^{2k+1}\frac{\partial^2 S}{\partial U^2}\mathrm{d}U^2 + \left(V\frac{\partial S}{\partial V}\right)^{2k+1}\frac{\partial^2 S}{\partial V^2}\mathrm{d}V^2 + \left[\left(U\frac{\partial S}{\partial U}\right)^{2k+1} + \left(V\frac{\partial S}{\partial V}\right)^{2k+1}\right]\frac{\partial^2 S}{\partial U\partial V}\mathrm{d}U\mathrm{d}V\right\}. \quad (22)$$

This form of the thermodynamic metric is valid for any system with two degrees of freedom represented by the extensive variables U and V. To completely determine the metric it is only necessary to specify the fundamental equation $S = S(U, V)$. For an ideal gas $S(U, V) = \frac{3\kappa}{2}\ln U + \kappa\ln V$, and the metric becomes

$$g = -\kappa^{2k+2}\Lambda\left[\left(\frac{3}{2}\right)^{2k+2}\frac{\mathrm{d}U^2}{U^2} + \frac{\mathrm{d}V^2}{V^2}\right]. \quad (23)$$

All the geometrothermodynamical information about the ideal gas must be contained in the metrics (21) and (23). First, we must show that the subspace of equilibrium $(\mathcal{E}, g)$ determines an extremal hypersurface in the phase manifold $(\mathcal{T}, G)$. Introducing (21) and (23) into the Nambu–Goto equations (12), the system reduces to

$$\frac{\partial\Lambda}{\partial U} + \frac{3\kappa}{2U^2}\frac{\partial\Lambda}{\partial Z^3} + 2(k+1)\frac{\Lambda}{U} = 0, \quad (24)$$

$$\frac{\partial\Lambda}{\partial V} + \frac{\kappa}{V^2}\frac{\partial\Lambda}{\partial Z^4} + 2(k+1)\frac{\Lambda}{V} = 0. \quad (25)$$

If we choose $\Lambda = \text{const.}$ and $k = -1$, we obtain a particular solution which is probably the simplest one. This shows that the geometry of the ideal gas is a solution to the differential equations of GTD and, consequently, determines an extremal hypersurface of the thermodynamic phase space.

We now investigate the geometry of the space of equilibrium states of the ideal gas. As can be seen from Eq. (23), the geometry is described by a 2-dimensional conformally flat metric. If we calculate the curvature scalar R, and replace in the result the differential conditions (24) and (25), we obtain

$$R \propto 3V^2\left\{2U^2\Lambda\frac{\partial^2\Lambda}{\partial U\partial Z^3} + \frac{\partial\Lambda}{\partial Z^3}\left[3\kappa\frac{\partial\Lambda}{\partial Z^3} + 2(k+1)U\Lambda\right]\right\} + 4\left(\frac{3}{2}\right)^{2k+2}U^2\left\{V^2\Lambda\frac{\partial^2\Lambda}{\partial V\partial Z^4} + \frac{\partial\Lambda}{\partial Z^4}\left[\kappa\frac{\partial\Lambda}{\partial Z^4} + 2(k+1)V\Lambda\right]\right\}. \quad (26)$$

We see that it is possible to choose the conformal factor Λ such that $R = 0$. For instance, the choice $\Lambda = \text{const.}$ is a particular solution which also satisfies the differential conditions (24) and (25) for $k = -1$. Consequently, we have shown that the ideal gas can be represented by a flat metric in the space of equilibrium states. This result agrees with our intuitive expectation that a thermodynamic metric with zero curvature should describe a system in which no thermodynamic interaction is present. The freedom involved in the choice of the function Λ is associated to the well-known fact that any 2-dimensional space is conformally flat.

