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Nonlinear closure relations theory for transport processes in nonequilibrium systems

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A decade ago, a macroscopic theory for closure relations has been proposed for systems out of Onsager's region. This theory is referred to as the *thermodynamic field theory* (TFT). The aim of this work was to determine the nonlinear flux-force relations that respect the thermodynamic theorems for systems far from equilibrium. We propose a formulation of the TFT where one of the basic restrictions, namely, the closed-form solution for the skew-symmetric piece of the transport coefficients, has been removed. In addition, the general covariance principle is replaced by the De Donder-Prigogine thermodynamic covariance principle (TCP). The introduction of TCP requires the application of an appropriate mathematical formalism, which is referred to as the *entropy-covariant formalism*. By geometrical arguments, we prove the validity of the Glansdorff-Prigogine universal criterion of evolution. A new set of closure equations determining the nonlinear corrections to the linear ("Onsager") transport coefficients is also derived. The geometry of the thermodynamic space is non-Riemannian. However, it tends to be Riemannian for high values of the entropy production. In this limit, we recover the transport equations found by the old theory. Applications of our approach to transport in magnetically confined plasmas, materials submitted to temperature, and electric potential gradients or to unimolecular triangular chemical reactions can be found at references cited herein. Transport processes in tokamak plasmas are of particular interest. In this case, even in the absence of turbulence, the state of the plasma remains close to (but, it is not in) a state of local equilibrium. This prevents the transport relations from being linear.

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I. INTRODUCTION

It is well known that the basic theory of dynamical systems should provide with an algorithm for the determination of the moments of the particle distribution functions f^{α} (i.e., the average values of the power of particle momenta $\mathbf{p}$), which are determined by the (fluctuating) fields through the kinetic equations. In the case of turbulent plasmas, for example, the most fundamental approach is the study of the stochastic kinetic equation coupled to the stochastic Maxwell equations. Such a self-consistent theory should not require any arbitrary assumption: it should produce equations of evolution for all the moments. In practice, however, an exact solution of this problem is impossible. Indeed, the equations of evolution of the moments have a hierarchical structure. The determination of a moment on the order n requires the knowledge of order $n+1$. Hence, the equations for the third moments will involve the fourth moments and so on *ad infinitum*. Because of these difficulties, the fundamental studies—in spite of their basic importance—cannot easily produce explicit results that can be directly compared to experiments. In order to obtain such results, one is led to make compromises. We must introduce additional simplifying assumptions allowing *to truncate* the hierarchy. As a result, we obtain a set of dynamical moments equations with a number of undetermined quantities: the equations are *not closed*. These quantities are of four kinds: thermodynamic quantities (such as temperature, pressure, etc.), electromagnetic fields, moments and energy exchanges (such as the collisional friction forces or the collisional particles heat exchange), and fluxes (such as, the particle flux, the heat flux, etc.). The dynamics of a thermodynamic system is finally based on the set of balance equations coupled to a (macroscopic) *theory for the closure relations*. Thus, in a macroscopic picture of thermodynamic systems, the formulation of a theory for the closure relations plays a fundamental role. The connection between the macroscopic equation and a microscopic distribution of particles should be established analyzing case by case (for example, for magnetically confined plasmas, see Ref. [1] and Sec. II E).

The most important closure relations are the so-called *transport equations*, relating the dissipative fluxes to the thermodynamic forces that produce them. The latter is related to the spatial inhomogeneity and is expressed as gradients of the thermodynamic quantities. The study of these relations is the object of nonequilibrium thermodynamics. Close to equilibrium, the transport equations of a thermodynamic system are provided by the well-known Onsager theory. Indicating with X^{μ} and J_{μ} the thermodynamic forces and fluxes, respectively, the Onsager relations read as

$$J_{\mu} = \tau_{0\mu\nu}X^{\nu}, \tag{1}$$

where $\tau_{0\mu\nu}$ are the transport coefficients. We suppose that all quantities involved in Eq. (1) are written in dimensionless form. In this equation, as in the remainder of this paper, the Einstein summation convention on the repeated indexes is adopted. Matrix $\tau_{0\mu\nu}$ can be decomposed into a sum of two matrices, one symmetric and the other skew symmetric, which we denote with $L_{\mu\nu}$ and $f_{0\mu\nu}$, respectively. The second principle of thermodynamics imposes that $L_{\mu\nu}$ be a positive-definite matrix. The most important property of Eq. (1) is that near equilibrium, the coefficients $\tau_{\mu\nu}$ are independent of the thermodynamic forces, so that

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$$\frac{\partial \tau_{0\mu\nu}}{\partial X^{\lambda}} = 0. \qquad (2)$$

The region where Eq. (2) holds is called *Onsager's region* or the *linear region*. A well-founded microscopic explanation on the validity of the linear phenomenological laws was developed by Onsager [2] in 1931. Onsager's theory is based on three assumptions: (i) the probability distribution function for the fluctuations of thermodynamic quantities (temperature, pressure, degree of advancement of a chemical reaction, etc.) is a *Maxwellian*, (ii) fluctuations decay according to a *linear law*, and (iii) the principle of the detailed balance (or the microscopic reversibility) is satisfied. Onsager showed the equivalence of Eqs. (1) and (2) with the assumptions (i)–(iii) [assumption (iii) allows deriving the *reciprocity relations* $\tau_{0\mu\nu}=\tau_{0\nu\mu}$]. The Onsager theory of fluctuations starts from the Einstein formula linking the probability of a fluctuation $\mathcal{W}$, with the entropy change ΔS associated with the fluctuations from the state of equilibrium,

$$\mathcal{W} = W_0 \exp[\Delta S/k_B]. \qquad (3)$$

In Eq. (3), k_B is the Boltzmann's constant and W_0 is a normalization constant that ensures the sum of all probabilities equals one. The first assumption in the Onsager theory consists in postulating that the entropy variation is a bilinear expression of fluctuations.

Many important theorems have been demonstrated for thermodynamic systems in the linear region. Among them, the most important one is the *minimum entropy production theorem* (MEPT) showed by Prigogine [3] in 1947. This theorem establishes that in the Onsager region, for $a-a$ or $b-b$ processes (i.e., when the Onsager matrix is symmetric. See also the definition of $a-a$ and $b-b$ processes reported in the footnote [4]), a thermodynamic system relaxes toward a steady state in such a way that the rate of the entropy production is negative

$$\frac{d\sigma}{dt} \leq 0 \quad \left(\frac{d\sigma}{dt} = 0 \quad \text{at the steady state}\right), \qquad (4)$$

where $\sigma = L_{\mu\nu}X^{\mu}X^{\nu}$ indicates the entropy production and t is time. Prigogine generalized Eq. (3), which applies only to adiabatic or isothermal transformations, by introducing the entropy production due to fluctuations. Denoting by ξ_i ($i=1,\ldots m$) the m deviations of the thermodynamic quantities from their equilibrium value, Prigogine proposed that the probability distribution of finding a state in which the values ξ_i lie between ξ_i and $\xi_i + d\xi_i$ is given by [3]

$$\mathcal{W} = W_0 \exp[\Delta_I S/k_B],$$

where

$$\Delta_I S = \int_E^F d_I s \qquad \frac{d_I s}{dt} \equiv \sigma, \qquad (5)$$

E and F indicate the equilibrium state and the state to which a fluctuation has driven the system, respectively. Note that this probability distribution remains unaltered for flux-force transformations leaving invariant the entropy production.

In 1954, Glansdorff and Prigogine [5] demonstrated a more general theorem valid also when the system is out of Onsager's region. They showed that regardless of the type of processes, a thermodynamic system relaxes toward a steady state in such a way that the following quantity $\mathcal{P}$ is negative:

$$\mathcal{P} \equiv J_{\mu}\frac{dX^{\mu}}{dt} \leq 0 \quad (\mathcal{P}=0 \quad \text{at the steady state}). \qquad (6)$$

Inequality (6) reduces to inequality (4) for $a-a$ or $b-b$ processes in the Onsager region. For spatially extended systems, the expression in Eq. (6) should be replaced by

$$\mathcal{P} \equiv \int_{\Omega} \mathcal{J}_{\mu}\frac{d\mathcal{X}^{\mu}}{dt}dv \leq 0 \quad (\mathcal{P}=0 \quad \text{at the steady state}), \qquad (7)$$

where dv is the (spatial) volume element and the integration is over the entire space Ω occupied by the system in question. $\mathcal{J}_{\mu}(\mathbf{r},t)$ and $\mathcal{X}^{\mu}(\mathbf{r},t)$ denote the space-time-dependent fluxes and forces, respectively. The phenomenological equations are not needed for deriving this more general theorem and no restrictions are imposed to the transport coefficients (apart from the validity of the second principle of thermodynamics). Therefore, no use is made of the Onsager reciprocal relations nor it is necessary to assume that the phenomenological coefficients are constants. The inequality expressed in Eq. (6) [or in Eq. (7)] is referred to as the *universal criterion of evolution* (UCE) and it is the most general result obtained up to now in thermodynamics of irreversible processes. Out of Onsager's region, the transport coefficients may depend on the thermodynamic forces and Eq. (2) may lose their validity. This happens when the first end/or the second assumption of the Onsager theory [i.e., the above-mentioned assumption (i) end/or assumption (ii)] is not satisfied. Magnetically confined tokamak plasmas are a typical example of thermodynamic systems out of Onsager's region. In this case, even in the absence of turbulence, the local distribution functions of species (electrons and ions) deviate from the (local) Maxwellian. After a short transition time, the plasma remains close to (but, it is not in) a state of local equilibrium (see, for example, [6] and Sec. II E).

Transport in the nonlinear region has been largely studied both experimentally and theoretically. In particular, many theories based on the Fourier expansion of the transport coefficients in terms of the thermodynamic forces have been proposed (see, for example, Refs. [7–9]). The theoretical predictions are however in disagreement with the experiments and this is mainly due to the fact that, in the series expansion, the terms of superior order are greater than those of inferior order. Therefore, the truncation of the series at some order is not mathematically justified.

A thermodynamic field theory (TFT) has been developed in 1999 for proposing a closure relations theory for thermodynamic systems out of the Onsager region [10]. In particular, the main objective of this work is to determine how the linear flux-force relations [i.e., Eq. (1)] should be "deformed" in such a way that the thermodynamic theorems for systems far from equilibrium are respected [10]. The Onsager coefficients enter in the theory as an input in the equations and they have to be calculated by the kinetic theory. Attempts to derive a generally covariant thermodynamic field theory (GTFT) can be found in Ref, [11]. The characteristic feature of the TFT is its purely macroscopic nature. This does not mean a formulation based on the macroscopic evolution equations but rather a purely thermodynamic formulation starting solely from the entropy production and from the transport equations. The latter provides the possibility of defining an abstract space (the thermodynamic space) covered by the n independent thermodynamic forces X^μ, whose metric is identified with the symmetric part of the transport matrix. The law of evolution is not the dynamical law of particle motion or the set of two-fluid macroscopic equations of plasma dynamics. The evolution in the thermodynamic space is rather determined by postulating three purely geometrical principles: the shortest path principle, the skew-symmetric piece of the transport coefficients in closed form, and the principle of least action. From theses principles, a set of closure equations, constraints, and boundary conditions are derived. These equations determine the nonlinear corrections to the linear ("Onsager") transport coefficients. However, the formulation of the thermodynamic field theory, as reported in Ref. [10], raises the following fundamental objection. There are no strong experimental evidences supporting the requirement that the skew-symmetric piece of the transport coefficients is in a closed form.

Moreover, the principle of general covariance, which in Ref. [11] has been assumed to be valid for general transformations in the space of thermodynamic configurations, is—in reality—respected only by a very limited class of thermodynamic processes. In this paper, through an appropriate mathematical formalism, the *entropy-covariant formalism*, the entire TFT is reformulated removing the assumptions regarding the closed form of the skew-symmetric piece of the transport coefficients and the general covariance principle (GCP). The GCP is replaced by the *thermodynamic covariance principle* (TCP) or the De Donder-Prigogine [12,13] statement, establishing that thermodynamic systems obtained by a transformation of forces and fluxes in such a way that the entropy production remains unaltered are thermodynamically equivalent. This principle applies to transformations in the thermodynamic space and they may be referred to as the *thermodynamic coordinate transformations* (TCTs). It is worthwhile mentioning that the TCP is actually largely used in a wide variety of thermodynamic processes ranging from nonequilibrium chemical reactions to transport processes in tokamak plasmas (see, for examples, the papers and books cited in Refs. [6,14]). To the author's knowledge, the validity of the thermodynamic covariance principle has been verified empirically without exception in physics until now.

The analysis starts from the following observation. Consider a relaxation process of a thermodynamic system in the Onsager region. If the system relaxes toward a steady state along the shortest path in the thermodynamic space then the universal criterion of evolution is automatically satisfied. Indeed, in this case, we can write

$$J_\mu \dot{X}^\mu = (L_{\mu\nu} + f_{0\mu\nu}) X^\nu \dot{X}^\mu, \tag{8}$$

where the dot over the variables indicates the derivative with respect to the arc parameter ς defined as

$$d\varsigma^2 = L_{\mu\nu} dX^\mu dX^\nu. \tag{9}$$

Parameter ς can be chosen in such a way that it vanishes when the system begins to evolve and it assumes the value, say l, when the system reaches the steady state. In the Onsager region, the thermodynamic space is an Euclidean space with metric $L_{\mu\nu}$. The equation of the shortest path reads $\ddot{X}^\mu = 0$, with solution of the form

$$X^\mu = a^\mu \varsigma + b^\mu, \tag{10}$$

where a^μ and b^μ are arbitrary constant independent of the arc parameter. Inserting Eq. (10) into Eq. (8) and observing that $L_{\mu\nu}a^\mu a^\nu = 1$ and $f_{0\mu\nu}a^\mu a^\nu = 0$, we find

$$J_\mu \dot{X}^\mu = \varsigma + \tau_{0\mu\nu} a^\mu b^\nu. \tag{11}$$

At the steady state (i.e., for $\varsigma = l$) $J_\mu \dot{X}^\mu|_{st\ state} = 0$. (because $\mathcal{P}|_{st\ state} = 0$). Equation (11) can then be written as

$$P = -(l - \varsigma) \leq 0 \quad (\text{with} \quad P \equiv J_\mu \dot{X}^\mu) \tag{12}$$

or

$$\mathcal{P} = -(l - \varsigma)\left(L_{\mu\nu}\frac{dX^\mu}{dt}\frac{dX^\nu}{dt}\right)^{1/2} \leq 0. \tag{13}$$

The equation for the dissipative quantity P, when the thermodynamic system relaxes in the linear region, is thus given by Eq. (11)

$$\frac{dP}{d\varsigma} = 1. \tag{14}$$

Also note that $\dot{\sigma} = 2P \leq 0$, i.e., the minimum entropy production theorem is also satisfied during relaxation. Now, our question is "How can we deform the linear flux-force relations in such a way that the universal criterion of evolution remains automatically satisfied, without imposing any restrictions to the transport coefficients, also out of Onsager's region?." Outside the linear region, one may be tempted to construct a Riemannian space (of three or more dimensions) which is projectively flat, i.e., having a vanishing Weyl's [15] projective curvature tensor. In this case, indeed, there exists a coordinate system such that the equations of the shortest path are linear in the coordinates [i.e., the shortest paths are given by equations of the form (10)]. In this respect, we have the following Weyl theorem. A necessary and sufficient condition that a Riemannian space be projectively flat is that its Riemannian curvature be constant everywhere. On the other hand, to reobtain the Onsager relations, we should also require that near equilibrium, the Riemannian space reduces to a flat space (which has zero Riemannian curvature). The Weyl theorem can be conciliated with our request only if there exists a coordinate system such that Eq. (2) is valid everywhere, which is in contrast with experiments. Thus one wants the universal criterion of evolution satisfied also out of the Onsager region, without imposing *a priori any* restrictions on transport coefficients, a *non-Riemannian* thermodynamic space is required. Clearly, a transport theory without knowledge of microscopic dynamical laws cannot be developed. Transport theory is only but an aspect of nonequilibrium statistical mechanics, which provides the link between microlevel and macrolevel. This link appears indirectly in the "unperturbed" matrices, i.e., the $L_{\mu\nu}$ and the $f_{0\mu\nu}$ coefficients used as an input in the equations. These coefficients, which depend on the specific material under consideration, have to be calculated in the usual way by kinetic theory.

