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On contact and metric structures on thermodynamic spaces *

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Abstract

In this article there are introduced and discussed two basic geometrical structures of the state space of classical thermodynamics. One of them is the so-called contact structure which is related to the first law of thermodynamics. The other is the metrical (Riemannian) structure related to the second law of thermodynamics. It is shown how these structures can be introduced either on the phenomenological or statistical way.

1 Introduction

The basic problem of any physical theory is to find the proper set M of all plausible states, i.e. the so-called *state space* of the system. The other necessary ingredient is the structure of this space. The structure is usually defined by means of a tensor, vector or covector field, or by connection. The group preserving the geometrical structure of M is considered as the symmetry group of the theory. From this point of view any physical theory can treated as a branch of geometry in the broadest meaning of this word. This approach is well known for instance in classical mechanics, special and general relativity, electrodynamics, gauge fields, quantum mechanics, and so on.

Contrary to the above-mentioned theories the situation is not so clear in thermodynamics. First of all there are two: phenomenological and statistical approaches to the thermal phenomena. For the second, the situation is relatively simple only for homogeneous equilibrium systems. It complicates remarkably for general nonequilibrium systems where one has to deal with a big number of macroscopic variables of various types.

The aim of this paper is to study some general aspects of classical thermodynamics from geometrical point of view. We shall show that the contact and the metric geometries can be associated with the first and second laws of thermodynamics, respectively. These two structures can be defined on the so-called *thermodynamic phase space* (TPS). For a thermodynamic system

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having n macroscopic degrees of freedom, TPS is a $(2n+1)$-dimensional manifold. Its contact structure may be given by a nondegenerate Pfaff form θ, for instance by $\theta = dU - TdS + PdV - \mu dN$ for $n = 3$ in the energy representation. It is important that all variables in θ are treated as independent. The basic idea is to take the state space as big as possible, i.e. to keep thermodynamic parameters independent as long as possible. Without that we would not be able to find the full group of symmetries of thermodynamics, and in particular the continuous symmetries. Only when we wish to draw thermodynamic conclusions from our considerations, we impose constraints on the thermodynamic parameters resulting from the laws of thermodynamics, and thus we reduce the description to some submanifolds of TPS.

The developed formalism is in many points similar to the symplectic formalism of classical Hamiltonian mechanics, with TPS and contact form playing in a sense the role analogous to the mechanical phase space and symplectic form. An important example of this similarity is the fact that to every function f on TPS one can associate a contact tangent vector field X_f generating a 1-parameter group of continuous contact transformations. The analogy is, however, not complete because under some conditions such transformations can be regarded as thermodynamic processes while in other cases only as a 1-parameter deformations of some submanifolds (the so-called Legendre submanifolds $\mathcal{S} \subset M$) representing thermodynamic states. In the latter case from a given thermodynamic system we may obtain a 1-parameter family of thermodynamic systems with different constitutive relations.

Although both these geometrical structures (contact and metric) can be obtained on a purely phenomenological as well as on a statistical way, in this article the metric structure will be discussed only in the statistical framework.

2 Contact manifolds and thermodynamic phase space

In this section we present some basic facts about contact geometry [2–8] and about its applications to thermodynamics.

DEFINITION 2.1. A differentiable $(2n+1)$-dimensional manifold M is said to be a *contact manifold* if it caries a global differential 1-form θ such that

$$\theta \wedge (d\,\theta)^n \neq 0\,, \tag{2.1}$$

where $\wedge$ denotes exterior product and $(d\,\theta)^n = d\,\theta \wedge \cdots \wedge d\,\theta$ (n times). The above condition means that θ is nondegenerate; it is called the *contact form.*

According to the Darboux theorem [2], there exist local canonical (contact) coordinates (x^0, x^i, p_i), $i = 1, \ldots, n$, in which θ has the simplest canonical form

$$\theta = dx^0 + p_i\,dx^i\,, \qquad i = 1, \ldots, n\,. \tag{2.2}$$

The summation convention, i.e. summation over repeated indices, has been assumed from now on. The nondegeneracy condition (2.1) can be geometrically interpreted in several ways. The simplest one results from (2.2) from which we see that $\theta \wedge (d\theta)^n$ is the volume form on M.

In thermodynamics M is usually a subset of $\mathbb{R}^{2n+1}$ and in the energy representation [1] we have the following correspondence

$$(x^0; x^1, x^2, x^3, \ldots; p_1, p_2, p_3, \ldots) \Longleftrightarrow (U; S, V, N_1, \ldots; -T, P, -\mu_1, \ldots), \tag{2.3}$$

and respectively,

$$\theta^U = dU - T\,dS + P\,dV - \mu_k\,dN^k, \qquad k = 1, \ldots, n-2, \tag{2.4}$$

or in the entropy representation

$$(x^0; x^1, x^2, x^3, \ldots; p_1, p_2, p_3, \ldots) \Longleftrightarrow (S; U, V, N_1, \ldots; \frac{-1}{T}, \frac{-P}{T}, \frac{\mu_1}{T}, \ldots) \tag{2.5}$$

$$\theta^S = dS - \frac{1}{T}dU - \frac{P}{T}dV + \frac{\mu_k}{T}dN^k, \qquad k = 1, \ldots, n-2, \tag{2.6}$$

where all the symbols have their standard thermodynamic meaning [1]. It is important that in each case all these $2n+1$ variables are treated as independent on M. Of course, we could have worked in any other representation. Note that $\theta^S = -T^{-1}\theta^U$.

