EMERGY SYNTHESIS 3:
Theory and Applications of the Emergy Methodology

Proceedings from the Third Biennial Emergy Conference,
Gainesville, Florida

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November 2005

The Center for Environmental Policy
Department of Environmental Engineering Sciences
University of Florida
Gainesville, FL

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How Many "Fourth" Principles Are There in Thermodynamics?

Corrado Giannantoni

ABSTRACT

The paper considers four different proposals (*found in Literature*) *concerning a possible Fourth Thermodynamic Principle, namely: Onsager's* Reciprocal Relations (*1931*)*, Prigogine's* Excess Entropy Production (*1971*)*, Georgescou-Roegen's* Matter Entropy (*1972*) *and Jorgensen's* Ecological Law of Thermodynamics (*1992*). *Such Principles, when analyzed in the light of Odum's* Maximum Em-Power Principle (*1994*)*, appear as being four different reductive* quantitative *versions of the latter. Consequently, the* Maximum Em-Power Principle *can be considered as being not only a* new *Thermodynamic Principle* (*as already shown in* (*Giannantoni 2001, 2002*))*, but also the* only *candidate to be recognized as the real* Fourth *Thermodynamic Principle.*

INTRODUCTION

In the 1870's Thermodynamics had already reached (in less than 50 years) its almost definitive and systematic formulation. Scientists consequently thought that all the physical phenomena substantially obeyed two fundamental Principles: the First and the Second Principles of Thermodynamics. Science seemed to have reached a definitive result. Everything seemed to be "under control". However some "creaking" could already be heard in that theoretical structure.

The first problematic aspect appeared in the application of those two Thermodynamic Principles to the analysis of *Biological Systems*. It was immediately clear that those Principles (although *globally* valid even in the case of living systems), could not be considered as being Laws sufficient to explain, by themselves, how and why organisms develop through self-organization processes, during which they lose Entropy (by increasing their own order), in open contrast with the surrounding universe. Those Principles in fact are only able to "tell us that certain things cannot happen, but they do not tell us what does happen" (Lotka, 1922b).

As is well-known Boltzmann (1887) first had the original idea of looking for a direct relationship between Classical Thermodynamics and the Evolutionary Theory of the organic world.
Lotka in 1922 reconsidered Boltzmann's initial ideas and, on the basis a thorough analysis of wide classes of living systems, formulated the *Maximum Power Principle* and contemporaneously proposed that it was the Fourth Thermodynamic Principle (ib.) (Nernst's Principle (1906) had already reached the status of a Third Thermodynamic Principle). Subsequently Odum (1994), in the early 1990's, after having introduced the new physical quantity termed Emergy, gave a more general formulation of Lotka's Principle in the form of the "*Maximum Em-Power Principle*".

Parallel to this line of thought, some other scientists discovered new Thermodynamic aspects and systematically proposed them as an expression of a "Fourth" Thermodynamic Principle.

"*Reciprocal Relations*", discovered by Onsager in 1931, represented a substantial novelty with respect to Classical Thermodynamics. The same can be said with reference to "*Excess Entropy Production Principle*" discovered by Prigogine in 1971. Even from Economics a new Fourth Principle was suggested: the "*Matter Entropy Principle*", proposed by Georgescou-Roegen in 1972. More recently another tentative Fourth Thermodynamic Principle was proposed by Jorgensen in 1992, termed as "*the Ecological Law of Thermodynamics*".

In this respect we can observe that: i) the mathematical formulation of the Maximum Em-Power Principle, achieved in 2001 (Giannantoni, 2001, 2002), finally clarified in what sense the latter can be considered as a *Thermo-dynamic* Principle; ii) and now, the availability of such a formulation (together with the appropriate associated mathematical language) enables us to show that all the other Principles are simple and different reductive *quantitative* versions of the Maximum Em-Power Principle.

ONSAGER'S PRINCIPLE (RECIPROCAL RELATIONS)

This Principle states that: "*Near thermal equilibrium an affinity* X_j (*also termed as generalized thermodynamic* "*force*") *produces a linear effect, in a flux* J_k, *which is symmetrical with respect to that produced by the affinity* X_k *in the flux* J_j" (Onsager, 1931). In other words, given two *coupled* processes, two *linear* force-flux equations can be written by means of transport coefficients L_{jk} as

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad (2.1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad (2.2)$$

where

$$L_{12} = L_{21} \qquad (2.3).$$

Such a Principle *has not the same generality* as the other well-known Thermodynamic Principles (and Onsager was aware of this). In fact it is only valid under very restricted conditions (Haken, 1984): i) an isolated System; ii) flows, at a given time t, are supposed to be only dependent on affinities (at the same time); iii) flows are always time derivatives of extensive quantities (pseudo-thermodynamic variables); iv) processes are supposed to be linear (near the equilibrium); v) there exists a dynamic equilibrium in a very restricted neighborhood of the thermal equilibrium; vi) subjacent statistical processes are supposed to be without memory (Markov's assumption); vii) microscopic reversibility of processes is also assumed.