In Sec. II, we introduce a non-Riemannian space whose geometry is constructed in such a way that (A) the theorems, valid when a generic thermodynamic system relaxes out of equilibrium, are satisfied; (B) the nonlinear closure equations are covariant under the TCTs.

We shall see that the properties of geometry do not depend on the shortest paths but upon a particular expression of the *affine connection*. Our geometry is then of affine type and not of projective type. At the end of Sec. II, we derive the nonlinear closure equations through an appropriate mathematical formalism: the entropy-covariant formalism. This formalism allows to respect the De Donder-Prigogine statement. New geometrical objects such as *thermodynamic covariant differentiation* or the *thermodynamic curvature* are also introduced. We shall see that under the weak-field approximation and when $\sigma \gg 1$, but only in these limits, the new nonlinear closure equations reduce to the ones obtained in Ref. [10]. So that, all results found in Ref. [1] (for magnetically confined plasmas) and in Ref. [16] (for the nonlinear thermoelectric effect and the unimolecular triangular reaction) remain valid. In Sec. III we show that this formalism is able to verify the thermodynamic theorems (in particular, the universal criterion of evolution) for systems relaxing out of the Onsager region. Mathematical details and demonstrations of the theorems are reported in Appendixes A and D.

It should be noted that geometrical formalisms have been applied for treating topics different to the transport closure theory such as the use of the matrix of the second derivatives of the entropy as a metric tensor in the analysis of fluctuations (see, for example, [17]) and the use of symplectic geometries in the analysis of nonlinear evolution equations of dynamical systems [18].

II. ENTROPY-COVARIANT FORMALISM

Consider a thermodynamic system driven out from equilibrium by a set of n independent thermodynamic forces $\{X^\mu\}$ $(\mu = 1, \ldots n)$. It is also assumed that the system is submitted to time-independent boundary conditions. The set of conjugate flows $\{J_\mu\}$ is coupled to the thermodynamic forces through the relation,

$$J_\mu = \tau_{\mu\nu}(X) X^\nu, \tag{15}$$

where the transport coefficients $\tau_{\mu\nu}(X)$ may now depend on the thermodynamic forces. The symmetric piece of $\tau_{\mu\nu}(X)$ is denoted with $g_{\mu\nu}(X)$ and the skew-symmetric piece as $f_{\mu\nu}(X)$,

$$\begin{aligned}\tau_{\mu\nu}(X) &= \frac{1}{2}[\tau_{\mu\nu}(X) + \tau_{\nu\mu}(X)] + \frac{1}{2}[\tau_{\mu\nu}(X) - \tau_{\nu\mu}(X)]\\ &= g_{\mu\nu}(X) + f_{\mu\nu}(X),\end{aligned} \tag{16}$$

where

$$g_{\mu\nu}(X) = \frac{1}{2}[\tau_{\mu\nu}(X) + \tau_{\nu\mu}(X)] = g_{\nu\mu}(X), \tag{17}$$

$$f_{\mu\nu}(X) = \frac{1}{2}[\tau_{\mu\nu}(X) - \tau_{\nu\mu}(X)] = -f_{\nu\mu}(X). \tag{18}$$

It is assumed that $g_{\mu\nu}(X)$ is a positive-definite matrix. For conciseness, in the sequel we drop the symbol (X) in $\tau_{\mu\nu}$, $g_{\mu\nu}$, and $f_{\mu\nu}$, being implicitly understood that these matrices may depend on the thermodynamic forces. With the elements of the transport coefficients two objects are constructed: *operators*, which may act on thermodynamic tensorial objects and *thermodynamic tensorial objects*, which under coordinate (forces) transformations, obey to well-specified transformation rules.

A. Operators

Two operators are introduced, the entropy production operator $\sigma(X)$ and the dissipative quantity operator $P(X)$, acting on the thermodynamic forces in the following manner:

$$\begin{aligned}&\sigma(X): \rightarrow \sigma(X) \equiv X g X^T,\\ &P(X): \rightarrow P(X) \equiv X \tau \dot{X}^T.\end{aligned} \tag{19}$$

In Eq. (19), the transport coefficients are then considered as elements of the two $n \times n$ matrices, τ and g. The positive definiteness of the matrix $g_{\mu\nu}$ ensures the validity of the second principle of thermodynamics $\sigma \geq 0$. These matrices multiply the thermodynamic forces X expressed as $n \times 1$ column matrices. The dot symbol stands for derivative with respect to parameter ς defined in Eq. (31). We anticipate that this parameter is invariant under the thermodynamic coordinate transformations. Thermodynamic states X_s such that

$$P(X_s) = 0 \tag{20}$$

are referred to as *steady states*. Of course, the steady states should be invariant expressions under the thermodynamic coordinate transformations. Equations (19) should not be interpreted as the metric tensor $g_{\mu\nu}$, which acts on the coordinates. The metric tensor acts only on elements of the tangent space (such as dX^μ, see the forthcoming paragraphs) or on the thermodynamic tensorial objects.

B. Transformation rules of entropy production, forces, and flows

According to the De Donder-Prigogine [12,13] statement, thermodynamic systems are thermodynamically equivalent if—under the transformation of fluxes and forces—the bilinear form of the entropy production σ remains unaltered [19]. In mathematical terms, this implies

$$\sigma = J_\mu X^\mu = J'_\mu X'^\mu. \tag{21}$$

This condition and the condition that also the dissipative quantity [cf. Eqs. (19)] must be an invariant expression require that the transformed thermodynamic forces and flows satisfy the relation

$$X'^{\mu} = \frac{\partial X'^{\mu}}{\partial X^{\nu}} X^{\nu},$$

$$J'_{\mu} = \frac{\partial X^{\nu}}{\partial X'^{\mu}} J_{\nu}. \tag{22}$$

These transformations may be referred to as TCTs. The expression of entropy production becomes accordingly

$$\sigma = J_{\mu} X^{\mu} = \tau_{\mu\nu} X^{\mu} X^{\nu} = g_{\mu\nu} X^{\mu} X^{\nu} = g'_{\mu\nu} X'^{\mu} X'^{\nu} = \sigma'. \tag{23}$$

From Eqs. (22) and (23) we derive

$$g'_{\lambda\kappa} = g_{\mu\nu} \frac{\partial X^{\mu}}{\partial X'^{\lambda}} \frac{\partial X^{\nu}}{\partial X'^{\kappa}}. \tag{24}$$

Moreover, inserting Eqs. (22) and (24) into relation $J_{\mu} = (g_{\mu\nu} + f_{\mu\nu}) X^{\nu}$, we obtain

$$J'_{\lambda} = \left(g'_{\lambda\kappa} + f_{\mu\nu} \frac{\partial X^{\mu}}{\partial X'^{\lambda}} \frac{\partial X^{\nu}}{\partial X'^{\kappa}} \right) X'^{\kappa} \tag{25}$$

or

$$J'_{\lambda} = (g'_{\lambda\kappa} + f'_{\lambda\kappa}) X'^{\kappa} \quad \text{with} \quad f'_{\lambda\kappa} = f_{\mu\nu} \frac{\partial X^{\mu}}{\partial X'^{\lambda}} \frac{\partial X^{\nu}}{\partial X'^{\kappa}}. \tag{26}$$

Hence, the transport coefficients transform like a thermodynamic tensor of second order [20].

C. Properties of the TCT

By direct inspection, it is easy to verify that the general solutions of Eq. (22) are

$$X'^{\mu} = X^{1} F^{\mu} \left(\frac{X^{2}}{X^{1}}, \frac{X^{3}}{X^{2}}, \cdots \frac{X^{n}}{X^{n-1}} \right), \tag{27}$$

where F^{μ} are *arbitrary functions* of variables X^{j}/X^{j-1} with $(j=2, \ldots, n)$. Hence, the TCT may be *highly nonlinear coordinate transformations* but, in the Onsager region, we may (or we must) require that they have to reduce to

$$X'^{\mu} = c^{\mu}_{\nu} X^{\nu}, \tag{28}$$

where c^{μ}_{ν} are constant coefficients (i.e., independent of the thermodynamic forces). Note that from Eq. (22), the following important identities are derived:

$$X^{\nu} \frac{\partial^{2} X'^{\mu}}{\partial X^{\nu} \partial X^{\kappa}} = 0; \quad X'^{\nu} \frac{\partial^{2} X^{\mu}}{\partial X'^{\nu} \partial X'^{\kappa}} = 0. \tag{29}$$

Moreover

$$dX'^{\mu} = \frac{\partial X'^{\mu}}{\partial X^{\nu}} dX^{\nu},$$

$$\frac{\partial}{\partial X'^{\mu}} = \frac{\partial X^{\nu}}{\partial X'^{\mu}} \frac{\partial}{\partial X^{\nu}}, \tag{30}$$

i.e., dX^{μ} and $\partial/\partial X^{\mu}$ transform like a thermodynamic contravariant and a thermodynamic covariant vector, respectively. According to Eq. (30), thermodynamic vectors dX^{μ} define the *tangent space* to T_{s}. It also follows that the operator $P(X)$, i.e., the dissipation quantity, and in particular the definition of steady states are invariant under TCT. Parameter ς defined as

$$d\varsigma^{2} = g_{\mu\nu} dX^{\mu} dX^{\nu} \tag{31}$$

is a scalar under TCT. The operator $\mathcal{O}$

$$\mathcal{O} \equiv X^{\mu} \frac{\partial}{\partial X^{\mu}} = X'^{\mu} \frac{\partial}{\partial X'^{\mu}} = \mathcal{O}' \tag{32}$$

is also invariant under TCT. This operator plays an important role in the formalism.

D. Thermodynamic space, thermodynamic covariant derivatives, and thermodynamic curvature

A non-Riemannian space with an affine connection $\Gamma^{\mu}_{\alpha\beta}$ is now introduced (see also Appendix D). Consider an n space in which the set of quantities $\Gamma^{\mu}_{\alpha\beta}$ is assigned as functions of the n independent thermodynamic forces X^{μ} chosen as coordinate system. Under a coordinate (forces) transformation, it is required that the functions $\Gamma^{\mu}_{\alpha\beta}$ transform according to the law,

$$\Gamma'^{\mu}_{\alpha\beta} = \Gamma^{\nu}_{\lambda\kappa} \frac{\partial X'^{\mu}}{\partial X^{\nu}} \frac{\partial X^{\lambda}}{\partial X'^{\alpha}} \frac{\partial X^{\kappa}}{\partial X'^{\beta}} + \frac{\partial X'^{\mu}}{\partial X^{\nu}} \frac{\partial^{2} X^{\nu}}{\partial X'^{\alpha} \partial X'^{\beta}}. \tag{33}$$

With the linear connection $\Gamma^{\mu}_{\alpha\beta}$, the absolute derivative of an arbitrary thermodynamic contravariant vector denoted by T^{μ} along a curve can be defined as

$$\frac{\delta T^{\mu}}{\delta\varsigma} = \frac{dT^{\mu}}{d\varsigma} + \Gamma^{\mu}_{\alpha\beta} T^{\alpha} \frac{dX^{\beta}}{d\varsigma}. \tag{34}$$

It is easily checked that if the parameter along the curve is changed from ς to ϱ then the absolute derivative of a thermodynamic tensor field with respect to ϱ is $d\varsigma/d\varrho$ times the absolute derivative with respect to ς. The absolute derivative of any contravariant thermodynamic tensor may be easily obtained generalizing Eq. (34). In addition, the linear connection $\Gamma^{\mu}_{\alpha\beta}$ is submitted to the following basic postulates:

(1) the absolute derivative of a thermodynamic contravariant tensor is a thermodynamic tensor of the same order and type,

(2) the absolute derivative of an outer product of thermodynamic tensors, is given—in terms of factors—by the usual rule for differentiating a product, and

(3) the absolute derivative of the sum of thermodynamic tensors of the same type is equal to the sum of the absolute derivatives of the thermodynamic tensors.