The 1-form θ defines on M a $2n$-dimensional distribution, i.e. a field of tangent $2n$-dimensional hyperplanes which locally can be given (spanned) by $2n$ vector fields, e.g. by [8]

$$\mathcal{P}_k = \partial/\partial p_k, \qquad \mathcal{X}_k = \partial/\partial x^k - p_k\,\partial/\partial x^0, \qquad k = 1, \ldots, n. \tag{2.7}$$

The geometrical meaning of this distribution follows from the fact that $\theta(\mathcal{P}_k) = \theta(\mathcal{X}_k) = 0$, i.e. θ annihilates all the fields (2.7). This distribution is called a *contact distribution* or a *contact structure* on M [2]. Note that another 1-form $h\theta$, where $h \neq 0$ is any function on M, also annihilates the fields (2.7). Therefore, the notion of contact structure is unique, whereas the associated contact form is determined only up to a nonzero factor.

There exists also a dual 1-dimensional *characteristic distribution* defined by a global *characteristic vector field* ξ such that

$$i_\xi\, d\theta = 0, \qquad i_\xi\,\theta \equiv \theta(\xi) = 1, \qquad (\text{or} \quad i_\xi\,(\theta \wedge (d\theta)^n) = (d\theta)^n), \tag{2.8}$$

where i_ξ denotes the interior product (contraction) of θ with ξ. In contact coordinates

$$\xi = \partial/\partial x^0. \tag{2.9}$$

The fields $\mathcal{P}_k$, $\mathcal{X}_k$ and ξ satisfy the following commutation relations [8],

$$[\mathcal{X}_i, \mathcal{X}_j] = [\mathcal{P}_i, \mathcal{P}_j] = [\mathcal{X}_i, \xi] = [\mathcal{P}_i, \xi] = 0, \quad [\mathcal{X}_i, \mathcal{P}_j] = \delta_{ij}\xi. \tag{2.10}$$

The last commutator shows that the contact distribution is not involutive. Geometrically it means that the contact distribution is nonintegrable. In fact, due to (2.1) it is maximally nonintegrable.

3 Legendre submanifolds and the first law of thermodynamics

In thermodynamics the major role is played by the maximum dimensional integral submanifolds of the contact distribution, by the so-called *Legendre submanifolds* denoted here by $\mathcal{S}$. The name given to $\mathcal{S}$ is justified by the fact that the well-known Legendre transformations preserve $\mathcal{S}$, i.e. they map any Legendre submanifold onto itself. Because the contact distribution is maximally nonintegrable, the dimension of any Legendre submanifold coincides with the number of thermodynamic degrees of freedom n.

THEOREM 3.1. *Let (M,θ) be a $(2n+1)$-dimensional contact manifold. The maximal dimension of integral submanifolds of the contact distribution (or, equivalently, of integral submanifolds of the eq. $\theta = 0$) is equal to n.*

Instead of a formal proof we only show that the existence of n-dimensional integral submanifolds is guaranteed because they may be given for instance by $n+1$ equations $x^l = C^l$, $l = 0, 1, \ldots, n$, where C^l are arbitrary constants, or by $n+1$ equations

$$x^0 = \phi(x^1, \ldots, x^n)\,, \qquad p_i = -\frac{\partial\phi(x^1, \ldots, x^n)}{\partial x^i}\,, \qquad i = 1, \ldots, n\,. \tag{3.1}$$

A local description of Legendre submanifolds in terms of a generating function ϕ is given by the following theorem [2] which generalizes the formulae (3.1).

THEOREM 3.2. *For any partition $I \cup J$ of the set of indices $\{1, \ldots, n\}$ into two disjoint subsets I and J, and for a function $\phi(p_I, x^J)$ of n variables p_i, $i \in I$, and x^j, $j \in J$, the $n+1$ equations*

$$x^i \;=\; \frac{\partial\phi}{\partial p_i}\,, \qquad p_j \;=\; -\frac{\partial\phi}{\partial x^j}\,, \qquad x^0 \;=\; \phi - p_i\frac{\partial\phi}{\partial p_i} \tag{3.2}$$

define a Legendre submanifold $\mathcal{S}$ of M^{2n+1}. Conversely, every Legendre submanifold of (M,θ) in a neighbourhood of any point is defined by these equations for at least one of the 2^n possible choices of the subset I.

Let us stress that ϕ is a function of only n variables and that these variables cannot belong to the same pair of conjugate variables (x^i, p_i), conjugate in the sense as they appear in θ.

The first law of thermodynamics can be geometrically expressed in TPS in terms of Legendre submanifolds according to the following postulate.

POSTULATE (first law of thermodynamics). Any equilibrium thermodynamic system is represented in an appropriate thermodynamic phase space (M,θ) by Legendre submanifolds of the eq. $\theta = 0$.

We have used here plural because for any real thermodynamic system we need several Legendre submanifolds to represent its states. Actually, each thermodynamic phase will be represented by a fragment of a Legendre submanifold. Only ideal gas, for which no phase transitions occur, will be represented by one smooth Legendre submanifold.

