Atti Accademia Nazionale Lincei Classe Scienze Fisiche Matematiche Naturali

# Rendiconti Lincei Matematica e Applicazioni

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## Remarks on Riemannian Thermodynamics

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti Lincei. Matematica e Applicazioni, Serie 9*, Vol. **3** (1992), n.1, p. 45–50.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLIN_1992_9_3_1_45_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti Lincei. Matematica e Applicazioni, Accademia Nazionale dei Lincei, 1992.

*Rend. Mat. Acc. Lincei*
*s. 9, v. 3:45-50 (1992)*

**Meccanica dei continui.** — *Remarks on Riemannian Thermodynamics.* Nota di Luigi G. Napolitano e Carlo Albanese, presentata (*) dal Corrisp. L. G. Napolitano.

Abstract. — The postulates of macroscopic thermodynamics give us the possibility to endow the set of thermodynamic states with the structure of a riemannian manifold. Two alternatives are available: the first one is to introduce on the set of thermodynamic equilibrium states a metric induced by an embedding metric space (extrinsic approach), the second one is to introduce the stability metric (intrinsic approach). Between the two choices the second one looks more promising on the basis of its capability of yielding physical informations. An open problem is however the tensoriality of the stability metric.

Key words: Thermodynamics; Riemannian geometry; Hypersonics.

Riassunto. — *Contributo alla Termodinamica Riemanniana.* A partire dai postulati della termodinamica macroscopica viene dimostrato come l'insieme degli stati termodinamici può essere dotato di struttura di varietà riemanniana. A tale scopo ci sono due modi di introdurre una metrica: un modo estrinseco, derivandola da uno spazio metrico immergente, oppure un modo intrinseco usando una metrica autonoma. Tra le due scelte la seconda sembra migliore per le informazioni di carattere fisico che è capace di fornire. Resta un problema aperto: il carattere tensoriale della metrica scelta. Per finire viene delineata l'applicazione dei metodi geometrici introdotti a sistemi complessi.

## Introduction

In the last two decades there have been a number of attempts to endow thermodynamics with geometrical and/or topological structures to parallel similar previous developments in other branches of physics and to yield the sophisticated mathematical tools needed to cope efficiently with the complex problems connected with hypersonic transatmospheric flights of aircrafts such as the European Hermes or the USA transatmospheric plane.

For such complex and demanding machines the empirical phenomenological approach becomes too costly and a rational theoretical foundation relying on modern mathematical tools may be the answer.

In this *Note* we shall focus only on one of the several problems and challenges that arise when one attempts to thread these patterns. In particular we shall deal with the so-called Riemannian thermodynamics which intends to introduce and exploit, in thermodynamics, the tools of Riemannian manifolds.

## The Problem

The starting point is the basic postulates of macroscopic thermodynamics as formulated by Callen and by Tisza [1, 2] and as embodied in the assumed existence of the so-called energy fundamental equation $U = U(X^i)$, containing all needed information

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(*) Nella seduta del 14 giugno 1991.

about an isolated system $\Sigma$ in thermodynamic equilibrium. Here $X^i (0 \leq i \leq n+1)$ are the $(n+1)$ extensive (natural) variables (among which the entropy $S$) necessary and sufficient to uniquely define the extensive state ($P$) of $\Sigma$; $U$ is its internal energy, a first order homogeneous function of its natural variables $X^i$. The Euler theorems yield what are known in thermodynamics as equations of Gibbs, Euler and Gibbs-Duhem (GD).

$$(1) \qquad dU = Y_i\, dX^i\,, \quad U = Y_i\, X^i\,, \quad 0 = X^i\, dY_i\,, \qquad (0 \leqslant i \leqslant n)$$

where Einstein convention on repeated indexes has been used. The $(n+1)$ $Y_i$'s are the intensive parameters (zeroth order homogeneous functions) conjugated to $X^i$ in the energy representation. Only $(n)$ of them are independent on account of GD equation (see Mistura [3] for an illuminating analysis of the properties of the GD equation and of their consequences).