In a space with a linear connection, we can introduce the notion of the *shortest path* defined as a curve such that a thermodynamic vector, initially tangent to the curve and propagated parallelly along it, remains tangent to the curve at all points. By a suitable choice of the parameter ϱ, the differential equation for the shortest path is simplified reducing to

$$\frac{d^2X^\mu}{d\varrho^2}+\Gamma^\mu_{\alpha\beta}\frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho}=0. \tag{35}$$

To satisfy the general requirement (A) (see Sec. III), it is required that the absolute derivative of the entropy production satisfies the equality

$$\frac{\delta\sigma}{\delta\varsigma}=J_\mu\frac{\delta X^\mu}{\delta\varsigma}+X^\mu\frac{\delta J_\mu}{\delta\varsigma}. \tag{36}$$

More in general, it is required that the operations of contraction and absolute differentiation commute for all thermodynamic vectors. As a consequence, the considered space should be a space with a single connection. The absolute derivative of an arbitrary covariant thermodynamic vector denoted by T_μ is then defined as

$$\frac{\delta T_\mu}{\delta\varsigma}=\frac{dT_\mu}{d\varsigma}-\Gamma^\alpha_{\mu\beta}T_\alpha\frac{dX^\beta}{d\varsigma}. \tag{37}$$

The absolute derivative of the most general contravariant, covariant. and mixed thermodynamic tensors may be obtained generalizing Eqs. (34) and (37). The derivatives, covariant under TCT, of thermodynamic vectors are defined as

$$T^\mu_{|\nu}=\frac{\partial T^\mu}{\partial X^\nu}+\Gamma^\mu_{\alpha\nu}T^\alpha,$$

$$T_{\mu|\nu}=\frac{\partial T_\mu}{\partial X^\nu}-\Gamma^\alpha_{\mu\nu}T_\alpha. \tag{38}$$

For the entropy production, it is also required that

$$\sigma_{|\mu|\nu}=\sigma_{|\nu|\mu}. \tag{39}$$

More in general, Eq. (39) should be verified for any thermodynamic scalar T. This postulate requires that the linear single connection $\Gamma^\mu_{\alpha\beta}$ is also symmetric, i.e., $\Gamma^\mu_{\alpha\beta}=\Gamma^\mu_{\beta\alpha}$. A non-Riemannian geometry can now be constructed out of $n^2(n+1)/2$ quantities, the components of $\Gamma^\mu_{\alpha\beta}$, according to the general requirements (A) and (B) mentioned in the introduction.

In the forthcoming paragraph, the expression of the affine connection $\Gamma^\mu_{\alpha\beta}$ is determined from assumption (A). In Sec. III it is shown that the universal criterion of evolution applied to thermodynamic systems relaxing toward a steady state, is automatically satisfied along the shortest path if, in case of symmetric processes (i.e., for $a-a$ or $b-b$ processes), we impose

$$\Gamma^\mu_{\alpha\beta}=\frac{1}{2}g^{\mu\lambda}\left(\frac{\partial g_{\lambda\alpha}}{\partial X^\beta}+\frac{\partial g_{\lambda\beta}}{\partial X^\alpha}-\frac{\partial g_{\alpha\beta}}{\partial X^\lambda}\right)+\frac{1}{2\sigma}X^\mu\mathcal{O}(g_{\alpha\beta}),$$

where

$$\mathcal{O}(g_{\alpha\beta})\equiv X^\eta\frac{\partial g_{\alpha\beta}}{\partial X^\eta}. \tag{40}$$

In the general case, we have

$$\begin{aligned}\Gamma^\mu_{\alpha\beta}={}&\check{N}^{\mu\kappa}g_{\kappa\lambda}\left\{\begin{matrix}\lambda\\ \alpha\beta\end{matrix}\right\}+\frac{\check{N}^{\mu\kappa}}{2\sigma}X_\kappa\mathcal{O}(g_{\alpha\beta})\\ &+\frac{\check{N}^{\mu\kappa}}{2\sigma}X_\kappa X^\lambda\left(\frac{\partial f_{\alpha\lambda}}{\partial X^\beta}+\frac{\partial f_{\beta\lambda}}{\partial X^\alpha}\right)\\ &+\frac{\check{N}^{\mu\kappa}}{2\sigma}f_{\kappa\varsigma}X^\varsigma X^\lambda\left(\frac{\partial g_{\alpha\lambda}}{\partial X^\beta}+\frac{\partial g_{\beta\lambda}}{\partial X^\alpha}\right),\end{aligned} \tag{41}$$

where the thermodynamic Christoffel symbols of the second kind are introduced

$$\left\{\begin{matrix}\mu\\ \alpha\beta\end{matrix}\right\}=\frac{1}{2}g^{\mu\lambda}\left(\frac{\partial g_{\lambda\alpha}}{\partial X^\beta}+\frac{\partial g_{\lambda\beta}}{\partial X^\alpha}-\frac{\partial g_{\alpha\beta}}{\partial X^\lambda}\right) \tag{42}$$

and matrix $\check{N}^{\mu\kappa}$ is defined as

$$N_{\mu\nu}\equiv g_{\mu\nu}+\frac{1}{\sigma}f_{\mu\kappa}X^\kappa X_\nu+\frac{1}{\sigma}f_{\nu\kappa}X^\kappa X_\mu$$

$$\text{with}\quad \check{N}^{\mu\kappa}{:}\check{N}^{\mu\kappa}N_{\nu\kappa}=\delta^\mu_\nu. \tag{43}$$

In Appendix A it is proven that the affine connections (40) and (41) transform, under a TCT, as in Eq. (33) and satisfy the postulates (1)–(3). From Eq. (43) we easily check that

$$N_{\mu\nu}=N_{\nu\mu},$$

$$N_{\mu\nu}X^\nu=\left(g_{\mu\nu}+\frac{1}{\sigma}f_{\mu\kappa}X^\kappa X_\nu+\frac{1}{\sigma}f_{\nu\kappa}X^\kappa X_\mu\right)X^\nu=J_\mu,$$

$$N_{\mu\nu}X^\mu=N_{\nu\mu}X^\mu=J_\nu,$$

$$N_{\mu\nu}X^\nu X^\mu=J_\mu X^\mu=\sigma, \tag{44}$$

while

$$\check{N}^{\mu\kappa}=\check{N}^{\kappa\mu},$$

$$\check{N}^{\mu\kappa}J_\mu=\check{N}^{\mu\kappa}N_{\mu\nu}X^\nu=\check{N}^{\kappa\mu}N_{\nu\mu}X^\nu=X^\kappa,$$

$$\check{N}^{\mu\kappa}J_\kappa=\check{N}^{\kappa\mu}J_\kappa=X^\mu,$$

$$\check{N}^{\mu\kappa}J_\kappa J_\mu=X^\mu J_\mu=\sigma. \tag{45}$$

At this point, we are confronted with the following theorem [21] for two symmetric connections, the most general change which preserves the paths is:

$$\bar{\Gamma}^\mu_{\alpha\beta}=\Gamma^\mu_{\alpha\beta}+\delta^\mu_\alpha\psi_\beta+\delta^\mu_\beta\psi_\alpha, \tag{46}$$

where ψ_α is an arbitrary covariant thermodynamic vector and δ^μ_ν denotes the Kronecker tensor. In literature, the modifications of the connection similar to Eq. (46) are referred to as *projective transformations* of the connection and ψ_α the *projective covariant vector*. The introduction of the affine connection gives rise, then, to the following difficulty. The universal criterion of evolution is satisfied for every shortest path constructed with affine connections $\bar{\Gamma}^\mu_{\alpha\beta}$ linked to $\Gamma^\mu_{\alpha\beta}$ by projective transformations. This leads to an indetermination of the expression for the affine connection, which is not possible to remove by using the De Donder-Prigogine statement and the thermodynamic theorems alone. This problem can be solved by postulating that the *nonlinear closure equations* (i.e., the equations for the affine connection and the transport coefficients) be *symmetric* and *projective invariant* (i.e., invariant under projective transformations).

For any arbitrary covariant thermodynamic vector field denoted by $T_\mu(X)$, we can form the thermodynamic tensor $R^\mu_{\nu\lambda\kappa}(X)$ in the following manner [22]:

$$T_{\nu|\lambda|\kappa}(X) - T_{\nu|\kappa|\lambda}(X) = T_\mu(X) R^\mu_{\nu\lambda\kappa}(X), \tag{47}$$

where [by omitting, for conciseness, the symbol (X)]

$$R^\mu_{\nu\lambda\kappa} = \frac{\partial\Gamma^\mu_{\nu\kappa}}{\partial X^\lambda} - \frac{\partial\Gamma^\mu_{\nu\lambda}}{\partial X^\kappa} + \Gamma^\eta_{\nu\kappa}\Gamma^\mu_{\eta\lambda} - \Gamma^\eta_{\nu\lambda}\Gamma^\mu_{\eta\kappa}, \tag{48}$$

with $R^\mu_{\nu\lambda\kappa}$ satisfying the following identities:

$$R^\mu_{\nu\lambda\kappa} = -R^\mu_{\nu\kappa\lambda},$$

$$R^\mu_{\nu\lambda\kappa} + R^\mu_{\lambda\kappa\nu} + R^\mu_{\lambda\nu\kappa} = 0,$$

$$R^\mu_{\nu\lambda\kappa|\eta} + R^\mu_{\nu\kappa\eta|\lambda} + R^\mu_{\nu\eta\lambda|\kappa} = 0. \tag{49}$$

By contraction, we obtain two distinct thermodynamic tensors of second order

$$R_{\nu\lambda} = R^\mu_{\nu\lambda\mu} = \frac{\partial\Gamma^\mu_{\nu\mu}}{\partial X^\lambda} - \frac{\partial\Gamma^\mu_{\nu\lambda}}{\partial X^\mu} + \Gamma^\eta_{\nu\mu}\Gamma^\mu_{\eta\lambda} - \Gamma^\eta_{\nu\lambda}\Gamma^\mu_{\eta\mu},$$

$$F_{\lambda\nu} = \frac{1}{2}R^\mu_{\mu\lambda\nu} = \frac{1}{2}\left(\frac{\partial\Gamma^\mu_{\nu\mu}}{\partial X^\lambda} - \frac{\partial\Gamma^\mu_{\lambda\mu}}{\partial X^\nu}\right), \tag{50}$$

with $F_{\lambda\nu}$ being skew symmetric and $R_{\nu\lambda}$ being asymmetric. Tensor $R_{\nu\lambda}$ can be rewritten as

$$R_{\nu\lambda} = B_{\nu\lambda} + F_{\lambda\nu},$$

where

$$B_{\nu\lambda} = B_{\lambda\nu} = \frac{1}{2}\left(\frac{\partial\Gamma^\mu_{\nu\mu}}{\partial X^\lambda} + \frac{\partial\Gamma^\mu_{\lambda\mu}}{\partial X^\nu}\right) - \frac{\partial\Gamma^\mu_{\nu\lambda}}{\partial X^\mu} + \Gamma^\eta_{\nu\mu}\Gamma^\mu_{\eta\lambda} - \Gamma^\eta_{\nu\lambda}\Gamma^\mu_{\eta\mu}. \tag{51}$$

Hence, $F_{\lambda\nu}$ is the skew-symmetric part of $R_{\nu\lambda}$ [25]. It is argued that the closure equations can be derived by the variation in a stationary action, which involves $R_{\nu\lambda}$. Symmetric and projective invariant closure equations may be obtained by adopting the following strategy: (1) a suitable projective transformation of the affine connection is derived so that $R_{\nu\lambda}$ be symmetric and $F_{\lambda\nu}$ be a zero thermodynamic tensor and (2) the most general projective transformation that leave unaltered $R_{\nu\lambda}$ and $F_{\lambda\nu}$ (=0) is determined. By a projective transformation, it is found that

$$\bar{B}_{\nu\lambda} = B_{\nu\lambda} + n\left(\frac{\partial\psi_\nu}{\partial X^\lambda} - \psi_\nu\psi_\lambda\right) - \left(\frac{\partial\psi_\lambda}{\partial X^\nu} - \psi_\nu\psi_\lambda\right),$$

$$\bar{F}_{\lambda\nu} = F_{\lambda\nu} + \frac{n+1}{2}\left(\frac{\partial\psi_\lambda}{\partial X^\nu} - \frac{\partial\psi_\nu}{\partial X^\lambda}\right). \tag{52}$$

Equation (50) shows that $F_{\lambda\nu}$ can be written as the curl of the vector $a_\nu/2$ defined as [21]

$$a_\nu = \Gamma^\kappa_{\kappa\nu} - \left\{\begin{matrix}\kappa\\ \kappa\nu\end{matrix}\right\}. \tag{53}$$

Consequently, by choosing

$$\psi_\nu = -\frac{1}{n+1}\left(\Gamma^\kappa_{\kappa\nu} - \left\{\begin{matrix}\kappa\\ \kappa\nu\end{matrix}\right\}\right), \tag{54}$$

we have $\bar{F}_{\lambda\nu}=0$ and $\bar{R}_{\nu\lambda}=\bar{B}_{\nu\lambda}$. From Eq. (52), we also have that the thermodynamic tensor $\bar{\bar{R}}_{\nu\lambda}$ remains symmetric for projective transformations of connection if, and only if, the projective covariant vector is the gradient of an arbitrary function of the X's [21]. In this case, the thermodynamic tensor $\bar{\bar{F}}_{\lambda\nu}$ remains unaltered, i.e., $\bar{\bar{F}}_{\lambda\nu}=0$. Hence, at this stage, the expression of the affine connection is determined up to the gradient of a function, say ϕ, of the thermodynamic forces, which is also scalar under TCT. Let us impose now the projective invariance. Equation (52) indicate that a necessary and sufficient condition that $\bar{R}_{\nu\lambda}$ be projective invariant is that

$$\frac{\partial^2\phi}{\partial X^\lambda\,\partial X^\nu} - \frac{\partial\phi}{\partial X^\lambda}\frac{\partial\phi}{\partial X^\nu} = 0,$$

with

$$\phi = 0 \text{ (in the Onsager region)},$$

$$\frac{\partial\phi}{\partial X^\mu} = 0 \text{ (in the Onsager region)},$$

$$\frac{\partial^2\phi}{\partial X^\mu\,\partial X^\nu} = 0 \text{ (in the Onsager region)}, \tag{55}$$

where ϕ is a function, invariant under TCT. The solution of Eq. (55) is $\phi\equiv0$ everywhere. The final expression of the affine connection for symmetric processes reads then

$$\Gamma^\mu_{\alpha\beta} = \left\{\begin{matrix}\mu\\ \alpha\beta\end{matrix}\right\} + \frac{1}{2\sigma}X^\mu\mathcal{O}(g_{\alpha\beta}) - \frac{1}{2(n+1)\sigma}[\delta^\mu_\alpha X^\nu\mathcal{O}(g_{\beta\nu}) + \delta^\mu_\beta X^\nu\mathcal{O}(g_{\alpha\nu})]. \tag{56}$$

The general case is given by

$$\begin{aligned}\Gamma^{\mu}_{\alpha\beta}=\check{N}^{\mu\kappa}g_{\kappa\lambda}\left\{\begin{matrix}\lambda\\ \alpha\beta\end{matrix}\right\}+\frac{\check{N}^{\mu\kappa}}{2\sigma}X_{\kappa}\mathcal{O}(g_{\alpha\beta})\\ +\frac{\check{N}^{\mu\kappa}}{2\sigma}X_{\kappa}X^{\lambda}\left(\frac{\partial f_{\alpha\lambda}}{\partial X^{\beta}}+\frac{\partial f_{\beta\lambda}}{\partial X^{\alpha}}\right)\\ +\frac{\check{N}^{\mu\kappa}}{2\sigma}f_{\kappa\varsigma}X^{\varsigma}X^{\lambda}\left(\frac{\partial g_{\alpha\lambda}}{\partial X^{\beta}}+\frac{\partial g_{\beta\lambda}}{\partial X^{\alpha}}\right)+\psi_{\alpha}\delta^{\mu}_{\beta}+\psi_{\beta}\delta^{\mu}_{\alpha},\end{aligned} \tag{57}$$

where

$$\begin{aligned}\psi_{\nu}=-\frac{\check{N}^{\eta\kappa}g_{\kappa\lambda}}{n+1}\left\{\begin{matrix}\lambda\\ \eta\nu\end{matrix}\right\}-\frac{\check{N}^{\eta\kappa}X_{\kappa}}{2(n+1)\sigma}\mathcal{O}(g_{\nu\eta})\\ -\frac{\check{N}^{\eta\kappa}}{2(n+1)\sigma}X_{\kappa}X^{\lambda}\left(\frac{\partial f_{\eta\lambda}}{\partial X^{\nu}}+\frac{\partial f_{\nu\lambda}}{\partial X^{\eta}}\right)\\ -\frac{\check{N}^{\eta\kappa}}{2(n+1)\sigma}f_{\kappa\varsigma}X^{\varsigma}X^{\lambda}\left(\frac{\partial g_{\eta\lambda}}{\partial X^{\nu}}+\frac{\partial g_{\nu\lambda}}{\partial X^{\eta}}\right)+\frac{1}{n+1}\frac{\partial\log\sqrt{g}}{\partial X^{\nu}}.\end{aligned} \tag{58}$$

Note that the thermodynamic space tends to reduce to a (thermodynamic) Riemannian space when $\sigma^{-1}\ll 1$. The following definitions are adopted:

(i) The space covered by n independent thermodynamic forces X^{μ}, with metric tensor $g_{\mu\nu}$ and a linear single connection given by Eq. (57), may be referred to as *thermodynamic space* T_s (or, space of the thermodynamic forces).