The total number of Legendre submanifolds in M is infinite. In fact, through every point of M one has an infinite number of them. However, only some of these submanifolds represent states of real thermodynamic systems.

From Theorem 3.2 we see that in the contact coordinates (cf. (2.2)) any $\mathcal{S}$ can be, in principle, represented in equivalent ways by various functions ϕ of n variables (one has 2^n choices of n independent variables). These functions correspond to various thermodynamic potentials, e.g. to energy, entropy, enthalpy, and so on. Therefore, for a given ϕ the set of equations (3.2) may be interpreted as one fundamental relation and n equations of state [1], cf. also (3.1).

4 Contact transformations and thermodynamic symmetries

We shall consider now a group of diffeomorphisms (symmetries) Λ of M which preserve its contact structure. Usually in thermodynamics there are considered only discrete Legendre transformations. On the contrary, we shall concentrate here on the continuous transformations and on their generators, i.e. on contact vector fields.

DEFINITION 4.1. A diffeomorphism $\lambda : M \to M$ is said to be a *contact diffeomorphism* if it preserves the contact distribution of M, i.e. if λ is such that

$$\lambda^* \theta = \rho \theta, \qquad \lambda \in \Lambda, \tag{4.1}$$

where ρ is a nowhere vanishing function on M and λ^* is the pull-back map induced by λ.

The new transformed form $\lambda^*\theta$ is again a contact form because it is also nondegenerate, $\rho\theta \wedge (d(\rho\theta))^n = \rho^{n+1}\theta \wedge (d\theta)^n \neq 0$. Thus λ preserves the contact structure but not the contact form. Diffeomorphisms with $\rho = 1$ preserve also the contact form and are called strict contact transformations.

Consequently, by a 1-parameter group of *continuous contact transformations* we mean a subgroup of mappings $\lambda_t : M \to M$ of Λ which preserve the contact distribution, i.e. λ_t are such that

$$\lambda_t^* \theta = \rho_t \theta, \qquad \lambda_t \in \Lambda, \qquad \rho_t \neq 0. \tag{4.2}$$

Let X be a generator of this 1-parameter subgroup of Λ, that is X satisfies the formula

$$(Xh)(m) = \frac{d}{dt}\bigg|_{t=0} \lambda_t^* h(m) \equiv \frac{d}{dt}\bigg|_{t=0} h(\lambda_t(m)), \qquad \forall m \in M, \tag{4.3}$$

for any smooth function h on M. Hence X is a vector field associated to λ_t.

The definition (4.2) of λ_t is equivalent to

$$\mathcal{L}_X\theta \equiv \frac{d}{dt}\bigg|_{t=0} \lambda_t^*\theta = \tau_t\theta, \tag{4.4}$$

where $\tau_t = d\rho_t/dt$ and $\mathcal{L}_X$ denotes Lie derivative [9,10]. Thus we see that $\mathcal{L}_X\theta$ is a product of θ and a function τ_t on M. If $\tau_t = 0$, we say that θ is invariant of λ_t. This justifies the following more general definition.

DEFINITION 4.2. A vector field X on M is said to be a *contact vector field* if it preserves the contact structure of M or, equivalently, if

$$\mathcal{L}_X\theta \;=\; \tau\,\theta\,, \qquad \text{i.e.} \qquad \mathcal{L}_X\theta\wedge\theta = 0\,. \tag{4.5}$$

Contact vector fields do not belong to the contact distribution but they do form a Lie algebra (see below the properties of X_f).

The contact distribution, spanned by $\mathcal{P}_k$ and $\mathcal{X}_k$, and the characteristic distribution spanned by ξ can be called the horizontal and vertical distributions, respectively. This is justified by the fact that actually θ is a connection form [9–11] on M. Thus, taking these $2n+1$ vector fields as a basis, any vector field X on M may be then decomposed into the horizontal hX and vertical vX components,

$$X = vX + hX\,, \qquad \text{where} \qquad vX \;:=\; \theta(X)\xi\,, \quad hX \;:=\; X - vX\,. \tag{4.6}$$

This decomposition allows one to introduce the notion of covariant differentiation on M. For a real-valued function f on M its covariant differential Df is defined by

$$Df(X) \;=\; df(hX)\,, \qquad \text{i.e.} \qquad Df \;=\; df - (\xi f)\theta\,, \tag{4.7}$$

for any vector field X on M.

DEFINITION 4.3. By a contact vector field *associated* to a function f on M we mean a vector field X_f defined by

$$i_{X_f}\theta \;\equiv\; \theta(X_f) \;=\; f\,, \qquad i_{X_f}d\theta \;=\; -Df\,. \tag{4.8}$$

The two above equations define the vertical and horizontal components of X_f, respectively. To sum up, the construction of X_f requires the three steps: $f \to df \to Df = df - (\xi f)\theta \to X_f$.