All these hypotheses are generally and synthetically referred to as *linear Thermodynamics of irreversible processes*.

Derivation from the Maximum Em-Power Principle

Given its very limited field of validity, Onsager's Principle can be derived from the Maximum Em-Power Principle by simply starting from the general definition of Emergy (see Giannantoni, 2002)

$$Em = Tr \cdot Ex = Tr_{\phi} \cdot Tr_{ex} \cdot Ex \qquad (2.4)$$

and by remembering that

$$\frac{d}{dt} Em \rightarrow Max \qquad (2.5).$$

In fact:
i) Eq. (2.5) can be explicitly written as follows

$$\frac{d}{dt}Em = Tr_{ex}\left(\frac{d}{dt}Tr_{\phi}\cdot Ex + Tr_{\phi}\frac{dEx}{dt}\right)\rightarrow Max \qquad (2.6)$$

because, by hypothesis, the system has no "memory" near equilibrium. This implies that the factor Tr_{ex}, accounting for Exergy dissipation, is constant, whereas the factor Tr_{ϕ}, which accounts for Emergy "source terms" may vary.
ii) If we now take into account that, for an isolated System

$$\frac{dEx}{dt} = -\frac{(\delta Ex)_{irr}}{dt} = -T_0\cdot\frac{dS}{dt} \qquad (2.7) \qquad \text{and} \qquad \frac{dS}{dt}\geq 0 \qquad (2.8),$$

Eq. (2.6) becomes

$$\frac{d}{dt}Em = Tr_{ex}\left(\frac{d}{dt}Tr_{\phi}\cdot Ex - Tr_{\phi}T_0\frac{dS}{dt}\right)\rightarrow Max \qquad (2.9)$$

which is satisfied when two distinct and independent conditions are verified : $\frac{d}{dt}Tr_{\phi}\rightarrow Max$ (that is Emergy source terms give their maximum contribution) and contemporaneously

$$\frac{dS}{dt}\rightarrow \min \qquad (2.10).$$

The much wider generality of the Maximum Em-Power Principle can be shown by the fact that Onsager's Principle can be derived from the sole latter condition.
iii) Condition (2.10), on the other hand, considered in the context of the hypotheses mentioned above, expresses Prigogine's well-known *minimum entropy production Principle* (1947).
iv) By remembering that the Entropy production can be expressed as

$$\frac{dS}{dt} = X_1J_1 + X_2J_2 = L_{11}J_1^2 + L_{12}J_1J_2 + L_{21}J_1J_2 + L_{22}J_2^2 \qquad (2.11)$$

and that it must also satisfy condition (2.8), we recognize that the structure (2.11) cannot be, strictly speaking, minimized, but it must have (at least) an extremum.
vi) This can be found on the basis of variational calculus via Silvester's criterion, valid for quadratic forms (see Krasnov et al., 1984) and it is really achieved when

$$L_{12} = L_{21} \qquad (2.12) \qquad \text{and} \qquad L_{11}L_{22} - L_{12}^2 \geq 0 \qquad (2.13).$$

PRIGOGINE'S PRINCIPLE (EXCESS ENTROPY PRODUCTION)

This Principle states that: "*Under the hypotheses which characterize Thermodynamics of irreversible processes* (see previous paragraph), *a stationary non-equilibrium state is stable if any perturbation* (δ) *of the system leads to the following conditions* (Prigogine, 1980; Haken, 1984):

$$(\delta^2 S)_{st}\leq 0 \qquad (3.1) \qquad\qquad \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 S)_{st} = \sum_i \delta X_i\cdot\delta J_i \geq 0 \qquad (3.2),$$

where (3.1) represents the extension of the analogous stability condition valid in the case of r*eversible*

Thermodynamics, while (3.2) gives the *excess entropy production*.[1] The equal sign only holds at the threshold of a new regime.
This Principle is a more sophisticated *stability criterion* introduced by Prigogine (1971) in addition to the already mentioned *Minimum Entropy Production Principle* (see previous paragraph), which was too limited to be considered a Fourth Thermodynamic Principle.