In T_s, the length of an arc is defined by the formula

$$L=\int_{\varsigma_1}^{\varsigma_2}\left(g_{\mu\nu}\frac{dX^{\mu}}{d\varsigma}\frac{dX^{\nu}}{d\varsigma}\right)^{1/2}d\varsigma. \tag{59}$$

The positive definiteness of matrix $g_{\mu\nu}$ ensures that $L\geq 0$. Consider a coordinate system X^{μ}, defining the thermodynamic space T_s.

(i) All thermodynamic spaces obtained from T_s by a TCT transformation may be called entropy-covariant spaces. In the TFT description, a thermodynamic configuration corresponds to a point in the thermodynamic space T_s. The equilibrium state is the origin of the axes. Consider a thermodynamic system out of equilibrium, represented by a certain point, say a, in the thermodynamic space.

(ii) A thermodynamic system is said to *relax* (from the geometrical point of view) toward another point of the thermodynamic space, say b, if it moves from point a to point b following the shortest path (35), with the affine connection given in Eq. (57). Note that in this context the term relaxation refers to a relaxation in a geometrical sense.

(iii) With Eq. (57), Eq. (38) may be called the thermodynamic covariant differentiation of a thermodynamic vector, while Eqs. (34) and (37) as the thermodynamic covariant differentiation *along a curve* of a thermodynamic vector.

(iv) With affine connection (57), $R^{\mu}_{\nu\lambda\kappa}$ may be called the *thermodynamic curvature tensor*.

(v) The scalar R obtained by contracting the thermodynamic tensor $R_{\nu\lambda}$ with the symmetric piece of the transport coefficients (i.e., $R=R_{\nu\lambda}g^{\nu\lambda}$) may be called the thermodynamic curvature *scalar*.

The principle of least action. From expression (57), the following mixed thermodynamic tensor on the third order can be constructed:

$$\begin{aligned}\Psi^{\mu}_{\alpha\beta}\equiv\check{N}^{\mu\kappa}g_{\kappa\lambda}\left\{\begin{matrix}\lambda\\ \alpha\beta\end{matrix}\right\}+\frac{\check{N}^{\mu\kappa}}{2\sigma}X_{\kappa}\mathcal{O}(g_{\alpha\beta})\\ +\frac{\check{N}^{\mu\kappa}}{2\sigma}X_{\kappa}X^{\lambda}\left(\frac{\partial f_{\alpha\lambda}}{\partial X^{\beta}}+\frac{\partial f_{\beta\lambda}}{\partial X^{\alpha}}\right)\\ +\frac{\check{N}^{\mu\kappa}}{2\sigma}f_{\kappa\varsigma}X^{\varsigma}X^{\lambda}\left(\frac{\partial g_{\alpha\lambda}}{\partial X^{\beta}}+\frac{\partial g_{\beta\lambda}}{\partial X^{\alpha}}\right)\\ +\psi_{\alpha}\delta^{\mu}_{\beta}+\psi_{\beta}\delta^{\mu}_{\alpha}-\left\{\begin{matrix}\mu\\ \alpha\beta\end{matrix}\right\}.\end{aligned} \tag{60}$$

This thermodynamic tensor satisfies the important identities

$$\Psi^{\alpha}_{\alpha\beta}=\Psi^{\beta}_{\alpha\beta}=0. \tag{61}$$

Again, from $\Psi^{\mu}_{\alpha\beta}$ the mixed thermodynamic tensor on the fifth order can be constructed

$$\begin{aligned}S^{\mu\nu}_{\lambda\alpha\beta}\equiv\frac{1}{2}(\Psi^{\mu}_{\beta\lambda}\delta^{\nu}_{\alpha}+\Psi^{\mu}_{\alpha\lambda}\delta^{\nu}_{\beta}+\Psi^{\nu}_{\beta\lambda}\delta^{\mu}_{\alpha}\\ +\Psi^{\nu}_{\alpha\lambda}\delta^{\mu}_{\beta}-\Psi^{\mu}_{\alpha\beta}\delta^{\nu}_{\lambda}-\Psi^{\nu}_{\alpha\beta}\delta^{\mu}_{\lambda}).\end{aligned} \tag{62}$$

By contraction, a thermodynamic tensor on the third order, a thermodynamic vector, and a thermodynamic scalar can be formed as follows:

$$\begin{aligned}S^{\mu\nu}_{\lambda}\equiv S^{\mu\nu}_{\lambda\alpha\beta}g^{\alpha\beta}=\Psi^{\mu}_{\lambda\alpha}g^{\nu\alpha}+\Psi^{\nu}_{\lambda\alpha}g^{\mu\alpha}\\ -\frac{1}{2}\Psi^{\mu}_{\alpha\beta}g^{\alpha\beta}\delta^{\nu}_{\lambda}-\frac{1}{2}\Psi^{\nu}_{\alpha\beta}g^{\alpha\beta}\delta^{\mu}_{\lambda},\\ S^{\mu}\equiv S^{\mu\lambda}_{\lambda}=\frac{1-n}{2}\Psi^{\mu}_{\alpha\beta}g^{\alpha\beta},\\ S\equiv S^{\mu\nu}_{\lambda}\Psi^{\lambda}_{\mu\nu}=2\Psi^{\kappa}_{\lambda\mu}\Psi^{\lambda}_{\kappa\nu}g^{\mu\nu}.\end{aligned} \tag{63}$$

The following postulate is now introduced. There exists a thermodynamic action I, scalar under TCT, which is stationary with respect to arbitrary variations in the transport coefficients and the affine connection.

This action, scalar under TCT, is constructed from the transport coefficients, the affine connection, and their first derivatives. In addition, it should have linear second derivatives of the transport coefficients and it should not contain second (or higher) derivatives of the affine connection. We also require that the action is stationary when the affine connection takes the expression given in Eq. (57). The only action satisfying these requirements is

$$I=\int[R_{\mu\nu}-(\Gamma^{\lambda}_{\alpha\beta}-\tilde{\Gamma}^{\lambda}_{\alpha\beta})S^{\alpha\beta}_{\lambda\mu\nu}]g^{\mu\nu}\sqrt{g}d^{n}X, \tag{64}$$

where d^nX denotes an infinitesimal volume element in T_s and $\tilde{\Gamma}^{\kappa}_{\mu\nu}$ is the expression given in Eq. (57), i.e., $\tilde{\Gamma}^{\kappa}_{\mu\nu}=\Psi^{\kappa}_{\mu\nu}$

$+\left\{ {\kappa \atop \mu\nu} \right\}$. To avoid misunderstanding, while it is correct to mention that this postulate affirms the possibility of deriving the nonlinear closure equations by a variational principle it does not state that the expressions and theorems obtained from the solutions of these equations can also be derived by a variational principle. In particular, the well-known universal criterion of evolution established by Glansdorff-Prigogine *cannot* be derived by a variational principle (see also Sec. III).

E. Nonlinear closure equations

The transport coefficients and the affine connection should be considered as independent dynamical variables (as opposed to X^μ, which is a mere variable of integration) [26]. Therefore, the action (64) is stationary with respect to arbitrary variations in $g_{\mu\nu}$, $f_{\mu\nu}$, and $\Gamma^\lambda_{\mu\nu}$. As a first step, we suppose that the transport coefficients and the affine connection be subject to infinitesimal variations, i.e., $g_{\mu\nu}\to g_{\mu\nu}+\delta g_{\mu\nu}$, $f_{\mu\nu}\to f_{\mu\nu}+\delta f_{\mu\nu}$, and $\Gamma^\kappa_{\mu\nu}\to\Gamma^\kappa_{\mu\nu}+\delta\Gamma^\kappa_{\mu\nu}$, where $\delta g_{\mu\nu}$, $\delta f_{\mu\nu}$, and $\delta\Gamma^\kappa_{\mu\nu}$ are arbitrary, except that they are required to vanish as $|X^\mu|\to\infty$. Upon the application of the principle of stationary action, the following nonlinear closure equations (i.e., the equations for the transport coefficients and the affine connection) are derived (see Appendix B):

$$R_{\mu\nu}-\frac{1}{2}g_{\mu\nu}R=-S_\lambda^{\alpha\beta}\frac{\delta\tilde{\Gamma}^\lambda_{\alpha\beta}}{\delta g^{\mu\nu}},$$

$$S_\lambda^{\alpha\beta}\frac{\delta\tilde{\Gamma}^\lambda_{\alpha\beta}}{\delta f^{\mu\nu}}=0,$$

$$g_{\mu\nu|\lambda}=-\Psi^\alpha_{\mu\lambda}g_{\alpha\nu}-\Psi^\alpha_{\nu\lambda}g_{\alpha\mu}, \qquad (65)$$

where the variations in the affine connection (57) with respect to the transport coefficients appear in the first two equations. Notice that $R_{\mu\nu}-\frac{1}{2}g_{\mu\nu}R$ does not coincide with Einstein's tensor (see also Appendix C). From the first equation in Eq. (65) and for $n\neq 2$, the expression for the thermodynamic curvature scalar is obtained [28]

$$R=\frac{2}{n-2}g^{\mu\nu}S_\lambda^{\alpha\beta}\frac{\delta\tilde{\Gamma}^\lambda_{\alpha\beta}}{\delta g^{\mu\nu}}\quad (n\neq 2). \qquad (66)$$

The third equation in Eq. (65) can be rewritten as

$$g_{\mu\nu,\lambda}-\Gamma^\alpha_{\mu\lambda}g_{\alpha\nu}-\Gamma^\alpha_{\nu\lambda}g_{\alpha\mu}=-\Psi^\alpha_{\mu\lambda}g_{\alpha\nu}-\Psi^\alpha_{\nu\lambda}g_{\alpha\mu}, \qquad (67)$$

where the comma (,) denotes partial differentiation. Adding to this equation, the same equation with μ and λ interchanged and subtracting the same equation with ν and λ interchanged gives

$$g_{\mu\nu,\lambda}+g_{\lambda\nu,\mu}-g_{\mu\lambda,\nu}=2g_{\alpha\nu}\Gamma^\alpha_{\lambda\mu}-2g_{\alpha\nu}\Psi^\alpha_{\lambda\mu} \qquad (68)$$

or

$$\Gamma^\kappa_{\lambda\mu}=\left\{ {\kappa \atop \lambda\mu} \right\}+\Psi^\kappa_{\lambda\mu}=\tilde{\Gamma}^\kappa_{\lambda\mu}. \qquad (69)$$

Hence, action (64) is stationary when the affine connection takes the expression given in Eq. (57). For $a-a$ or $b-b$ processes, close to the Onsager region, it holds that

$$g_{\mu\nu}=L_{\mu\nu}+h_{\mu\nu}+O(\epsilon^2),$$

$$\lambda_\sigma=O(\epsilon)\quad\text{with}\quad\epsilon=\max\left\{\frac{|\text{eigenvalues}[g_{\mu\nu}-L_{\mu\nu}]|}{\text{eigenvalues}[L_{\mu\nu}]}\right\}\ll 1, \qquad (70)$$

where $\lambda_\sigma\equiv 1/\sigma$ and $h_{\mu\nu}$ are small variations with respect to Onsager's coefficients. In this region, Eq. (64) is stationary for arbitrary variations of $h_{\mu\nu}$ and $\Gamma^\kappa_{\mu\nu}$. It can be shown that [10]

$$L^{\lambda\kappa}\frac{\partial^2 h_{\mu\nu}}{\partial X^\lambda\,\partial X^\kappa}+L^{\lambda\kappa}\frac{\partial^2 h_{\lambda\kappa}}{\partial X^\mu\,\partial X^\nu}-L^{\lambda\kappa}\frac{\partial^2 h_{\lambda\nu}}{\partial X^\kappa\,\partial X^\mu}-L^{\lambda\kappa}\frac{\partial^2 h_{\lambda\mu}}{\partial X^\kappa\,\partial X^\nu}$$
$$=0+O(\epsilon^2),$$

$$\Gamma^\kappa_{\mu\nu}=\frac{1}{2}L^{\kappa\eta}(h_{\mu\eta,\nu}+h_{\nu\eta,\mu}-h_{\mu\nu,\eta})+O(\epsilon^2). \qquad (71)$$

Equation (71) should be solved with the appropriate gauge choice and boundary conditions.