In contact coordinates X_f is given by [11–13]:

$$X_f = \frac{\partial f}{\partial p_i}\frac{\partial}{\partial x^i} + \left(p_i\frac{\partial f}{\partial x^0} - \frac{\partial f}{\partial x^i}\right)\frac{\partial}{\partial p_i} + \left(f - p_i\frac{\partial f}{\partial p_i}\right)\frac{\partial}{\partial x^0}\,. \tag{4.9}$$

Note that X_f is a linear combination of the vector fields $\mathcal{X}_k$, $\mathcal{P}_k$ and ξ, namely $X_f = (\mathcal{P}_i f)\mathcal{X}_i - (\mathcal{X}_i f)\mathcal{P}_i + f\xi$, and hence we see that X_f does not belong to the contact distribution because of the last term $f\xi$.

From the definition of X_f and the property of Lie derivative, $\mathcal{L}_X = i_X d + d i_X$ [9,10], it is easy to see that X_f is a contact vector field because

$$\mathcal{L}_{X_f}\theta = d\,i_{X_f}\theta + i_{X_f}d\theta \;=\; df - Df \;=\; (\xi f)\theta \sim \tau\theta\,. \tag{4.10}$$

This also shows that X_f is a generator of a continuous contact transformation on M with $\tau = \xi f$. Moreover, the fields X_f form a Lie algebra because

$$\begin{aligned}\mathcal{L}_{[X_f,X_g]}\theta &= [\mathcal{L}_{X_f},\mathcal{L}_{X_g}]\theta \\ &= \mathcal{L}_{X_f}((\xi g)\theta) - \mathcal{L}_{X_g}((\xi f)\theta) = \left(\mathcal{L}_{X_f}(\xi g) - \mathcal{L}_{X_g}(\xi f)\right)\theta \sim \tau\theta\,.\end{aligned} \tag{4.11}$$

Taking now into account the general form of vector fields X on M (cf. (4.3) written in coordinates),

$$X = \dot{x}^i \frac{\partial}{\partial x^i} + \dot{p}_i \frac{\partial}{\partial p_i} + \dot{x}^0 \frac{\partial}{\partial x^0}, \tag{4.12}$$

we see that the components of X_f define a flow on M

$$\begin{aligned} \dot{x}^i &= \frac{\partial f}{\partial p_i}, \\ \dot{p}_i &= p_i \frac{\partial f}{\partial x^0} - \frac{\partial f}{\partial x^i}, \\ \dot{x}^0 &= f - p_i \frac{\partial f}{\partial p_i}. \end{aligned} \tag{4.13}$$

For a given f we can view (4.13) as a system of $2n + 1$ ordinary differential equations for the integral curves of this flow.

The situation is similar but more general than in Hamiltonian conservative mechanics in which one has a $2n$-dimensional phase space (usually a cotangent bundle) endowed with a symplectic 2-form ω ($\omega = dp_i \wedge dq^i$, $\omega^n \neq 0$, $d\omega = 0$). The dynamics of a system with a Hamilton function $H(p, q)$ is governed by a Hamiltonian vector field X_H defined by H and ω according to the formula $i_{X_H} \omega = -dH$. X_H is given by

$$X_H = \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q^i} - \frac{\partial H}{\partial q^i} \frac{\partial}{\partial p_i} \left(\equiv \dot{q}^i \frac{\partial}{\partial q^i} - \dot{p}_i \frac{\partial}{\partial p_i} \right), \tag{4.14}$$

which means that the Hamiltonian flow is given by $2n$ Hamilton equations

$$\dot{q}^i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q^i}. \tag{4.15}$$

By analogy, the flow induced by X_f represents a sort of *contact Hamilton equations* with a *contact Hamiltonian* $f(x^0, x^i, p_i)$. Unfortunately, the form of X_f is far more complicated than the form of X_H in the symplectic case. The components of the contact Hamiltonian flow X_f depend not only on the derivatives of f but also on f itself. Therefore $X_f \neq 0$ even for $f = \text{const}$. Moreover, X_H is tangent to every level surface $H = \text{const}$ because $X_H H \equiv dH(X_H) = 0$. This is not the case with X_f because $X_f f \equiv df(X_f) = f(\xi f)$, and hence X_f in the general case is tangent only to one level surface for which $f = 0$. This property of X_f opens new possibilities for the thermodynamic formalism.

In particular, if it happens that a Legendre manifold $\mathcal{S}$ is contained in the zero level surface of f, i.e. $\mathcal{S} \subset f^{-1}(0)$, then X_f is tangent to $\mathcal{S}$ [11]. In such a case the contact Hamilton equations (4.13) can be interpreted as a thermodynamic process (next section).

5 Examples of X_f and their associated contact flows

As mentioned previously, in thermodynamics M is usually a subset of $\mathbb{R}^{2n+1}$. In this section we shall work in the energy representation [1] in which (cf. (2.3))

$$(x^0; x^1, x^2, x^3, \ldots; p_1, p_2, p_3, \ldots) \Longleftrightarrow (U; S, V, N_1, \ldots; -T, P, -\mu_1, \ldots), \tag{5.1}$$

and respectively,

$$\theta = dU - T\,dS + P\,dV - \mu_k\,dN^k\,, \qquad k = 1, \ldots, n-2\,. \tag{5.2}$$

It is important that, unless restricted to a Legendre submanifold, all these $2n+1$ variables are treated as independent.

Now we shall present some examples of X_f, their associated contact Hamilton equations and integral curves. Some of them describe thermodynamic processes while the other map Legendre submanifolds representing one kind of systems onto submanifolds representing another kind of systems.