We now investigate the geodesic equations (14). For concreteness we take the values $\Lambda = -1$ and $k = -1$. Then, the metric takes the form $g = \mathrm{d}U^2/U^2 + \mathrm{d}V^2/V^2$ which can be put in the obvious flat form

$$g = \mathrm{d}\xi^2 + \mathrm{d}\eta^2 \quad (27)$$

by means of the transformation $\xi = \ln U$, $\eta = \ln V$, where for simplicity we set the additive constants of integration such that $\xi, \eta \geq 0$. The solutions of the geodesic equations are represented by straight lines, $\xi = c_1\eta + c_0$, with constants c_0 and c_1. In this representation, the entropy becomes a simple linear function of the coordinates, $S = (3\kappa/2)\xi + \kappa\eta$. Since each point on the $\xi\eta$-plane can represent an equilibrium state, the geodesics should connect those states which are allowed by the laws of thermodynamics. For instance, consider all geodesics with initial state $\xi = 0$ and $\eta = 0$. Then, any straight line pointing outwards of the initial state and contained inside the allowed positive quadrant connect states with increasing entropy. A quasi-static process connecting states in the inverse direction is not allowed by the second law. Consequently, the affine parameter τ along the geodesics can actually be interpreted as a time parameter and the direction of the geodesics indicates the "direction of time". A detailed analysis of these geodesics is presented elsewhere [19].

5.2. The van der Waals gas

A more realistic model of a gas, which takes into account the size of the particles and a pairwise attractive force between the particles of the gas, is based upon the van der Waals fundamental equation

$$S = \frac{3\kappa}{2}\ln\left(U + \frac{a}{V}\right) + \kappa\ln(V-b), \tag{28}$$

where a and b are constants. The metric of the manifold $\mathcal{T}$ is as before (21). For simplicity we consider the particular case with $k = -1$. Then, introducing the fundamental equations (28) into the metric (22), the metric of the manifold $\mathcal{E}$ reads

$$g = \frac{\Lambda}{U(U+a/V)}\left[-\mathrm{d}U^2 + \frac{U}{V^3}\frac{a(a+2UV)(3b^2-6bV+V^2)-2U^2V^4}{(V-b)(3ab-aV+2UV^2)}\mathrm{d}V^2 \right.$$
$$\left. + \frac{a}{V^2}\frac{3ab-aV-3bUV+5UV^2}{3ab-aV+2UV^2}\mathrm{d}U\mathrm{d}V\right]. \tag{29}$$

The curvature of this thermodynamic metric is in general nonzero, reflecting the fact that the thermodynamic interaction of the van der Waals gas is nontrivial. The differential equations (12) can be computed for this case by using the phase space metric (21), with $k = -1$, and the metric (29) for the space of equilibrium. It turns out that they reduce to only two first-order partial differential equations

$$\frac{\partial\Lambda}{\partial U} + F_3\frac{\partial\Lambda}{\partial Z^3} + F_4\frac{\partial\Lambda}{\partial Z^4} + F_0\Lambda = 0, \tag{30}$$

$$\frac{\partial\Lambda}{\partial V} + G_3\frac{\partial\Lambda}{\partial Z^3} + G_4\frac{\partial\Lambda}{\partial Z^4} + G_0\Lambda = 0, \tag{31}$$

where F_0, F_3, F_4, G_0, G_3, and G_4 are fixed rational functions of U and V. Because of the arbitrariness of the conformal factor Λ, it is always possible to find solutions to the above system. We conclude that there exists a family of nonflat thermodynamic metrics that determines an extremal hypersurface in the phase space, and can be used to describe the geometry of the van der Waals gas. The corresponding geodesic equations are highly nontrivial and require a detailed numerical analysis which is beyond the scope of the present work.

5.3. New solutions

The above applications of GTD show that from a given fundamental equation one can find the corresponding geometric representation. It is also possible to handle the inverse problem, i.e., we can find fundamental equations which are compatible with the geometric structures of GTD and correspond to thermodynamic systems. Consider a very simple generalization of the ideal gas