The validity of Eq. (71) has been largely tested by analyzing several symmetric processes such as the thermoelectric effect and the unimolecular triangular chemical reactions [10]. More recently, these equations have been also used to study transport processes in magnetically confined plasmas. In all examined examples, the theoretical results of the TFT are in line with experiments. It is worthwhile mentioning that for transport processes in tokamak plasmas, the predictions of the TFT for radial energy and matter fluxes are much closer to the experimental data than the neoclassical theory, which fails with a factor $10^3\div 10^4$ [1,6]. The physical origin of this failure can be easily understood. As mentioned in the introduction, even in the absence of turbulence, the state of the plasma is close to—but not in—a state of local equilibrium. Indeed, starting from an arbitrary initial state, the collisions would tend, if they were alone, to bring the system very quickly to a local equilibrium state. But slow processes, i.e., free-flow and electromagnetic processes, prevent the plasma from reaching this state. The distribution function for the fluctuations of the thermodynamic quantities also deviates from a Maxwellian preventing the thermodynamic fluxes from being linearly connected with the conjugate forces (refer to the Onsager theory [2] and, for example, [29]). In tokamak plasmas, the thermodynamic forces and the conjugate flows are the generalized frictions and the Hermitian moments, respectively [6]. In the neoclassical theory, the flux-force relations have been truncated at the linear order (refer, for example, to [30]), in contrast with the fact that the distribution function of the thermodynamic fluctuations is not a Maxwellian. This may be one of the main causes of the strong disagreement between the neoclassical previsions and the experimental profiles [1,31]. It is, however, important to mention that it is well accepted that another main reason of this discrepancy is attributed to turbulent phenomena existing in tokamak plasmas. Fluctuations in plasmas can become unstable and therefore amplified, with their nonlinear interaction successively leading the plasma to a state, which is far away from equilibrium. In this condition, the transport properties are supposed to change significantly and to exhibit qualitative features and properties that could not be explained by collisional transport processes, e.g., size scaling with machine dimensions and nonlocal behaviors that clearly point at turbulence spreading, etc. The scope of the work cited in Ref. [1] is mainly to demonstrate that collisional transport processes in fusion plasmas can be computed via a nonlinear theory on a more rigorous and sound basis than that provided by the well-known classical and/or neoclassical theory. The proposed approach includes prior-known results as a limiting case, where nonlinear and nonlocal effects in collisional transport processes can be ignored. More generally, the TFT estimates of collisional transport fluxes can be amplified by up to 2 or 3 orders of magnitude with respect to the classical/neoclassical levels in the electron-transport channel, while ions corrections are much smaller. However, TFT collisional transport levels remain a fraction of the values observed experimentally, confirming that the turbulent transport is the generally dominant process determining particle and heat fluxes in magnetically confined plasmas. In this specific example, the nonlinear corrections provide with an evaluation of the (parallel) Hermitian moments of the electron and ion distribution functions [1].

F. Some remarks on spatially extended thermodynamic systems

The macroscopic description of thermodynamic systems gives rise to state variables that depend continuously on space coordinates. In this case, the thermodynamic forces possess an infinity associated to each point of the space coordinates. The system may be subdivided into N cells ($N \times N \times N$ in three dimensions), each of which labeled by a wave number $\mathbf{k}$, and we follow their relaxation. Without loss of generality, we consider a thermodynamic system confined in a rectangular box with sizes l_x, l_y, and l_z. We write the wave number as

$$\mathbf{k} = 2\pi\left(\frac{n_x}{l_x}, \frac{n_y}{l_y}, \frac{n_z}{l_z}\right) \quad \text{with} \quad \begin{cases} n_x = 0, \pm 1, \cdots \pm N_x \\ n_y = 0, \pm 1, \cdots \pm N_y \\ n_z = 0, \pm 1, \cdots \pm N_z . \end{cases} \tag{72}$$

The fluxes and forces developed in (spatial) Fourier's series read as

$$\mathcal{J}_\mu(\mathbf{r},t) = \sum_{\mathbf{n}=-\mathbf{N}}^{\mathbf{N}} \hat{J}_{\mu(\mathbf{k})}(t)\exp(i\mathbf{k}\cdot\mathbf{r}),$$

$$\mathcal{X}^\mu(\mathbf{r},t) = \sum_{\mathbf{n}'=-\mathbf{N}}^{\mathbf{N}} \hat{X}^\mu_{(\mathbf{k}')}(t)\exp(i\mathbf{k}'\cdot\mathbf{r}) \tag{73}$$

where, for brevity, $\mathbf{n}$ and $\mathbf{N}$ stand for $\mathbf{n}=(n_x,n_y,n_z)$ and $\mathbf{N}=(N_x,N_y,N_z)$, respectively. The Fourier coefficients are given by

$$\hat{J}_{\mu(\mathbf{k})}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{J}_\mu(\mathbf{r},t)\exp(-i\mathbf{k}\cdot\mathbf{r})dv,$$

$$\hat{X}^\mu_{(\mathbf{k}')}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{X}^\mu(\mathbf{r},t)\exp(-i\mathbf{k}'\cdot\mathbf{r})dv. \tag{74}$$

In particular, the contributions at the thermodynamic limit (i.e., for $\mathbf{k}\to 0$) are expressed as

$$\hat{J}_{\mu(0)}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{J}_\mu(\mathbf{r},t)dv = J_\mu(t),$$

$$\hat{X}^\mu_{(0)}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{X}^\mu(\mathbf{r},t)dv = X^\mu(t). \tag{75}$$

The entropy production and the fluxes-forces relations take, respectively, the form

$$\sigma(\mathbf{r},t) = \mathcal{J}_\mu(\mathbf{r},t)\mathcal{X}^\mu(\mathbf{r},t) \geq 0,$$

$$\mathcal{J}_\mu(\mathbf{r},t) = \tau_{\mu\nu}(\mathbf{r},t)\mathcal{X}^\nu(\mathbf{r},t). \tag{76}$$

Considering that

$$\int_0^{l_x}\int_0^{l_y}\int_0^{l_z} \exp[i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}]dv = \Omega\,\delta_{\mathbf{k}+\mathbf{k}',0}$$

with

$$\delta_{\mathbf{k}+\mathbf{k}',0} = \begin{cases} 0 & \text{if } \mathbf{k}+\mathbf{k}' \neq 0 \\ 1 & \text{if } \mathbf{k}+\mathbf{k}' = 0 \end{cases} \qquad \Omega = l_x l_y l_z \tag{77}$$

from the first equation in Eq. (76), we also find

$$\int_\Omega \mathcal{J}_\mu(\mathbf{r},t)\mathcal{X}^\mu(\mathbf{r},t)dv = \Omega\left[\hat{J}_{\mu(0)}(t)\hat{X}^\mu_{(0)}(t) + \sum_{\mathbf{k}\neq 0}\hat{J}_{\mu(\mathbf{k})}(t)\hat{X}^\mu_{(-k)}(t)\right] \geq 0. \tag{78}$$

On the other hand, we have

$$\hat{J}_{\mu(0)}(t) = \hat{\tau}_{\mu\nu(0)}(t)\hat{X}^\nu_{(0)}(t) + \sum_{\mathbf{k}\neq 0}\hat{\tau}_{\mu\nu(\mathbf{k})}(t)\hat{X}^\nu_{(-k)}(t), \tag{79}$$

where

$$\hat{\tau}_{\mu\nu(\mathbf{k})}(t) = \frac{1}{\Omega}\int_\Omega \tau_{\mu\nu}(\mathbf{r},t)\exp(-i\mathbf{k}\cdot\mathbf{r})dv. \tag{80}$$

Equation (78) can then be brought into the form

$$\int_\Omega \sigma dv = \Omega\hat{g}_{\mu\nu(0)}(t)\hat{X}^\mu_{(0)}(t)\hat{X}^\nu_{(0)}(t) + \Omega\sum_{\mathbf{k}\neq 0}[\hat{\tau}_{\mu\nu(\mathbf{k})}(t)\hat{X}^\nu_{(-k)}(t)\hat{X}^\nu_{(0)}(t) + \hat{J}_{\mu(\mathbf{k})}(t)\hat{X}^\mu_{(-k)}(t)] \geq 0, \tag{81}$$

where

$$\hat{g}_{\mu\nu(\mathbf{k})}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{G}_{\mu\nu}(\mathbf{r},t)\exp(-i\mathbf{k}\cdot\mathbf{r})dv,$$

$$\mathcal{G}_{\mu\nu}(\mathbf{r},t) \equiv \frac{1}{2}[\tau_{\mu\nu}(\mathbf{r},t) + \tau_{\nu\mu}(\mathbf{r},t)]. \tag{82}$$

In Eq. (81), the first term is the contribution at the thermodynamic limit, whereas the second expression reflects the interactions between the **k** cell and the other cells. In a relaxation process, contributions from different wave numbers are negligible with respect to those with same wave numbers (the *slaving principle* [32]) and, hence, we finally obtain

$$\int_\Omega \sigma dv \simeq \Omega \hat{g}_{\mu\nu(0)}(t)\hat{X}^{\mu}_{(0)}(t)\hat{X}^{\nu}_{(0)}(t) > 0 \qquad \forall\, \hat{X}^{\mu}_{(0)}(t)(\sigma \neq 0). \tag{83}$$

Last inequality is satisfied for any $\hat{X}^{\mu}_{(0)}(t)$ if, and only if

$$\hat{g}_{\mu\nu(0)}(t) = \frac{1}{\Omega}\int_\Omega \mathcal{G}_{\mu\nu}(\mathbf{r},t)dv = g_{\mu\nu}(t) \tag{84}$$

is a *positive-definite matrix*. Therefore, for spatially extended thermodynamic systems, we replace $X^{\mu}(t) \to X^{\mu}_{(\mathbf{k})}(t)$ and $\tau_{\mu\nu}(t) \to \tau_{\mu\nu(\mathbf{k})}(t)$. Under these conditions, Eq. (65) determines the nonlinear corrections to the Onsager coefficients, while Eqs. (34) and (38), with affine connection (57), are the thermodynamic covariant differentiation along a curve and the thermodynamic covariant differentiation of a thermodynamic vector, respectively.

G. Privileged thermodynamic coordinate system

By definition, a thermodynamic coordinate system is a set of coordinates defined so that the expression of the entropy production takes the form of Eq. (21). Once a particular set of thermodynamic coordinates is determined; the other sets of coordinates are linked to the first one through a TCT [see Eq. (22)]. The simplest way to determine a particular set of coordinates is to quote the entropy balance equation

$$\frac{\partial \rho s}{\partial t} + \nabla \cdot \mathbf{J}_s = \sigma, \tag{85}$$

where ρs is the local total entropy per unit volume and $\mathbf{J}_s$ is the entropy flux. Let us consider, as an example, a thermodynamic system confined in a rectangular box where chemical reactions, diffusion of matter, macroscopic motion of the volume element (convection), and heat current take place simultaneously. The entropy flux and the entropy production read [33,34] as

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}_q - \sum_i \mathbf{J}_i\mu_i\right) + \sum_i \rho_i v_i s_i, \tag{86}$$

$$\sigma = \mathbf{J}_q \cdot \nabla\frac{1}{T} - \frac{1}{T}\sum_i \mathbf{J}_i \cdot \left[\nabla\left(\frac{\mu_i}{T}\right) - \mathbf{F}_i\right] + \sum_i \frac{w_i A_i}{T} - \frac{1}{T}\sum_{ij}\Pi_{ij}\partial_{\mathbf{r}_i}v_j \geq 0, \tag{87}$$

where μ_i, $\rho_i s_i$, and A_i are the chemical potential, the local entropy, and the affinity of species "i," respectively. Moreover, $\mathbf{F}_i$ indicates the external force per unit mass acting on i, Π_{ij} indicate the components of the dissipative part of the pressure tensor $\mathcal{M}_{ij}$ ($\mathcal{M}_{ij}=p\delta_{ij}+\Pi_{ij}$; p is the hydrostatic pressure), and v_j is the component of the hydrodynamic velocity (see, for example, Ref. [35]). The set of thermodynamic coordinates is given as

$$\left\{\nabla\frac{1}{T};-\frac{1}{T}\left[\nabla\left(\frac{\mu_i}{T}\right)-\mathbf{F}_i\right];\frac{A_i}{T};-\frac{1}{T}\partial_{\mathbf{r}_i}v_j\right\}. \tag{88}$$

For this particular example, this set may be referred to as the *privileged thermodynamic coordinate system*. Other examples of privileged thermodynamic coordinate system, concerning magnetically confined plasmas, can be found in Refs. [16,30].

III. THERMODYNAMIC THEOREMS FOR SYSTEMS OUT OF EQUILIBRIUM

In 1947, Prigogine [3] proved the minimum entropy production theorem, which concerns the relaxation of thermodynamic systems near equilibrium. This theorem states as follows.

A. MEPT

For $a-a$ or $b-b$ processes, a thermodynamic system near equilibrium relaxes to a steady state X_s in such a way that the inequality

$$\frac{d\sigma}{dt} \leq 0 \tag{89}$$

is satisfied throughout the evolution and is only saturated at X_s.

The minimum entropy production theorem is generally not satisfied far from equilibrium. Indeed, under TCT, the rate of the entropy production transforms as

$$\frac{d\sigma'}{dt} = \frac{d\sigma}{dt} + \frac{\partial X'^{\kappa}}{\partial X^{\eta}}\frac{\partial^2 X^{\mu}}{\partial X^{\nu}\partial X'^{\kappa}}X^{\eta}J_{\mu}\frac{dX^{\nu}}{dt}. \tag{89a}$$

In particular, we find

$$J'_{\mu}\frac{dX'^{\mu}}{dt} = J_{\mu}\frac{dX^{\mu}}{dt},$$

$$X'^{\mu}\frac{dJ'_{\mu}}{dt} = X^{\mu}\frac{dJ_{\mu}}{dt} + \frac{\partial X'^{\kappa}}{\partial X^{\eta}}\frac{\partial^2 X^{\mu}}{\partial X^{\nu}\partial X'^{\kappa}}X^{\eta}J_{\mu}\frac{dX^{\nu}}{dt}. \tag{89b}$$

The second expression of Eqs. (89b) tells us that nothing can be said about the sign of $X^{\mu}{}_{dJ_\mu/dt}$. Concerning the quantity $J_{\mu\, dX^\mu/dt}$, Glansdorff and Prigogine [5] demonstrated in 1954 a theorem, which reads

B. UCE

When the thermodynamic forces and conjugate flows are related by a generic asymmetric tensor, regardless of the type of processes, for time-independent boundary conditions a thermodynamic system—even in strong nonequilibrium conditions—relaxes toward a steady state in such a way that the following universal criterion of evolution is satisfied:

$$\mathcal{P} \equiv J_\mu \frac{dX^\mu}{dt} \leq 0. \tag{90}$$

This *inequality* is only saturated at X_s.

For $a-a$ or $b-b$ processes, the UCE reduces to the MEPT in the Onsager region. As mentioned in the introduction of this paper, Glansdorff and Prigogine demonstrated this theorem using a purely thermodynamical approach. In this section, we shall see that if the system relaxes toward a steady state along the shortest path then the universal criterion of evolution is automatically satisfied.