EXAMPLE 5.1. For $f = U - TS + RNT - \mu N$, according to (4.9), (5.1) and (5.2) we have

$$X_f = (S - RN)\frac{\partial}{\partial S} + N\frac{\partial}{\partial N} + P\frac{\partial}{\partial P} + RT\frac{\partial}{\partial \mu} + U\frac{\partial}{\partial U}\,, \tag{5.3}$$

and hence the contact Hamilton equations (4.13) (defined by components of X_f) have the form

$$\dot{T} = \dot{V} = 0\,, \quad \dot{P} = P\,, \quad \dot{\mu} = RT\,, \quad \dot{S} = S - RN\,, \quad \dot{N} = N\,, \quad \dot{U} = U\,. \tag{5.4}$$

Their integral curves are given by

$$\begin{gathered} T = T_0\,, \quad P = P_0\,e^t\,, \quad \mu = RT_0 t + \mu_0\,, \\ S = (S_0 - RN_0 t)e^t\,, \quad V = V_0\,, \quad N = N_0\,e^t\,, \quad U = U_0 e^t\,. \end{gathered} \tag{5.5}$$

Because for ideal gas $f = 0$, X_f is tangent to the Legendre submanifold $\mathcal{S}$ representing this gas and describes a 'thermodynamic process' with constant volume V_0 and temperature T_0. It is easy to check that during this 'process' all relations between thermodynamic parameters for ideal gas are preserved, for instance

$$PV = NRT\,, \qquad U = \frac{3}{2}NRT\,, \qquad \text{or} \qquad U = TS - PV + \mu N\,. \tag{5.6}$$

EXAMPLE 5.2. For $f = NRT - \frac{2}{5}TS - \frac{2}{5}\mu N$ one obtains

$$X_f = \left(\frac{2}{5}S - RN\right)\frac{\partial}{\partial S} + \frac{2}{5}N\frac{\partial}{\partial N} - \frac{2}{5}T\frac{\partial}{\partial T} + \left(RT - \frac{2}{5}\mu\right)\frac{\partial}{\partial \mu}\,, \tag{5.7}$$

and thus the integral curves of X_f take the form

$$\begin{gathered} S = (S_0 - RN_o t)\,e^{2t/5}\,, \qquad V = V_0\,, \qquad N = N_0\,e^{2t/5}\,, \\ T = T_0\,e^{-2t/5}\,, \quad P = P_0\,, \quad \mu = (\mu_0 + RT_0 t)\,e^{-2t/5}\,, \quad U = U_0\,. \end{gathered} \tag{5.8}$$

They describe an isobaric, isochoric and isoenergetic 'process'. Again it is easy to prove that the relations (5.6) are preserved.

In the two examples above the functions f have been chosen in such a way that the Legendre submanifold $\mathcal{S}$ of the ideal gas was placed on the level hypersurfaces $f^{-1}(0)$. Therefore, X_f was tangent to $\mathcal{S}$ and could be treated as a 'thermodynamic process'. The situation is quite different if $\mathcal{S}$ is not placed on $f^{-1}(0)$. In the following examples X_f is not tangent to $\mathcal{S}$ and cannot be treated as a generator of a thermodynamic process; but rather as a generator of a 1-parameter family of thermodynamic systems.

EXAMPLE 5.3. Let f be an affine function of the intensive parameters only, $f = a + b^i p_i$. Then the components of X_f have the form

$$\dot{x}^i = b^i\,, \qquad \dot{p}_i = 0\,, \qquad \dot{x}^0 = a\,, \tag{5.9}$$

and subsequently

$$x^i = x^i_0 + b^i t\,, \qquad p_i = p_{i0}\,, \qquad x^0 = x^0_0 + at\,. \tag{5.10}$$

Thus the intensive parameters are kept constant, whereas the extensive ones are linear functions of t. None of Eqs. (5.6) is preserved in this case. Instead, X_f produces a continuous 1-parameter family of thermodynamic systems (1-parameter family of Legendre submanifolds $\mathcal{S}_t$). An interesting situation occurs for f reduced to $f = bP$ [11]. Then $V = V_0 + bT$ while all the other parameters are fixed. For a fixed b, $\mathcal{S}_t$ represents a 1-parameter family of gases of hard spheres (cf. also Example 5.6.).

EXAMPLE 5.4. If $f = a + b_i x^i$ is an affine function of the extensive parameters, then X_f belongs also to the new class of contact vector fields. The integral curves of X_f assume now the form

$$\dot{x}^i = x^i_0\,, \qquad \dot{p}_i = p_{i0} - b_i t\,, \qquad \dot{x}^0 = x^0_0 + (a + b_i x^i_0)\,t\,, \tag{5.11}$$

and they do not represent a thermodynamic process. The meaning of X_f in this case is not clear.

EXAMPLE 5.5. Let us take now $f = x^0 - \phi(x^1, \ldots, x^n)$. Then

$$\dot{x}^i = 0\,, \qquad \dot{p}_i = p_i + \frac{\partial\phi}{\partial x^i}\,, \qquad \dot{x}^0 = x^0 - \phi\,. \tag{5.12}$$

Again X_f produces a 1-parameter family of Legendre submanifolds $\mathcal{S}_t$ from a given $\mathcal{S}$. However, if it happens that $\phi(x^1, \ldots, x^n)$ is such that $x^0 = \phi(x^1, \ldots, x^n)$ represents the fundamental relation [1] for the system (cf. (2.5)), then $X_f|_{\mathcal{S}} = 0$ and $\mathcal{S}$ is obviously preserved.