The function $U$ is assumed to be of class $C^3$ at least and the symmetric matrix $|U_{ij}| = |\partial Y_i / \partial X_j|$ of its second derivatives is positive definite for all stable thermodynamic equilibrium states of $\Sigma$ (This condition, required by thermodynamic stability of the system, is often misleadingly referred to as the second law of thermodynamics, the first one being embodied in the postulated existence of $U$).

The extension of $\Sigma$ is characterized by a fixed scale parameter, which can be the value of any extensive parameter $X_i$. Usually (but by no means always) one assumes the total mass $M$ or total volume $V$ of $\Sigma$. One then speaks of a «specific» (*e.g.* per unit mass or volume) thermodynamic state of $\Sigma_s$ which has thus only $(n)$ degrees of freedom.

If low case letters denote specific extensive quantities, eqs. (1) read

$$(2) \qquad du = Y_i\, dx^i\,, \quad U = Y_i\, x^i + Y_0\,, \quad 0 = x^i\, dY_i + dY_0\,,$$

where $X^0$ is the scale parameter and $Y_0$ is its coniugate intensive parameter, $u = u(x^i)$ is the specific internal energy.

Assume, for the moment, a $(n+1)$ $[u, x_i]$ Euclidean space $E^{n+1}$ (however a coordinate-free approach can also be followed, in terms of appropriate manifolds), and consider the fundamental relation as defining an $n$-dimensional hypersurface embedded in $E^{n+1}$ [4].

To endow it with the structure of a Riemannian manifold $V_n$ a metric must be defined and it can either be induced from that of the embedding space (Gaussian approach, extrinsic) or prescribed arbitrarily (Riemannian approach, intrinsic).

The question is: in which alternative the tools of Riemannian geometry (distance, angles, tangent vectors, parallel transport, absolute derivation, connection, curvature tensors) can be given relevant physical interpretations and be used as discriminant measures?

## INDUCED METRIC

Let greek and latin indices run from 1 to $n$ and from 1 to $(n+1)$ respectively, denote by $\eta^\alpha$ coordinates on $V_n$, $g_{\alpha\beta}$ its metric coefficients, $\Gamma^\alpha_{\beta\gamma}$ its Christoffel coefficients of second type and $\mathcal{R}_{\alpha\beta,\gamma\delta}$ the coefficients of the Riemannian tensor.

The induced metric $g_{\alpha\beta}$ is related to the metric $G_{ij}$ of the embedding space by

$$g_{\alpha\beta}(\eta^\gamma) = \frac{\partial x^i}{\partial \eta^\alpha} \frac{\partial x^j}{\partial \eta^\beta} G_{ij}(x^k). \tag{3}$$

There seem to be no physical arguments that would single out a «preferred» metric $G_{ij}$. It is thus usually assumed that the embedding space is Euclidean and therefore $G_{ij}$ can be reduced to the Cartesian metric

$$g_{\alpha\beta}(\eta^\gamma) = \frac{\partial x^i}{\partial \eta^\alpha} \delta_{ij} \frac{\partial x^j}{\partial \eta^\beta}. \tag{4}$$

In this preliminary investigation we consider a simple gas, ($n = 2$), and assume for the fundamental relation two models, the perfect gas (*a*) and the Van der Waals gas (*b*) so that, in appropriate nondimensional variables per unit mass, the fundamental energy relation reads:

$$u(s, v) = \exp(s)\, v^{1-k}, \tag{5a}$$

$$u(s, v) = \exp(s)\, v^{1-k} - ab[(b-1)\, v + 1]^{-1} \tag{5b}$$

where $u = u(s, v)$ is the specific internal energy, $s, v$ the specific entropy and volume $k = c_p/c_v$, $a = A/v_0\, u_0$, $b = v_0/B$; $A$, $B$ constants; and the index (0) denotes values in a reference state.

With $\eta^1 = x^1 = s$; $\eta^2 = x^2 = v$; $x^3 = u(s, v)$ the metric coefficients are $g_{11} = 1 + T^2$, $g_{12} = -Tp$, $g_{22} = 1 + p^2$ where $T$, $p$ are the (nondimensional) absolute temperature and thermodynamic pressure. Substituting the expressions for $T$ and $p$ obtained from the energy equation the expressions for $g_{\alpha\beta}(s, v)$ for the perfect and Van der Waals gas are obtained.