$$S(U,V) = \frac{3\kappa}{2}\ln U + \kappa c\ln V, \tag{32}$$

where c is a constant. Although this seems to be a trivial generalization, we will see that it can contain interesting thermodynamic systems. As before, we choose the thermodynamic metrics in $\mathcal{T}$ and $\mathcal{E}$ as in Eqs. (21) and (22). The Nambu–Goto equations (12) are identically satisfied if we choose $\Lambda = -1$ and $k = -1$. Then, the space of states turns out to be flat and, according to our interpretation of thermodynamic curvature, the system is characterized by the absence of thermodynamic interaction. The geometric analysis of the manifold $\mathcal{E}$ is similar to that carried out in Section 5.1. To interpret this solution it is convenient to use the energy representation in which the fundamental equation is $U(S,V) = \frac{e^{2S/3\kappa}}{V^{2c/3}}$. The conditions for equilibrium (19) and Euler's identity (5) lead to

$$\frac{\partial U}{\partial S} = T = \frac{2}{3\kappa}U, \qquad \frac{\partial U}{\partial V} = -P = -\frac{2c}{3}\frac{U}{V}, \qquad S = \frac{3\beta\kappa}{2} + c\kappa, \tag{33}$$

where β is the degree of homogeneity of the thermodynamic potential. Hence,

$$U = \frac{3\kappa}{2}T, \qquad PV = \kappa cT, \tag{34}$$

are the equations of state. The internal energy of the system coincides with that of an ideal gas, and the only difference appears in the behavior of the pressure P which can be controlled by the constant c. If we define the energy density $\rho = U/V$, then from the above equations we obtain the "barotropic" equation of state $P = (2c/3)\rho$. For the particular choice $c = -3/2$, we obtain $P + \rho = 0$ with a negative value of the pressure. Consequently, the fundamental equation (32) describes a system with no thermodynamic interaction and negative pressure. This behavior resembles that of the dark energy which is responsible for the recently observed acceleration of the universe. A more detailed analysis will be necessary to determine if the above thermodynamic system can be used as a realistic model for dark energy.

The above example can be generalized to include a complete family of noninteracting thermodynamic systems. In fact, if we consider a system with n degrees of freedom and the separable fundamental equation

$$S(E^1, \ldots, E^n) = S_1(E^1) + \cdots + S_n(E^n), \tag{35}$$

where $S_1, \ldots, S_2$ are arbitrary smooth functions, we obtain from Eq. (16), with $\Lambda = \text{const}$, a diagonal thermodynamic metric of the form $g = g_{11}(E^1)(\mathrm{d}E^1)^2 + \cdots + g_{nn}(E^n)(\mathrm{d}E^n)^2$. The curvature of this metric vanishes as can be seen by applying the coordinate transformation $g_{aa}(E^a)\mathrm{d}E^a = \mathrm{d}X^a$ (no summation over repeated indices) which transforms the metric into the flat form $g = \delta_{ab}\mathrm{d}X^a\mathrm{d}X^b$. In this family of thermodynamically noninteracting systems one can include, for instance, all known multicomponent generalizations of the ideal gas.

Turning back to the case of systems with two degrees of freedom, we mention that it is possible to find complete classes of solutions of the form

$$S = S_0 U^\alpha V^\beta \quad \text{or} \quad S = S_0 \ln(U^\alpha + cV^\beta), \tag{36}$$

where S_0, α, β, and c are arbitrary real constants. It turns out that in all these cases, one can choose Λ and k in such a way that the resulting thermodynamic metric (22) is curved and satisfies the Nambu–Goto equations (12). This means that the above fundamental equations can, in principle, represent nontrivial thermodynamically interacting systems. It is not difficult to find exact solutions to the Nambu–Goto equations which are also compatible with the metric structure (21) of the phase manifold and, consequently, with the thermodynamic metric of the manifold of equilibrium states. Nevertheless, a more detailed analysis will be necessary in order to establish the physical significance of the solutions obtained in this manner.