EXAMPLE 5.6. If we take $f_1 = bP$, where b is a nonnegative constant, the integral curves of $X_{f_1} = b\partial/\partial V$ are such that all parameters are preserved but the volume V changes according to $V = V_0 + bt$. Therefore, X_{f_1} maps ideal gas into a gas of noninteracting hard spheres.

On the other hand, for $f_2 = -aV^{-1}$, $a > 0$, $X_{f_2} = (-a/V)\partial/\partial U - (a/V^2)\partial/\partial P$ is such that (notice a new parameter τ)

$$U = U_0 - \frac{a}{V_0}\tau\,, \qquad P = P_0 - \frac{a}{V_0^2}\tau\,, \tag{5.13}$$

while all the other parameters are preserved. This time one can say that X_{f_2} maps ideal gas into a gas of interacting point like particles.

Now let us take $f = f_1 + f_2 = bP - aV^{-1}$. The integral curves of X_f are such that T, S, N and μ do not change, whereas

$$V = V_0 + bt\,, \qquad U = U_0 - \frac{a}{b}\ln\frac{V_0 + bt}{V_0}\,, \qquad P = P_0 - \frac{at}{V_0(V_0 + bt)}\,. \tag{5.14}$$

The equation of state for the ideal gas, $P_0V_0 = N_0RT_0$, is no more preserved and it goes over into an equation of state

$$\left(P + \frac{at}{V(V - bt)}\right)(V - bt) = NRT\,, \tag{5.15}$$

which for $t = 1$ resembles the well-known van der Waals equation of state. In fact, for a fixed a and a fixed b we have obtained a 1-parameter family of van der Waals gases.

EXAMPLE 5.7. Two other modifications of the van der Waals gas can be obtained if, instead of one transformation induced by $X_{f_1+f_2}$, we consider two consecutive transformations [15]: the one associated to X_{f_1} followed by X_{f_2} and vice versa. We receive two different 2-parameter transformations since the transformations induced by f_1 and f_2 do not commute. This can be seen from the Lie bracket,

$$[X_{f_1}, X_{f_2}] = \left[b\frac{\partial}{\partial V}, -\frac{a}{V}\frac{\partial}{\partial U} - \frac{a}{V^2}\frac{\partial}{\partial P}\right] = \frac{ab}{V^2}\frac{\partial}{\partial U} + \frac{2ab}{V^3}\frac{\partial}{\partial P} \neq 0\,. \tag{5.16}$$

In the case when X_{f_1} is followed by X_{f_2}, instead of (5.15) we receive a 2-parameter family of equations of state

$$\left(P + \frac{a}{V^2}\tau\right)(V - bt) = NRT\,. \tag{5.17}$$

The result is different if X_{f_2} is followed by X_{f_1}, where

$$\left(P + \frac{a}{(V - bt)^2}\tau\right)(V - bt) = NRT\,. \tag{5.18}$$

As a matter of fact, Eq. (5.17) exactly reproduces the standard van der Waals equation.

The presented method allows us to obtain new equations of state and new fundamental relations from the known ones. Because of that it has very practical meaning in thermodynamics. Recently, this formalism was thoroughly studied in [16].

6 Statistical derivation of the contact and metric structures on M

In this section we show that using a generalized Gibbs (generalized canonical) probability distribution function ρ [17], and relaxing some standard conditions imposed on ρ, we can introduce a contact and a metric structure on the space of thermodynamic parameters M.

Statistical physics tries to explaining thermal properties of macroscopic bodies by taking into account their microscopic structure. However, it does not investigate detailed states of all individual microobjects in the system but tries to describe only their collective statistical behaviour. This collective behaviour is characterized by a function (or operator in the quantum case) defining a probability density over the space of all plausible microstates of the system. Having such a probability density it is possible to calculate mean values of physical quantities as well as their fluctuations around these mean values.

Let us consider a physical system with Γ as the space of its all microscopical states. These states will be labeled by $y = (y^1, \ldots, y^l)$, where $l/2$ denotes the number of all microscopic degrees of freedom. Let $\rho : \Gamma \to \mathbb{R}_+$ be a normalized or nonnormalized probability distribution on Γ and let $F^i : \Gamma \to \mathbb{R}$, $i = 1, ..., n$, be a set of linearly independent stochastic variables on Γ. Following the Jaynes *maximum entropy* (*information*) *principle* [18] we take ρ in the form

$$\rho(y; w, p_1, \ldots, p_n) \; = \; \exp[-w + p_i F^i(y)] \, , \qquad y \in \Gamma \, , \tag{6.1}$$

where $p = (p_1, \ldots, p_n)$ are some macroscopic (nonstochastic) parameters called statistical (or generalized) temperatures; they characterize the state of environment [19]. For a nonnormalized probability distribution, w is a free parameter, while for ρ normalized, w is a function of $p_1, \ldots, p_n$, namely

$$Z(p) \; \equiv \; e^w \; = \; \int \exp[p_i F^i(y)] \, d\Gamma \, . \tag{6.2}$$