In $V_2$ $\mathcal{R}_{12,12}$ is the only independent component of the Riemann tensor, and it turns out to be different from zero in both models. Thus this choice does not lead to any significant discriminating Riemannian parameter that would enable one to identify such physically widely different models as the perfect and Van der Waals gas.

## STABILITY METRIC

The other choice poses the problem of the appropriate definition of the metric coefficients $g_{\alpha\beta}$ which must transform as the covariant components of a symmetryc and positive definite tensor under any admissible change of coordinates $\bar{\eta}^\alpha = \bar{\eta}^\alpha(\eta^\beta)$ in $V_2$.

In all available works attention has been limited to the positive definite character of the matrix $g_{\alpha\beta}$ and only Ruppeiner [6] has addressed the covariance aspect. Both Gilmore and Ruppeiner [6, 7] have proposed metric related to the thermodynamic stability of the system (in our terminology).

We shall elaborate on this proposition and point out why it is not yet acceptable.

Suppose we introduce the stability metric: $g_{\alpha\beta} = \partial^2 u/\partial \eta^\alpha\, \partial \eta^\beta$. By thermodynamic stability (and *not*, as already mentioned, by the second law) $g_{\alpha\beta}$ is symmetric and positive definite. If these were the only requirements to be satisfied by a Riemannian metric it appears as a powerful «discriminating» metric.

Indeed, for the perfect gas model is given by $g_{11} = \exp(s)\, v^{1-k}$; $g_{12} = (1-k) \cdot \exp(s)\, v^{-k}$; $g_{22} = k(k-1)\exp(s)\, v^{-k-1}$ and for the Van der Waals model by $g_{11} = \exp(s)\, v^{1-k}$; $g_{12} = (1-k)\exp(s)\, v^{-k}$; $g_{22} = k(k-1)\exp(s)\, v^{-k-1} - 2ab(b-1)^2 \cdot [(b-1)\,v+1]^{-3}$.

Straightforward developments show that the only independent component of the Riemann tensor $\mathcal{R}_{12,12}$ vanishes for the perfect gas model and is instead given by $-4g\mathcal{R}_{12,12} = (1-k)\exp(s)\, v^{-2k} - 2ab(b-1)^2\, [(b-1)\,v+1]^{-3}$ where $g = \exp(s) \cdot v^{1-k}\{(k-1)(T/v^2) - ab(b-1)^2\, [(b-1)\,v+1]^{-3}\}$ for the Van der Waals gas.

Thus for perfect gases the Riemannian curvature vanishes ($V_2$ is flat) and there exists a coordinate system ($\xi^\alpha$) in which the stability metric reduces to the cartesian metric. Simple but somewhat lengthy developments lead to the following expression for the «principal» coordinates:

$$\xi^1 = K_1 \exp(s/2)\, v^{(1-k)/2} \cos\left(\left(C + \sqrt{k-1}\ln v\right)/2\right), \tag{6a}$$

$$\xi^2 = K_2 \exp(s/2)\, v^{(1-k)/2} \sin\left(\left(C + \sqrt{k-1}\ln v\right)/2\right), \tag{6b}$$

where $K_1$, $K_2$ and $C$ are integration constants. For a Van der Waals gas the Riemannian curvature is different from zero and there exists a value $T_c$ of the temperature $T_c = (k-1)^{-1}\, v^2\, ab\,(b-1)^2\,[(b-1)\,v+1]^{-3}$ (critical temperature in the language of thermodynamics) for which the determinant of the metric vanishes and below which $g_{\alpha\beta}$ is no longer positive definite. There follows, for instance, the possibility of interpreting the Riemannian curvature as a measure of the possibility that the system undergoes phase-transitions and to eventually transfer the study of phase-transition to the study of geometrical or topological properties of the Riemannian equilibrium manifold and of its submanifolds.

## DISCUSSION AND CONCLUSIONS

There is however, as anticipated, a crucial problem to be addressed and solved.