By definition, a necessary and sufficient condition for a curve to be the shortest path is that it satisfies the differential equation

$$\frac{d^2X^\mu}{dt^2} + \Gamma^\mu_{\alpha\beta}\frac{dX^\alpha}{dt}\frac{dX^\beta}{dt} = \varphi(t)\frac{dX^\mu}{dt}, \tag{91}$$

where $\varphi(t)$ is a determined function of time. If we define a parameter ϱ by

$$\frac{d\varrho}{dt} = c \exp \int \varphi^* dt \quad \text{with} \quad \varphi^* = \varphi - 2\psi_\nu \frac{dX^\nu}{dt}, \tag{92}$$

where c is an arbitrary constant and ψ_ν is the projective covariant vector, Eq. (91) reduces to Eq. (35) with $\Gamma^\mu_{\alpha\beta}$ given by Eq. (41). Parameter ϱ is not the affine parameter s of the shortest path. The relation between these two parameters is

$$\varrho = b \int \exp\left(-2\int \psi_\nu dX^\nu\right) ds, \tag{93}$$

where b is an arbitrary constant. Equation (92) allows us to choose the parameter ϱ in such a way that it increases monotonically as the thermodynamic system evolves in time. In this case, c is a positive constant and, without loss of generality, we can set $c=1$. Parameter ϱ can also be chosen so that it vanishes when the thermodynamic system begins to evolve and it takes the (positive) value, say $\bar{l}$, when the system reaches the steady state. Multiplying Eq. (35) with the flows J_μ and contracting, we obtain

$$J_\mu \frac{d^2X^\mu}{d\varrho^2} + J_\mu \Gamma^\mu_{\alpha\beta}\frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho} = 0. \tag{94}$$

However

$$\begin{aligned} J_\mu \frac{d^2X^\mu}{d\varrho^2} = {} & \frac{d\tilde{P}}{d\varrho} - \left(\frac{d\varsigma}{d\varrho}\right)^2 - \frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho}X^\lambda \frac{\partial g_{\alpha\lambda}}{\partial X^\beta} \\ & - \frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho}X^\lambda \frac{\partial f_{\alpha\lambda}}{\partial X^\beta}, \end{aligned} \tag{95}$$

where $\tilde{P}=J_\mu \frac{dX^\mu}{d\varrho}$ and after taking into account the identities $f_{\mu\nu}\frac{dX^\mu}{d\varrho}\frac{dX^\nu}{d\varrho}=0$ and $g_{\mu\nu}\frac{dX^\mu}{d\varsigma}\frac{dX^\nu}{d\varsigma}=1$. In addition, recalling Eq. (45) and the relations $X_\mu X^\mu=\sigma$ and $f_{\mu\nu}X^\mu X^\nu=0$, it can be shown that

$$J_\mu \Gamma^\mu_{\alpha\beta}\frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho} = \frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho}X^\lambda \frac{\partial g_{\alpha\lambda}}{\partial X^\beta} + \frac{dX^\alpha}{d\varrho}\frac{dX^\beta}{d\varrho}X^\lambda \frac{\partial f_{\alpha\lambda}}{\partial X^\beta}. \tag{96}$$

Summing Eq. (95) with Eq. (96) and considering Eq. (94) gives

$$\frac{d\tilde{P}}{d\varrho} = \left(\frac{d\varsigma}{d\varrho}\right)^2. \tag{97}$$

Integrating Eq. (97) from the initial condition to the steady state, we find

$$\tilde{P}(X_s) - \tilde{P} = \int \left(\frac{d\varsigma}{d\varrho}\right)^2 d\varrho \geq 0. \tag{98}$$

From Eq. (20) we have $\tilde{P}(X_s)=P(X_s)d\varsigma/d\varrho=0$, so we finally obtain

$$\tilde{P} = J_\mu \frac{dX^\mu}{d\varrho} = -\int \left(\frac{d\varsigma}{d\varrho}\right)^2 d\varrho \leq 0, \tag{99}$$

where the inequality is only saturated at the steady state. Recalling Eq. (92), the inequality established by the UCE can be derived

$$\mathcal{P} = \tilde{P}\frac{d\varrho}{dt} = J_\mu \frac{dX^\mu}{d\varrho}\left(\exp\int \varphi^* dt\right) \leq 0. \tag{100}$$

Equation (97) can be rewritten as

$$\frac{d}{d\varsigma}\left[\left(\frac{d\varsigma}{d\varrho}\right)P\right] = \left(\frac{d\varsigma}{d\varrho}\right). \tag{101}$$

This equation generalizes Eq. (14), which was valid only in the near-equilibrium region (notice that in the linear region, $d\varsigma/d\varrho=1/b=\text{const}$). Integrating Eq. (101), the expression of the dissipative quantity P is derived

$$\begin{aligned} P &= -\left(\frac{d\varrho}{d\varsigma}\right)\int_\varsigma^l \left(\frac{d\varsigma'}{d\varrho}\right)d\varsigma' \\ &= -\left(g_{\mu\nu}\frac{dX^\mu}{d\varrho}\frac{dX^\nu}{d\varrho}\right)^{-1/2}\int_\varsigma^l \left(g_{\mu\nu}\frac{dX^\mu}{d\varrho}\frac{dX^\nu}{d\varrho}\right)^{1/2} d\varsigma' \leq 0. \end{aligned} \tag{102}$$

On the right, it is understood that the X's are expressed in terms of $\varrho(\varsigma)$. Equation (102) generalizes Eq. (12), which was valid only in the linear region. For $a-a$ or $b-b$ processes in the Onsager region, Eq. (100) implies the validity of the inequality (89). Indeed, Eq. (36) gives

$$\frac{\delta\sigma}{\delta\varrho} = \frac{d\sigma}{d\varrho} = J_\mu \frac{\delta X^\mu}{\delta\varrho} + X^\mu \frac{\delta J_\mu}{d\varrho} = 2J_\mu \frac{\delta X^\mu}{\delta\varrho} + X^\mu X^\nu \frac{\delta L_{\mu\nu}}{\delta\varrho}. \tag{103}$$

In the linear region, the coefficients of the affine connection vanish. Equation (103) is simplified reducing to

$$\frac{d\sigma}{dt} = \frac{d\sigma}{d\varrho}\frac{d\varrho}{dt} = 2\left(J_\mu \frac{dX^\mu}{d\varrho}\frac{d\varrho}{dt}\right) = 2\mathcal{P} \leq 0, \tag{104}$$

where the inequality is saturated only at the steady state.

Let us now consider spatially extended thermodynamic systems. We say that a spatially-extended system *relaxes* (from the geometrical point of view) towards a steady state if the thermodynamic mode (i.e., the mode with $\mathbf{k}=\mathbf{0}$) relaxes to the steady state following the shortest path. In this case, the dissipative quantity should be expressed in the integral form

$$\mathcal{P} = \int_\Omega \mathcal{J}_\mu(\mathbf{r},t) d_t \mathcal{X}^\mu(\mathbf{r},t) dv, \tag{105}$$

where $d_t\mathcal{X}^\mu \equiv d\mathcal{X}^\mu/dt$. In terms of wave vectors $\mathbf{k}$, Eq. (105) can easily be brought into the form

$$\mathcal{P} = \Omega\left[\hat{J}_{\mu(0)}(t) d_t \hat{X}^\mu_{(0)}(t) + \sum_{\mathbf{k}\neq 0} \hat{J}_{\mu(\mathbf{k})}(t) d_t \hat{X}^\mu_{(-k)}(t)\right], \tag{106}$$

where Eq. (77) has been taken into account. As already mentioned in Sec. II, in a relaxation process, contributions from different wave numbers are negligible with respect to those with same wave numbers [32]. Thus, considering Eq. (75), we finally obtain

$$\mathcal{P} = \int_\Omega \mathcal{J}_\mu(\mathbf{r},t) d_t \mathcal{X}^\mu(\mathbf{r},t) dv \simeq \Omega J_\mu(t) d_t X^\mu(t) \leq 0, \tag{107}$$

where inequality (100) has also been taken into account. It is therefore proven that the universal criterion of evolution is automatically satisfied if the system relaxes along the shortest path. Indeed it would be more exact to say that the affine connection given in Eq. (41) has been constructed, in such a way that the UCE is satisfied without imposing *any* restrictions on the transport coefficients (i.e., on matrices $g_{\mu\nu}$ and $f_{\mu\nu}$). In addition, analogously to Christoffel's symbols, the elements of the new affine connection have been constructed from matrices $g_{\mu\nu}$ and $f_{\mu\nu}$ and their first derivatives in such a way that all coefficients vanish in the Onsager region. Equation (41) provides the simplest expression satisfying these requirements.

C. MRDP

In Ref. [11], the validity of the following theorem [minimum rate of dissipation principle (MRDP)] is shown. The generally covariant part of the Glansdorff-Prigogine quantity is always negative and is locally minimized when the evolution of a system traces out a geodesic in the space of thermodynamic configurations.

It is important to stress that this theorem does not refer to the Glansdorff-Prigogine expression reported in Eq. (90) but only to its *generally covariant part*. Moreover, it concerns the evolution of a system in the space of thermodynamic configurations and not in the thermodynamic space. One could consider the possibility that the shortest path in the thermodynamic space is an extremal for the functional

$$\int_{\varsigma_1}^{\varsigma_2} J_\mu \dot{X}^\mu d\varsigma. \tag{108}$$

The answer is negative. Indeed, a curve is an extremal for functional (108) if, and only if, it satisfies Euler's equations [36],

$$\dot{X}^\nu\left(\frac{\partial J_\nu}{\partial X^\mu} - \frac{\partial J_\mu}{\partial X^\nu}\right) = 0. \tag{109}$$

As it can be easily checked, this extremal coincides with the shortest path if

$$\frac{1}{2}\left(\frac{M_{\mu\alpha}}{\partial X^\beta} + \frac{M_{\mu\beta}}{\partial X^\alpha}\right) - \Gamma^\kappa_{\alpha\beta} M_{\mu\kappa} = 0,$$

where

$$\begin{aligned} M_{\mu\nu} \equiv J_{\nu,\mu} - J_{\mu,\nu} = 2f_{\nu\mu} + X^\kappa(g_{\nu\kappa,\mu} - g_{\mu\kappa,\nu}) \\ + X^\kappa(f_{\nu\kappa,\mu} - f_{\mu\kappa,\nu}) \end{aligned} \tag{110}$$

and $\Gamma^\kappa_{\alpha\beta}$ given in Eq. (57). However, Eq. (110) are $n^2(n+1)/2$ equations for n^2 variables (the transport coefficients) and, in general, for $n \neq 1$, they do not admit solutions. We have thus another proof that the universal criterion of evolution cannot be derived from a variational principle.

IV. CONCLUSIONS AND LIMIT OF VALIDITY OF THE APPROACH

A macroscopic description of thermodynamic systems requires the formulation of a theory for the closure relations. To this purpose, a thermodynamic field theory has been proposed a decade ago. The aim of this theory was to determine the (nonlinear) deviations from of the Onsager coefficients, which satisfy the thermodynamic theorems for systems out of equilibrium. The Onsager matrix, which depends on the materials under consideration, entered in the theory as an input. Magnetically confined tokamak plasmas are an example of thermodynamic systems where the first basic assumption of the Onsager microscopic theory of fluctuations is not satisfied. This prevents the phenomenological relations from being linear. Another interesting case may be met in hydrodynamics. In some circumstances, indeed, nonlinear terms of convective origin may arise [37], as, for instance, in frame-indifferent time derivatives as corotational Jaumann derivative or upper-convected Maxwell time derivatives, which do not modify the entropy production.

The main purpose of this paper is to present a formulation of the thermodynamic field theory where one of the basic restrictions, namely, the closed form of the skew-symmetric piece of the transport coefficients (see Ref. [10]), has been removed. Furthermore, the general covariance principle respected—in reality—only by a very limited class of thermodynamic processes has been replaced by the thermodynamic covariance principle first introduced by De Donder and Prigogine for treating nonequilibrium chemical reactions [12]. The validity of the De Donder-Prigogine statement has been successfully tested, without exception until now, in a wide variety of physical processes going beyond the domain of chemical reactions. The introduction of this principle requested, however, the application of an appropriate mathematical formalism, which may be referred to as the entropy-covariant formalism. The construction of the present theory rests on two assumptions:

(i) the thermodynamic theorems valid when a generic thermodynamic system relaxes out of equilibrium are satisfied;

(ii) there exists a thermodynamic action, scalar under thermodynamic coordinate transformations, which is stationary for general variations in the transport coefficients and the affine connection.

The second strong assumption can only be judged by its results. A non-Riemannian geometry has been constructed out of the components of the affine connection, which has been determined by imposing the validity of the universal criterion of evolution for nonequilibrium systems, relaxing toward a steady state. Relaxation expresses an intrinsic physical property of a thermodynamic system. The affine connection, on the other hand, is an intrinsic property of geometry allowing to determine the equation for the shortest path. It is the author's opinion that a correct thermodynamical-geometrical theory should correlate these two properties. It is important to mention that the thermodynamic space tends to be Riemannian for small values of the inverse of the entropy production. In this limit, we obtain again the same closure relations found in Ref. [10]. The results established for magnetically confined plasmas [1] and for the nonlinear thermoelectric effect and the unimolecular triangular reaction [16] remain then valid.

Finally, note that the transport equations may take even more general forms than Eq. (15). The fluxes and the forces can be defined locally as fields depending on space coordinates and time. The most general transport relation takes the form

$$J_\mu(\mathbf{r},t) = \int_\Omega d\mathbf{r}' \int_0^t dt' \mathcal{L}_{\mu\nu}[X(\mathbf{r}',t')]X^\nu(\mathbf{r}-\mathbf{r}',t-t'). \tag{111}$$

This type of nonlocal and non-Markovian equation expresses the fact that the flux at a given point $(\mathbf{r},t)$ could be influenced by the values of the forces in its spatial environment and by its history. Whenever the spatial and temporal ranges of influence are sufficiently small, the delocalization and the retardation of the forces can be neglected under the integral,

$$\begin{aligned}\mathcal{L}_{\mu\nu}&[X(\mathbf{r}',t')]X^\nu(\mathbf{r}-\mathbf{r}',t-t') \\ &\simeq 2\tau_{\mu\nu}[X(\mathbf{r},t)]X^\nu(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'),\end{aligned} \tag{112}$$

where δ denotes the Dirac delta function. In this case, the transport equations reduces to

$$J_\mu(\mathbf{r},t) \simeq \tau_{\mu\nu}[X(\mathbf{r},t)]X^\nu(\mathbf{r},t). \tag{113}$$

In the vast majority of cases studied at present in transport theory, it is assumed that the transport equations are of the form of Eq. (113). However, equations of the form (111) may be met when we deal with anomalous transport processes such as, for example, transport in turbulent tokamak plasmas [38]. Equation (112) establishes, in some sort, the limit of validity of the present approach. Equation (65) determines the nonlinear corrections to the linear (Onsager) transport coefficients whenever the width of the nonlocal coefficients can be neglected. It is worthwhile mentioning that in this paper, the thermodynamic quantities (number density, temperature, pressure, etc.) are evaluated at the local equilibrium state. This is not inconsistent with the fact that the arbitrary state of a thermodynamic system is close to (but not in) a state of local equilibrium. Indeed, as known, it is always possible to construct a representation in such a way that the thermodynamic quantities evaluated with a distribution function close to a Maxwellian do coincide *exactly* with those evaluated at the local equilibrium state (see, for example, the textbook [30]).