6. Discussion and conclusions

Geometrothermodynamics (GTD) is a formalism that has been developed recently to describe ordinary thermodynamics by using differential geometry. To this end, two known structures were joined together in a consistent manner: The natural contact structure of the thermodynamic phase space $\mathcal{T}$ and the metric structure of the space of equilibrium states $\mathcal{E}$. In GTD, one introduces a Legendre invariant metric G in $\mathcal{T}$ which naturally induces a thermodynamic metric g in $\mathcal{E}$ by means of the pullback φ^* associated to the map $\varphi : \mathcal{E} \mapsto \mathcal{T}$. This additional construction confers to $\mathcal{T}$ and $\mathcal{E}$ the geometric structure of Riemannian manifolds. In this work we established that φ can be handled as a harmonic map that allows us to introduce a Polyakov-like action in $\mathcal{E}$. Taking into account that the metric of $\mathcal{E}$ is induced by the metric of $\mathcal{T}$, the variation of the action of the harmonic map leads to a set of second-order differential equations which can be identified as the Nambu–Goto motion equations. This is the main result that allows us to interpret thermodynamic systems as classical bosonic strings. Thermodynamic systems are characterized in GTD by a specific metric g which determines the properties of $\mathcal{E}$. Therefore, if g satisfies the Nambu–Goto equations, we can conclude that it describes an n-dimensional membrane that "lives" in the background manifold $\mathcal{T}$. If we demand Legendre invariance of G, the background $\mathcal{T}$ turns out to be curved in general. So the explicit case of a thermodynamic system with two degrees of freedom and thermodynamic metric g resembles the dynamics of a string moving on a nonflat background G. The analogy, however, is only at the mathematical level. In fact, in string theory the metrics g and G must be Lorentzian metrics in order to incorporate into the theory a relativistic dynamical behavior with a genuine time parameter. In GTD the metrics are not necessarily Lorentzian and there is no explicit time parameter so that we cannot really talk about dynamics. This is in agreement with our intuitive understanding of ordinary thermodynamics of equilibrium states in which, strictly speaking, there is no dynamics at all and we are in fact handling with thermostatics. Non-equilibrium thermodynamics is a different subject that cannot be incorporated in a straightforward manner in GTD as formulated here. A generalization of the geometric structures considered in this work will be necessary in order to analyze more general scenarios in which non-equilibrium states cannot be neglected. This is a task for future investigations.

Starting from the most general Legendre invariant metric in $\mathcal{T}$ we were able to show that the ideal gas and the van der Waals gas are concrete examples of 2-dimensional extremal hypersurfaces $\mathcal{E}$ embedded in a 5-dimensional curved manifold $\mathcal{T}$. In the case of an ideal gas, the geometry of $\mathcal{E}$ is flat, whereas for the van der Waals gas the manifold $\mathcal{E}$ is curved. This reinforces the interpretation of the thermodynamic curvature as a measure of thermodynamic interaction. Our formalism is such that one only needs to postulate an arbitrary fundamental equation to derive the thermodynamic metric g of $\mathcal{E}$. One can then derive from the Nambu–Goto equations the conditions that the fundamental equation and g must satisfy in order to correspond to an extremal hypersurface of $\mathcal{T}$. In this manner, we obtained simple generalizations of the ideal gas with vanishing thermodynamic curvature. It is also possible to derive new solutions with nonvanishing thermodynamic curvature.

We used the concept of thermodynamic length in the manifold of equilibrium states $\mathcal{E}$ as a quantity representing the geometric distance between two different states. It involves the explicit form of the thermodynamic metric g. By demanding that the thermodynamic length be an extremal, we obtained that the geodesic equations for g must be satisfied. Not all the solutions of the geodesic equations need to be physically realizable since they could connect, in a given direction, equilibrium states that are not compatible with the laws of thermodynamics. We interpret geodesics which connect thermodynamically meaningful states as representing a dense succession of quasi-static states. Moreover, we showed that the affine parameter along a geodesic can be used to label each of the equilibrium states which can be reached in a specific quasi-static thermodynamic process. The affine parameter can then be chosen in such a way that it increases as the entropy of a quasi-static process increases. Then, a suitable selection allows us to interpret the affine parameter as a "time" parameter with a specific direction which coincides with the direction of entropy increase. The geodesic equations for the more general van der Waals gas cannot be solved analytically. It will be necessary to perform a detailed numerical study of these equations in order to corroborate the physical significance of the geodesics.

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