As it concerns the stability metric, its law of transformation under admissible coordinate transformations in $V_2$ is related to that of second derivatives of the energy fundamental relation:

$$\frac{\partial^2 u}{\partial \bar{\eta}^\alpha\, \partial \bar{\eta}^\beta} = \frac{\partial^2 u}{\partial \eta^\gamma\, \partial \eta^\varepsilon}\, \frac{\partial \eta^\gamma}{\partial \bar{\eta}^\alpha}\, \frac{\partial \eta^\varepsilon}{\partial \bar{\eta}^\beta} + \frac{\partial u}{\partial \eta^\delta}\, \frac{\partial^2 \eta^\delta}{\partial \bar{\eta}^\alpha\, \partial \bar{\eta}^\beta}\,. \tag{7}$$

The presence of the last term on the right hand side defeats satisfaction of the covariant tensorial character of $g_{\alpha\beta}$.

An analogous situation was met by Ruppeiner [6] who considered as metric the matrix of second derivatives of the entropy fundamental relation (obtained from (1) by interchanging the roles of $U$ and $S$). His arguments were as follows. He introduces the notion of the so-called bath-reservoirs $\Sigma^B$ that guarantees the constancy of scale factors, considers the system $\Sigma$ not isolated but in contact with reservoirs with the same scale and applies the basic equilibrium thermodynamics to the total system ($\Sigma + {} + \Sigma^B$). Then, in this case, the term $\partial s/\partial \bar{\eta}^\alpha$ would vanish identically in the considered condition of «mutual» equilibrium between $\Sigma$ and $\Sigma^B$. Ruppeiner speculation however cannot be considered as a proof of the needed tensorial character of $(\partial^2 s/\partial \bar{\eta}^\alpha \, \partial \bar{\eta}^\beta)$ because he considered changes of variables of the *reservoirs* and not the manifold $V_2\,(\eta)$. The tensorial covariant character of the metric is with respect to admissible changes of variables on $V_2$ and, for them, the Ruppeiner term $(\partial s/\partial \bar{\eta}^\alpha)$ corresponding to our $(\partial u/\partial \bar{\eta}^\alpha)$ does not vanish.

The question thus remains still open and further studies are needed to either solve it satisfactorily or to conceive other «discriminating» metric that do not present this shortcoming.

We conclude this *Note* by giving an indicative example of how complex the thermodynamics of the composite systems can become and therefore, how big is the need (aside from conceptual elegance and satisfaction) for developing mathematical tools capable of coping with it.

A gas mixture in which a single rate process (*e.g.* chemical reaction or excitation of internal degrees of freedom of a molecule) can take place, can be considered, to within the hypothesis of shifting equilibrium, Napolitano [8], as a composite thermodynamic system with three specific degrees of freedom $(s, v, \xi)$, where $\xi$ is the progress variable of the rate process and $(\partial u/\partial \xi = Y_3)$ its affinity.

The embedding space is four dimensional $(n = 3)$, the thermodynamic manifold $V_3\ (s, v, \xi)$ defined by the energy fundamental functions $u = u(s, v, \xi)$ is three dimensional. Upon stability the chemical equilibrium condition $Y_3 = 0$ defines implicitly the equilibrium value $\xi_e\,(s, v)$ of $\xi$ and the corresponding chemical equilibrium sub-manifold is a two-dimensional manifold, defined by $V_2\,[(v, s, \xi_e\,(s, v)]$ *embedded* in $V_3$. There is thus a cascade of embeddings and some of the questions are: how and why to choose the metric on $V_2$, embedded in $V_3$, in turns embedded in $V_4$; what are the physical implications of the different choices (if any); is there a Riemannian (or, more generally, topological) measure of the distance from (neighbourhood of) chemical equilibrium states?

The situation in practical cases is even more complex due to the presence of several rate processes. In studies of the aerothermodynamics of the Hermes plane thermo-kinetic models with up to tens of chemical reactions must be developed to adequately describe the physico-chemical phenomena occurring along its trajectories through the atmosphere at speeds of the order of kilometers per second. There are states of partial equilibria of different orders so that, in the subject terminology, one must consider in addition to the original $n$-dimensional manifold $V_n$, the net of embedded varieties $V_{t_1}, V_{t_2}, \ldots, V_{t_k}\,(t_{i+1} > t_i)$ where the $t_i = \binom{n-2}{i}$ denotes the numbers of different states of partial equilibrium of order $t_i$ for which $t_i$ affinities vanish.

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