The mean values x^i of $F^i(y)$ (denoted usually by $\langle F^i \rangle$ or $E[F^i]$) are given by means of ρ by

$$x^i \; = \; \langle F^i \rangle \; := \; \int \rho F^i(y) \, d\Gamma \; = \; \frac{\partial \ln Z}{\partial p_i} \; = \; \frac{\partial w}{\partial p_i} \, . \tag{6.3}$$

The two most useful examples for our purposes are the grand canonical distribution

$$\rho(y; w, p_1, p_2) = Z^{-1}(T, \mu) \, \exp\left[\frac{-H_N(y) + \mu N}{kT}\right] , \qquad p_1 = -\frac{1}{kT} \, , \quad p_2 = \frac{\mu}{kT} \, , \tag{6.4}$$

with

$$Z(T, \mu) = \sum_{N=0}^{\infty} \int_{\Gamma_N} \exp\left[\frac{-H_N(y) + \mu N}{kT}\right] d\Gamma_N \, , \quad U = kT^2 \, \frac{\partial \ln Z}{\partial T} \, , \quad \langle N \rangle \; = \frac{\partial \ln Z}{\partial (\mu / kT)} \, , \tag{6.5}$$

(U denotes the mean value of $H_N(y)$, N is the number of particles) and the Boguslavski (or isobaric-isothermal) distribution

$$\rho(y; w, p_1, p_2) = Z^{-1}(T, P) \exp\left[\frac{-H(y) - PV}{kT}\right] , \qquad p_1 = -\frac{1}{kT} \, , \quad p_2 = -\frac{P}{kT} \, , \tag{6.6}$$

with

$$Z(T, P) = \int_0^{\infty} dV \int_{\Gamma} \exp\left[\frac{-H(y) - PV}{kT}\right] d\Gamma \, , \qquad U = kT^2 \, \frac{\partial \ln Z}{\partial T} \, , \quad \langle V \rangle \; = \frac{\partial \ln Z}{\partial (-P/kT)} \, , \tag{6.7}$$

The standard Gibbs (canonical) distribution $\rho(y; w, p) \; = \; Z^{-1}(T) \exp\left[-H(y)/kT\right]$ is not good for our purposes because the dimension with $n = 1$ is too low from geometrical reasons.

To introduce a metric we will also need the variances of stochastic variables which are equal to

$$\langle (F^i - x^i)(F^j - x^j) \rangle \; = \; \frac{\partial^2 \ln Z}{\partial p_i \partial p_j} \; = \; \frac{\partial^2 w}{\partial p_i \partial p_j} \; = \; \frac{\partial x^i}{\partial p_j} \; = \; \frac{\partial x^j}{\partial p_i} \, . \tag{6.8}$$

From the last equation we infer that

$$dx^i \;=\; \langle (F^i - x^i)(F^j - x^j) \rangle dp_j \,, \tag{6.9}$$

which also holds for nonnormalized ρ.

Now let us define the microscopic entropy

$$s \;:=\; -\ln \rho \;=\; w - p_i F^i \,, \tag{6.10}$$

and its differential

$$ds \;=\; dw - F^i dp_i \,, \tag{6.11}$$

where differentiation was done only with respect to the macroscopic parameters w and p_i. The mean value of ds,

$$\vartheta \;=\; \langle ds \rangle \;=\; dw - x^i dp_i \,, \tag{6.12}$$

leads to a contact form on the space of parameters $w, p_1, \ldots, p_n, x^1, \ldots, x^n$. To this end one has to assume that ρ is (temporarily) nonnormalized, i.e. w is a free parameter, and moreover that x^i are independent parameters as well. Then ϑ becomes a contact form because under such assumptions one has $\vartheta \wedge (d\vartheta)^n \neq 0$. For ρ normalized, ϑ becomes zero and subsequently w and x^i become functions of p_i. These functions define a Legendre submanifold of ϑ. The full Legendre transformation transforms ϑ into another contact form θ^S equal to

$$\theta^S \;=\; dx^0 + p_i dx^i \,, \tag{6.13}$$

where $x^0 = w - p_i x^i$ and (x^0, p_i, x^i) correspond to the parameters in the entropy representation, cf. (2.5) and (2.6). In the energy representation the contact form is given by

$$\theta \equiv \theta^U = -T\theta^S = dx^0 + p_i dx^i \,, \tag{6.14}$$

where now (x^0, p_i, x^i) correspond to the parameters in the energy representation, cf. (2.3) and (2.4). Thus we see that the contact structure is based on the mean value (or the first moment) of ds.