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APPENDIX A: TRANSFORMATION LAW AND PROPERTIES OF THE AFFINE CONNECTION (57)

In this section we show that the affine connection (57) transforms, under TCT, as in Eq. (33) and satisfies the postulates (1)–(3). We first note that the quantity $\delta^\lambda_\alpha\psi_\beta+\delta^\lambda_\beta\psi_\alpha$ transforms like a mixed thermodynamic tensor of third rank

$$\delta^\lambda_\alpha\psi_\beta+\delta^\lambda_\beta\psi_\alpha=(\delta^\tau_\rho\psi_\nu+\delta^\tau_\nu\psi_\rho)\frac{\partial X'^\lambda}{\partial X^\tau}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}. \tag{A1}$$

Thus, if Eq. (41) transforms, under TCT, such as Eq. (33), then so will be Eq. (57). Consider the symmetric processes. From Eq. (24), we have

$$\begin{aligned}\frac{\partial g'_{\alpha\beta}}{\partial X'^\kappa}&=\frac{\partial g_{\rho\nu}}{\partial X^\varrho}\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+g_{\rho\nu}\frac{\partial^2X^\rho}{\partial X'^\kappa\,\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta} \\ &\quad+g_{\rho\nu}\frac{\partial^2X^\rho}{\partial X'^\kappa\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\alpha}.\end{aligned} \tag{A2}$$

The thermodynamic Christoffel symbols transform then as

$$\left\{\begin{matrix}\lambda\\ \alpha\beta\end{matrix}\right\}'=\left\{\begin{matrix}\tau\\ \rho\nu\end{matrix}\right\}\frac{\partial X'^\lambda}{\partial X^\tau}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+\frac{\partial X'^\lambda}{\partial X^\rho}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}. \tag{A3}$$

Recalling that $\sigma'=\sigma$, from Eq. (A2) we also find

$$\frac{\check{N}'^{\lambda\kappa}}{2\sigma'}X'_\kappa\mathcal{O}'(g'_{\alpha\beta})=\frac{\check{N}^{\tau\eta}}{2\sigma}X_\eta\mathcal{O}(g_{\rho\nu})\frac{\partial X'^\lambda}{\partial X^\tau}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta},$$

$$\frac{1}{2\sigma'}X'^\lambda\mathcal{O}'(g'_{\alpha\beta})=\frac{1}{2\sigma}X^\tau\mathcal{O}(g_{\rho\nu})\frac{\partial X'^\lambda}{\partial X^\tau}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta},\quad\text{(A4)}$$

where Eqs. (22) and (29) have been taken into account. Therefore, the affine connection

$$\Gamma^\tau_{\rho\nu}=\left\{\begin{matrix}\tau\\ \rho\nu\end{matrix}\right\}+\frac{1}{2\sigma}X^\tau\mathcal{O}(g_{\rho\nu})-\frac{1}{2(n+1)\sigma}[\delta^\tau_\rho X^\eta\mathcal{O}(g_{\nu\eta})+\delta^\tau_\nu X^\eta\mathcal{O}(g_{\rho\nu})]\quad\text{(A5)}$$

transforms as

$$\Gamma'^\lambda_{\alpha\beta}=\Gamma^\tau_{\rho\nu}\frac{\partial X'^\lambda}{\partial X^\tau}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+\frac{\partial X'^\lambda}{\partial X^\rho}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}.\quad\text{(A6)}$$

Consider now the general case. From Eq. (24) we obtain

$$\frac{1}{2}\left(\frac{\partial g'_{\alpha\kappa}}{\partial X'^\beta}+\frac{\partial g'_{\beta\kappa}}{\partial X'^\beta}-\frac{\partial g'_{\alpha\beta}}{\partial X'^\kappa}\right)=\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}\left[\frac{1}{2}\left(\frac{\partial g_{\nu\varrho}}{\partial X^\rho}+\frac{\partial g_{\rho\varrho}}{\partial X^\nu}-\frac{\partial g_{\rho\nu}}{\partial X^\varrho}\right)\right]+g_{\rho\nu}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\kappa}.\quad\text{(A7)}$$

From Eq. (26), we also have

$$\frac{\partial f'_{\alpha\mu}}{\partial X'^\beta}=\frac{\partial f_{\rho\eta}}{\partial X^\varsigma}\frac{\partial X^\varsigma}{\partial X'^\beta}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\beta\,\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\beta\,\partial X'^\mu}\frac{\partial X^\eta}{\partial X'^\alpha},$$

$$\frac{\partial f'_{\beta\mu}}{\partial X'^\alpha}=\frac{\partial f_{\varsigma\eta}}{\partial X^\rho}\frac{\partial X^\varsigma}{\partial X'^\beta}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\eta}{\partial X'^\mu}+f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\mu}\frac{\partial X^\eta}{\partial X'^\beta}.\quad\text{(A8)}$$

Taking into account Eqs. (22) and (29), we find

$$X'_\kappa X'^\mu\frac{\partial f'_{\alpha\mu}}{\partial X'^\beta}=X_\varrho X^\eta\frac{\partial f_{\rho\eta}}{\partial X^\nu}\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+X_\nu X^\eta f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\kappa},$$

$$X'_\kappa X'^\mu\frac{\partial f'_{\beta\mu}}{\partial X'^\alpha}=X_\varrho X^\eta\frac{\partial f_{\nu\eta}}{\partial X^\rho}\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+X_\nu X^\eta f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\kappa},\quad\text{(A9)}$$

from which we obtain

$$\frac{1}{2\sigma'}X'_\kappa X'^\mu\left(\frac{\partial f'_{\alpha\mu}}{\partial X'^\beta}+\frac{\partial f'_{\beta\mu}}{\partial X'^\alpha}\right)=\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}\left[\frac{1}{2\sigma}X_\varrho X^\eta\left(\frac{\partial f_{\rho\eta}}{\partial X^\nu}+\frac{\partial f_{\nu\eta}}{\partial X^\rho}\right)\right]+\frac{1}{\sigma}X_\nu X^\eta f_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\kappa}.\quad\text{(A10)}$$

Let us now reconsider the transformations of the following quantities:

$$\frac{\partial g'_{\alpha\mu}}{\partial X'^\beta}=\frac{\partial g_{\rho\eta}}{\partial X^\varsigma}\frac{\partial X^\varsigma}{\partial X'^\beta}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+g_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\beta\,\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+g_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\beta\,\partial X'^\mu}\frac{\partial X^\eta}{\partial X'^\alpha},$$

$$\frac{\partial g'_{\beta\mu}}{\partial X'^\alpha}=\frac{\partial g_{\varsigma\eta}}{\partial X^\rho}\frac{\partial X^\varsigma}{\partial X'^\beta}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+g_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\eta}{\partial X'^\mu}+g_{\rho\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\mu}\frac{\partial X^\eta}{\partial X'^\beta}.\quad\text{(A11)}$$

From these equations, we obtain

$$X'^\mu\frac{\partial g'_{\alpha\mu}}{\partial X'^\beta}+X'^\mu\frac{\partial g'_{\beta\mu}}{\partial X'^\alpha}=\left(X^\eta\frac{\partial g_{\rho\eta}}{\partial X^\varsigma}+\frac{\partial g_{\varsigma\eta}}{\partial X^\rho}\right)\frac{\partial X^\varsigma}{\partial X'^\beta}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\eta}{\partial X'^\mu}+2X_\rho\frac{\partial^2X^\rho}{\partial X'^\beta\,\partial X'^\alpha},\quad\text{(A12)}$$

where Eq. (29) has been taken into account. From Eq. (A12) we finally obtain

$$\frac{1}{2\sigma'}\left[X'^\varsigma\left(\frac{\partial g'_{\alpha\varsigma}}{\partial X'^\beta}+\frac{\partial g'_{\beta\varsigma}}{\partial X'^\alpha}\right)\right]f'_{\kappa\mu}X'^\mu=\frac{1}{2\sigma}\left[X^\eta\left(\frac{\partial g_{\rho\eta}}{\partial X^\nu}+\frac{\partial g_{\nu\eta}}{\partial X^\rho}\right)\right]f_{\varrho\varsigma}X^\varsigma\frac{\partial X^\varrho}{\partial X'^\kappa}\frac{\partial X^\rho}{\partial X'^\alpha}\frac{\partial X^\nu}{\partial X'^\beta}+\frac{1}{\sigma}X_\rho X^\eta f_{\nu\eta}\frac{\partial^2X^\rho}{\partial X'^\alpha\,\partial X'^\beta}\frac{\partial X^\nu}{\partial X'^\kappa}.\quad\text{(A13)}$$

Summing Eq. (A7) with Eqs. (A10) and (A13), it follows that:

$$\check{N}'^{\lambda}_{\alpha\beta} = \check{N}^{\tau}_{\rho\nu}\frac{\partial X'^{\lambda}}{\partial X^{\tau}}\frac{\partial X^{\rho}}{\partial X'^{\alpha}}\frac{\partial X^{\nu}}{\partial X'^{\beta}} + \frac{\partial X'^{\lambda}}{\partial X^{\rho}}\frac{\partial^2 X^{\rho}}{\partial X'^{\alpha}\,\partial X'^{\beta}}, \qquad (A14)$$

where

$$\check{N}^{\tau}_{\rho\nu} = \check{N}^{\tau\varrho}g_{\varrho\varsigma}\left\{ \begin{matrix} \varsigma \\ \rho\nu \end{matrix} \right\} + \frac{\check{N}^{\tau\varrho}X_{\varrho}X^{\eta}}{2\sigma}\left(\frac{\partial f_{\rho\eta}}{\partial X^{\nu}} + \frac{\partial f_{\nu\eta}}{\partial X^{\rho}}\right) + \frac{\check{N}^{\tau\varrho}f_{\varrho\varsigma}X^{\varsigma}X^{\eta}}{2\sigma}\left(\frac{\partial g_{\rho\eta}}{\partial X^{\nu}} + \frac{\partial g_{\nu\eta}}{\partial X^{\rho}}\right) \qquad (A15)$$

and

$$\check{N}^{\tau\varrho}N_{\rho\varrho} = \delta^{\tau}_{\rho} \quad \text{with} \quad N_{\rho\varrho} = g_{\rho\varrho} + \frac{1}{\sigma}f_{\rho\eta}X^{\eta}X_{\varrho} + \frac{1}{\sigma}f_{\varrho\eta}X^{\eta}X_{\rho}. \qquad (A16)$$

Summing again Eq. (A15) with Eq. (A1) and the first equation of Eq. (A4), we finally obtain

$$\Gamma'^{\lambda}_{\alpha\beta} = \Gamma^{\tau}_{\rho\nu}\frac{\partial X'^{\lambda}}{\partial X^{\tau}}\frac{\partial X^{\rho}}{\partial X'^{\alpha}}\frac{\partial X^{\nu}}{\partial X'^{\beta}} + \frac{\partial X'^{\lambda}}{\partial X^{\rho}}\frac{\partial^2 X^{\rho}}{\partial X'^{\alpha}\,\partial X'^{\beta}}, \qquad (A17)$$

where

$$\Gamma^{\tau}_{\rho\nu} = \check{\Gamma}^{\tau}_{\rho\nu} + \frac{\check{N}^{\tau\eta}}{2\sigma}X_{\eta}\mathcal{O}(g_{\rho\nu}) + \delta^{\tau}_{\rho}\psi_{\nu} + \delta^{\tau}_{\nu}\psi_{\rho}. \qquad (A18)$$

It is not difficult to prove that the affine connection (57) satisfies the postulates (1)–(3). Indeed, if A^{μ} indicates a thermodynamic vector, we have

$$A'^{\lambda} = A^{\eta}\frac{\partial X'^{\lambda}}{\partial X^{\eta}}. \qquad (A19)$$

Deriving this equation, with respect to parameter ς, we obtain

$$\frac{dA'^{\lambda}}{d\varsigma} = \frac{dA^{\eta}}{d\varsigma}\frac{\partial X'^{\lambda}}{\partial X^{\eta}} + A^{\eta}\frac{\partial^2 X'^{\lambda}}{\partial X^{\tau}\,\partial X^{\eta}}\frac{dX^{\tau}}{d\varsigma}. \qquad (A20)$$

Taking into account the following identities:

$$\frac{\partial^2 X'^{\lambda}}{\partial X^{\tau}\,\partial X^{\eta}} = -\frac{\partial X'^{\lambda}}{\partial X^{\rho}}\frac{\partial X'^{\alpha}}{\partial X^{\tau}}\frac{\partial^2 X^{\rho}}{\partial X^{\eta}\,\partial X'^{\alpha}} = -\frac{\partial X'^{\alpha}}{\partial X^{\tau}}\frac{\partial X'^{\beta}}{\partial X^{\eta}}\frac{\partial X'^{\lambda}}{\partial X^{\rho}}\frac{\partial^2 X^{\rho}}{\partial X'^{\alpha}\,\partial X'^{\beta}} \qquad (A21)$$

and Eq. (A17), we find

$$\frac{\delta A'^{\lambda}}{\delta\varsigma} = \frac{\delta A^{\eta}}{\delta\varsigma}\frac{\partial X'^{\lambda}}{\partial X^{\eta}}. \qquad (A22)$$

The validity of postulates (2) and (3) is immediately verified, by direct computation, using Eqs. (34) and (37). The validity of these postulates was shown above for a thermodynamic vector. By a closely analogous procedure, it can be checked that the postulated (1)–(3) are satisfied for any thermodynamic tensor.

APPENDIX B: DERIVATION OF THE NONLINEAR CLOSURE EQUATIONS FROM THE ACTION PRINCIPLE

In this appendix, the nonlinear closure equations by the principle of the least action are derived. Let us rewrite Eq. (64) as

$$I = \int [R_{\mu\nu}g^{\mu\nu} - (\Gamma^{\lambda}_{\mu\nu} - \tilde{\Gamma}^{\lambda}_{\mu\nu})S^{\mu\nu}_{\lambda}]\sqrt{g}d^nX, \qquad (B1)$$

where the expression of $S^{\mu\nu}_{\lambda}$ is given by Eq. (63). This action is stationary by varying independently the transport coefficients (i.e., by varying, separately, $g_{\mu\nu}$ and $f_{\mu\nu}$) and the affine connection $\Gamma^{\lambda}_{\mu\nu}$. A variation with respect to $\Gamma^{\lambda}_{\mu\nu}$ reads as

$$\delta I_{\Gamma} = \int [\delta R_{\mu\nu}g^{\mu\nu} - \delta\Gamma^{\lambda}_{\mu\nu}S^{\mu\nu}_{\lambda}]\sqrt{g}d^nX = 0. \qquad (B2)$$

By direct computation, we can check that

$$\delta R_{\mu\nu} = (\delta\Gamma^{\lambda}_{\mu\lambda})_{|\nu} - (\delta\Gamma^{\lambda}_{\mu\nu})_{|\lambda}. \qquad (B3)$$

Defining $\mathcal{K}^{\mu\nu} \equiv \sqrt{g}g^{\mu\nu}$, we have the identities

$$(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda})_{|\nu} = \mathcal{K}^{\mu\nu}_{|\nu}\delta\Gamma^{\lambda}_{\mu\lambda} + \mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda|\nu},$$

$$(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu})_{|\lambda} = \mathcal{K}^{\mu\nu}_{|\lambda}\delta\Gamma^{\lambda}_{\mu\nu} + \mathcal{K}^{\mu\nu}\delta\Gamma\lambda_{\mu\nu|\lambda}. \qquad (B4)$$

Equation (B2) can be rewritten as

$$\delta I_{\Gamma} = \int (\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda})_{|\nu}d^nX - \int \mathcal{K}^{\mu\nu}_{|\nu}\delta\Gamma^{\lambda}_{\mu\lambda}d^nX + \int \mathcal{K}^{\mu\nu}_{|\lambda}\delta\Gamma^{\lambda}_{\mu\nu}d^nX - \int (\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu})_{|\lambda}d^nX - \int S^{\mu\nu}_{\lambda}\delta\Gamma^{\lambda}_{\mu\nu}\sqrt{g}d^nX = 0. \qquad (B5)$$

The thermodynamic covariant derivative of the metric tensor reads as

$$g_{\alpha\beta|\lambda} = g_{\alpha\beta,\lambda} - \Gamma^{\eta}_{\alpha\lambda}g_{\eta\beta} - \Gamma^{\eta}_{\beta\lambda}g_{\eta\alpha}, \qquad (B6)$$

from which we find

$$\Gamma^{\beta}_{\lambda\beta} = -\frac{1}{2}g^{\alpha\beta}g_{\alpha\beta|\lambda} + \frac{1}{2}g^{\alpha\beta}g_{\alpha\beta,\lambda}. \qquad (B7)$$

Taking into account that $\delta\sqrt{g} = 1/2\sqrt{g}g^{\mu\nu}\delta g_{\mu\nu}$, Eq. (B7) can also be brought into the form

$$\Gamma^{\beta}_{\lambda\beta} - \frac{1}{\sqrt{g}}\sqrt{g}_{,\lambda} + \frac{1}{\sqrt{g}}\sqrt{g}_{|\lambda} = 0. \qquad (B8)$$

On the other hand, we can easily check the validity of the following identities:

$$(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda})_{|\nu} = (\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda})_{,\nu} + \left(\Gamma^{\beta}_{\nu\beta} - \frac{1}{\sqrt{g}}\sqrt{g}_{,\nu} + \frac{1}{\sqrt{g}}\sqrt{g}_{|\nu}\right)\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda},$$

TABLE I. Comparison between the General Relativity and the Thermodynamic Field Theory Geometries.

	General relativity	TFT
Geometry	Pseudo-Riemannian	Non-Riemannian
Field	Symmetric	Asymmetric
Metric	Minkowski (3+1) signature	Positive definite
Space	Pseudo-Riemannian	Thermodynamic space
Covariance	General covariance principle	Homogeneous functions of first degree
Equivalence principle	Satisfied	Not satisfied
Universal criterion of evolution	Not satisfied	Satisfied
Main invariant	Proper time	Entropy production
$\Gamma^{\mu}_{\alpha\beta}$	Levi-Civita's connection	New thermodynamic affine connection
$R^{\mu}_{\nu\lambda\kappa}$	Riemannian's tensor	New thermodynamic curvature tensor
$R_{\nu\lambda}$	Ricci's tensor	New thermodynamic tensor
$R_{\mu\nu}-1/2g_{\mu\nu}R$	Einstein's tensor	New thermodynamic tensor

$$(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu})_{|\lambda}=(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu})_{,\lambda}+\left(\Gamma^{\beta}_{\lambda\beta}-\frac{1}{\sqrt{g}}\sqrt{g}_{,\lambda}+\frac{1}{\sqrt{g}}\sqrt{g}_{|\lambda}\right)\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu}. \tag{B9}$$

Therefore, from Eq. (B8), the terms

$$\int(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\lambda})_{|\nu}d^nX,\qquad\int(\mathcal{K}^{\mu\nu}\delta\Gamma^{\lambda}_{\mu\nu})_{|\lambda}d^nX \tag{B10}$$

drop out when we integrate over all thermodynamic space. Equation (B5) reduces then to

$$\delta I_{\Gamma}=-\int\mathcal{K}^{\mu\nu}_{|\nu}\delta\Gamma^{\lambda}_{\mu\lambda}d^nX+\int\mathcal{K}^{\mu\nu}_{|\lambda}\delta\Gamma^{\lambda}_{\mu\nu}d^nX-\int S^{\mu\nu}_{\lambda}\delta\Gamma^{\lambda}_{\mu\nu}\sqrt{g}d^nX=0. \tag{B11}$$

It is seen that δI_{Γ} vanishes for general variation of $\delta\Gamma^{\lambda}_{\mu\nu}$ if, and only if,

$$-\frac{1}{2}\mathcal{K}^{\mu\alpha}_{|\alpha}\delta^{\nu}_{\lambda}-\frac{1}{2}\mathcal{K}^{\nu\alpha}_{|\alpha}\delta^{\mu}_{\lambda}+\mathcal{K}^{\mu\nu}_{|\lambda}-S^{\mu\nu}_{\lambda}\sqrt{g}=0. \tag{B12}$$

Contracting indexes ν with λ, we find

$$\mathcal{K}^{\mu\alpha}_{|\alpha}-\Psi^{\mu}_{\alpha\beta}g^{\alpha\beta}\sqrt{g}=0, \tag{B13}$$

where Eq. (63) has been taken into account. Thanks to Eq. (B13), Eq. (B12) becomes

TABLE II. Descriptions of terms appearing in the manuscript.

Term	Description
TCT	$X'^{\mu}=X^1F^{\mu}(\frac{X^2}{X^1},\frac{X^3}{X^2},\cdots\frac{X^n}{X^{n-1}})$, where F^{μ} are arbitrary functions
Covariant thermodynamic vector A^{μ}	A set of quantities transforming, under TCT, as $A'^{\mu}=\frac{\partial X'^{\mu}}{\partial X^{\nu}}A^{\nu}$
Contravariant thermodynamic vector A_{μ}	A set of quantities transforming, under TCT, as $A'_{\mu}=\frac{\partial X^{\nu}}{\partial X'^{\mu}}A_{\nu}$
Parallel transport	Moving a vector along a curve without changing its direction
Affine connection	A rule for parallel transport
Manifold	A set of points, which has a continuous 1−1 map *onto* a set of R^n
Differential manifold	A manifold with some additional structure allowing to do differential calculus on the manifold.
Linear connection	A differential-geometric structure on a differential manifold $\mathcal{M}$ associated with an affine connection on $\mathcal{M}$, which satisfies the transformation law (33)
Thermodynamic affine connection $\Gamma^{\nu}_{\lambda\kappa}$	The affine connection given in Eq. (57)
Tangent space	A real vector space, containing all possible directions, attached to every point of a differential manifold.
Riemannian geometry	A geometry constructed out of a symmetric positive-definite second-rank tensor
Riemannian manifold	A real differential manifold in which each tangent space is equipped with an inner product, which varies smoothly from point to point. The metric is a positive-definite metric tensor
Riemannian space	A space equipped with a positive-definite metric tensor and with the Levi-Civita connection.
Non-Riemannian geometry	A geometry constructed out of the components of the affine connections
Thermodynamic space	A space equipped with $g_{\mu\nu}$ as metric tensor and with the single affine connection given in Eq. (57)

$$\mathcal{K}^{\mu\nu}_{|\lambda}=\Psi^{\mu}_{\alpha\lambda}g^{\nu\alpha}\sqrt{g}+\Psi^{\nu}_{\alpha\lambda}g^{\mu\alpha}\sqrt{g}. \tag{B14}$$

From the identity $\delta g^{\mu\nu}=-g^{\mu\alpha}g^{\nu\beta}\delta g_{\alpha\beta}$, we also have

$$\mathcal{K}^{\mu\nu}_{|\lambda}=\sqrt{g}_{|\lambda}g^{\mu\nu}+\sqrt{g}g^{\mu\nu}_{|\lambda}=\frac{1}{2}\sqrt{g}g^{\mu\nu}g^{\alpha\beta}g_{\alpha\beta|\lambda}-\sqrt{g}g^{\mu\alpha}g^{\nu\beta}g_{\alpha\beta|\lambda}. \tag{B15}$$

Equation (B14) reads then

$$-g^{\mu\alpha}g^{\nu\beta}g_{\alpha\beta|\lambda}+\frac{1}{2}g^{\alpha\beta}g_{\alpha\beta|\lambda}g^{\mu\nu}=\Psi^{\mu}_{\alpha\lambda}g^{\nu\alpha}+\Psi^{\nu}_{\alpha\lambda}g^{\mu\alpha}. \tag{B16}$$

Contracting this equation with $g_{\mu\nu}$, we find, for $n\neq 2$

$$g^{\alpha\beta}g_{\alpha\beta|\lambda}=0, \tag{B17}$$

where Eq. (61) has been taken into account. Equation (B16) is simplified as

$$-g^{\mu\alpha}g^{\nu\beta}g_{\alpha\beta|\lambda}=\Psi^{\mu}_{\alpha\lambda}g^{\nu\alpha}+\Psi^{\nu}_{\alpha\lambda}g^{\mu\alpha}. \tag{B18}$$

Contracting again Eq. (B18) with $g_{\mu\eta}g_{\nu\rho}$, we finally obtain

$$g_{\eta\rho|\lambda}=-\Psi^{\alpha}_{\eta\lambda}g_{\alpha\rho}-\Psi^{\alpha}_{\rho\lambda}g_{\alpha\eta}. \tag{B19}$$

The first two equations in Eq. (65) are straightforwardly obtained considering that from Eq. (B19) we derive $\Gamma^{\lambda}_{\mu\nu}-\tilde{\Gamma}^{\lambda}_{\mu\nu}=0$ (see Sec. II).

APPENDIX C: COMPARISON BETWEEN THE GENERAL RELATIVITY AND THE THERMODYNAMIC FIELD THEORY GEOMETRIES

Although the mathematical symbols are similar, the geometries of the general relativity and of the TFT are quite different. Above all, in the former case, the geometry is pseudo-Riemannian whereas in the latter is non-Riemannian. The principle of *general covariance* respected in the general relativity is not satisfied in the TFT. In addition, the *equivalence principle* is not respected in the TFT. On the contrary, the universal criterion of evolution is satisfied only in the TFT. In the TFT, symbol $R^{\mu}_{\nu\lambda\kappa}$ should not be confused with the Riemannian curvature tensor and the curvature scalar is defined to as the contraction between the $R_{\nu\lambda}$ thermodynamictensor (which does not coincide with Ricci's tensor) and the symmetric piece of the transport coefficients (see also Ref. [21]). In this paper, it is mentioned that in case of (but only in this case) the dimensionless entropy production is much greater than unity then the space tends to be Riemannian. However, also in this limit case, a comparison with the general relativity geometry is not appropriate. Table I should help to avoid any possibility of confusion.

APPENDIX D: DESCRIPTIONS OF THE MATHEMATICAL TERMS

For easy reference, we provide below Table II with short descriptions of the terms appearing in this paper. This should help to make more readable this paper and we refer the reader to the specialized textbooks for rigorous definitions.

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[4] Here, we adopt the De Groot-Mazur terminology [29]. The state of the system can be described by a number of independent variables. In general, one distinguishes two types of macroscopic variables. The variables of the first type denoted by the symbol a are *even* functions of the particle velocities. The other variables denoted by the symbol b are *odd* functions of the particle velocities. Thermodynamic processes involving only variables a (b) are referred to as $a-a$ ($b-b$) processes. It is possible to show that the Onsager reciprocal relations read as $L^{a-a}_{\mu\nu}=L^{a-a}_{\nu\mu}$, $L^{b-b}_{\mu\nu}=L^{b-b}_{\nu\mu}$, and $L^{a-b}_{\mu\nu}=-L^{b-a}_{\nu\mu}$.
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[19] In some examples of chemical reactions, the only condition of invariance of entropy production may not be sufficient to

assure the equivalent character of two descriptions (J_μ, X^μ) and (J'_μ, X'^μ). In Ref. [3] we can find the case where it is also necessary to impose additional invariances of the rate of change in the number of moles. This is necessary to avoid certain paradoxes to which Verschaffelt [23] called its attention (cf., also [24]).

[20] We may qualify as thermodynamic tensor (taken as a single noun) a set of quantities where only transformation (22) is involved. This is in order to qualify as a tensor, a set of quantities, which satisfies certain laws of transformation when the coordinates undergo a general transformation. Consequently, every tensor is a thermodynamic tensor but the converse is not true.

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[28] Equation (66) does not apply in two dimensions. Two-dimensional problem may be met in the limit case of a system driven out of equilibrium by two (independent) scalar thermodynamic forces such as, for example, two chemical affinities (and *not* when we analyze, for example, a system submitted to two vectorial thermodynamic forces in one dimension), where the diffusion of the chemical species is neglected. This ideal example is, however, analyzed in Ref. [16]. Equation (66) should be replaced by $R=2R_{1212}/g$ where R_{1212} and g indicate the 1212 component of the thermodynamic curvature tensor and the determinant of the matrix $g_{\mu\nu}$, respectively (see, for example, Ref. [27]).

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[36] Notice that $J_{\nu,\mu}-J_{\mu,\nu}$ is a thermodynamic tensor of second order.

[37] H. C. Ottinger, *Beyond Equilibrium Thermodynamics* (Wiley, New York, 2005), p. 464; G. Lebon, J. Casas-Vázquez, and D. Jou, *Understanding Nonequilibrium Thermodynamics* (Springer, New York, 2008), p. 196.

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