The metric form is based on the variance (or the second moment) of ds which, due to (6.1), (6.3) and (6.11), is equal to

$$\Big\langle (ds - \langle ds \rangle)^2 \Big\rangle \;=\; \Big\langle (F^i - x^i)(F^j - x^j) \Big\rangle \, dp_i dp_j \;=\; dp_i dx^j \,. \tag{6.15}$$

Thus we see that this quantity is related to fluctuations of the stochastic variables F^i. To derive from $\langle (ds - \langle ds \rangle)^2 \rangle$ a metric form on M^{2n+1} we have to make two additional assumptions. First, we assume again that p_i and x^i are independent. Then $\langle (ds - \langle ds \rangle)^2 \rangle = dp_i dx^i$ becomes a bilinear, positive definite and symmetric form on the $(2n+1)$-dimensional space M^{2n+1} of parameters w, p_i and x^i. However, the form $dp_i dx^i$ is degenerate on M^{2n+1}. To remove this degeneracy we make another assumption that the sought for metric form G on M is the sum of $dp_i dx^i$ and $\vartheta \otimes \vartheta$, i.e.

$$G := dp_i dx^i + \vartheta \otimes \vartheta\,. \tag{6.16}$$

The degeneracy of $dp_i dx^i$ could have been removed in any other way, for instance by adding $dw\,dw$ or $dx^0 dx^0$. However, our choice has the advantage that G reduced to any Legendre submanifold $\mathcal{S}$ of ϑ,

$$g \;=\; G|_{\mathcal{S}} \;=\; \langle (ds - \langle ds \rangle)^2 \rangle|_{\mathcal{S}} \;=\; dp_i dx^i|_{\mathcal{S}}\,, \tag{6.17}$$

has a very simple form not depending on the way the degeneracy has been removed. Its statistical and physical interpretation can be deduced from (6.15).

Instead, an equivalent (up to a Legendre transformation) metric $\mathcal{H}$ on M could be defined as

$$\mathcal{H} \;:=\; \langle (ds)^2 \rangle \;=\; dwdw - 2x^i dwdp_i + x^i x^j dp_i dp_j + dx^i dp_i\,, \tag{6.18}$$

for nonnormalized ρ. The metric $\mathcal{H}$ is nondegenerate if we assume that p_i's and x^i's are independent.

7 Generalizations and remarks

Riemannian metrics can be defined at once on Legendre submanifolds in quite a different way if we use the notion of *relative information* (or relative entropy). This notion — also called *Kullback information* or *information gain* — for the two probability distributions $\rho(y;p)$ and $\sigma(y;p)$ is defined by

$$I\,(\rho|\sigma) = \int_\Gamma \rho\,(\ln\,\rho - \ln\,\sigma)\,d\Gamma\,, \tag{7.1}$$

if ρ is absolutely continuous with respect t0 σ.

For two close states $\rho = \rho\,(y;p)$ and $\sigma = \rho\,(y;p+dp)$, we have

$$I\,(\rho|\sigma) \approx \frac{1}{2}\frac{\partial^2 I}{\partial p_i \partial p_j} dp_i dp_j\,, \tag{7.2}$$

because $I(\rho\,(p)|\rho\,(p)) = 0$ and $\partial I/\partial p_i = 0$. Then the square infinitesimal distance dl^2 in the space of $p = (p_1, ..., p_r)$ we can define as

$$dl^2 = 2I(\rho\,(p)|\rho\,(p+dp) = g_{ij}(p) dp_i dp_j\,, \tag{7.3}$$

where

$$g_{ij}(p) = \frac{\partial^2 I}{\partial p_i \partial p_j} = E\left[\frac{\partial \ln\rho}{\partial p_i}\frac{\partial \ln\rho}{\partial p_j}\right] = -E\left[\frac{\partial^2 \ln\rho}{\partial p_i \partial p_j}\right] = \frac{\partial^2 \ln Z(p)}{\partial p_i \partial p_j} = E\left[(F_i - \langle F_i\rangle)\,(F_j - \langle F_j\rangle)\right], \tag{7.4}$$

where E denotes the mean (average) value. The metric tensor $g_{ij}(p)$ is equivalent to *Fisher's information matrix* (*covariance* or *correlation matrix*) well known from statistics. It is also equivalent to the metric introduced in Section 6.

This metric could be used to study irreversible phenomena such as relaxation, diffusion, transport processes, and dissipation. For instance, for a relaxation process $\rho(t) \to \sigma$, $I(\rho|\sigma)$ means entropy production and g_{ij} might be used to study the characteristic features of this process.

This metric will certainly find applications to communication theory, pattern recognition, biology, ecology, theoretical linguistics, and so on.

As a last remark let us stress that introducing the contact and metric structures we have used (generalized) Gibbs distributions with many stochastic variables $F^i(y)$. From the point of view of the maximum entropy principle [18] it means that to find ρ we have to know (e.g. from experiment) the mean values (first moments) of F^i. We could go further and include into the set of F^i's also some stochastic variables corresponding to higher-order moments. Then the conjugate parameters p_i (higher-order temperatures) would not have so simple thermodynamic meaning as for the grand canonical or the Boguslavski distribution. However, the probability distribution would be more concentrated (sharper) in this case.

With some necessary modifications the whole procedure could be repeated for quantum systems.

8 Perspectives

The described geometrical setting for thermodynamics opens new perspectives because it offers new mathematical tools previously not used, or used only rarely, in thermodynamics. To these tools belong:

- tensor calculus,
- group theory, and in particular Lie groups,
- Lie algebras,
- Lie derivative $\mathcal{L}_X$, to study invariants,
- the Poisson, Jacobi, Cartan, and Lagrange brackets [13],
- catastrophe theory, to study phase transitions.

We hope that this geometrical setting opens new possibilities to analyse cyclic processes and their invariants.

The metric structure can be used to study convexity and stability, and hence to study fluctuations, phase transitions and critical points.

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