Derivation from the Maximum Em-Power Principle

i) Let us first re-formulate conditions (3.1) and (3.2) in terms of Exergy. These, on the basis of the above mentioned hypotheses, can be written as follows (see also Eq. (2.7))

$$(\delta^2 Ex)_{st} \geq 0 \qquad (3.3) \qquad\qquad \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Ex)_{st} \leq 0 \qquad (3.4).$$

ii) If we then start from the mathematical formulation of the Maximum Em-Power Principle (Giannantoni, 2001)

$$\int_{D^*(t)} \Gamma \varphi_v^* d_3V \stackrel{\rightarrow}{=} \frac{d}{dt}\int_{D^*(t)} em_v^* d_3V \rightarrow Max \qquad , \qquad \forall D^*(t) \subseteq S_U(t) \qquad (3.5)$$

and express the Lagrangian derivative in explicit terms, we can write

$$\int_{D^*(t)} \Gamma \varphi_v^* d_3V \stackrel{\rightarrow}{=} \frac{\partial}{\partial t}\int_{D^*(t)} C\cdot\rho\cdot ex^* d_3V + \int_{\partial D^*(t)} C\cdot\rho\cdot ex^*\cdot v_{rn} d_2S \geq 0 \qquad (3.6).$$

For an *isolated* system, in a "reference" *stationary* state, a *perturbation* (δ) in the neighborhood of that state (under the assumption of *local dynamic equilibrium* and *linear processes*) can be written as

$$\int_{D^*(t)} \delta(\Gamma \varphi_v^*) d_3V \stackrel{\rightarrow}{=} \frac{\partial}{\partial t}\int_{D^*(t)} \delta(C\cdot\rho\cdot ex^*) d_3V = \frac{\partial}{\partial t}(\delta \int_{D^*(t)} C\cdot\rho\cdot ex^* d_3V) =$$

$$= \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Em)_{st} + .. \geq 0 \qquad (3.7)$$

because, under the mentioned hypotheses, the term of the first order $(\delta Em)_{st}$ equals zero.[2]

[1] The expression "*excess entropy production*" is due to the fact that, when the state of reference is an *equilibrium* state, the pertaining stability condition $(\delta^2 S)_{eq} \leq 0$ (analogous to condition (3.1)) is directly related to the *total entropy production* (expressed by Eq. (2.11)) as follows: $\frac{dS}{dt} = \sum_i X_i \cdot J_i = \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 S)_{eq}$. When, on the contrary, the state of reference is a stationary *non equilibrium* state, the derivative with respect to time of the quantity $(\delta^2 S)_{st}$ is no more related to the total entropy production of the system, but to the *sole* entropy production *in excess* due to the perturbation (the terms δX_i and δJ_i in Eq. (3.2) represent the corresponding variations with respect to the *equilibrium* values) (Prigogine, 1980).

[2] In *physical terms* this means that system Emergy, when evaluated on the basis of the *sole* first order perturbations, results as having already reached its maximum. In fact this is the only result *compatible with the considered boundary conditions*. Vice versa, if it is evaluated through higher order perturbations, the latter imply pertaining modifications of the previous boundary conditions and consequently allow us to calculate the corresponding Emergy *increase* (in accordance with the general tendency expressed by the Maximum Em-Power Principle).

iii) By taking into account that the system is also without memory, in stationary conditions, and undergoing microscopic reversible processes, we can assume $Tr_{ex}(t) = const$, whereas $Tr_{\phi}(t)$, which is due to perturbations of structural configuration, may vary. This means that condition (3.7) becomes

$$\frac{1}{2}\frac{\partial}{\partial t}[\delta^2(Tr \cdot Ex)]_{st} = [Ex \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Tr)]_{st} + [Tr \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Ex)]_{st} \geq 0 \qquad (3.8)$$

because the mixed products vanish.

iv) Condition (3.8), *derived from the Maximum Em-Power Principle*, represents a very *general stability criterion* which is *much wider* than Prigogine's Principle. In fact the former *includes* the latter, without being affected by its limitations. In addition it is able to explain why condition (3.2) (or equivalent condition (3.4)) is only a *sufficient* condition for *stability*. Whereas, *instability necessarily* implies its violation (Prigogine, 1980; Haken, 1984).

Let us now examine the various possible cases of this *more general criterion*:

a) Condition (3.4) is *a sufficient condition* for *stability*. In fact, on the basis of the Maximum Em-Power Principle, under *stability* conditions we have

$$\frac{\partial}{\partial t}[(\delta^2 Tr)]_{st} \geq 0 \qquad (3.9),$$

which is always verified if Prigogine's condition (3.4) is introduced into the general criterion (3.8).

The latter however implies, in addition, that the term

$$\frac{1}{2}\frac{\partial}{\partial t}[(\delta^2 Ex)]_{st} \qquad (3.10)$$

must satisfy the following condition

$$[Ex \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Tr)]_{st} - \left|[Tr \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Ex)]_{st}\right| \geq 0 \qquad (3.11),$$

which clearly shows that, according to criterion (3.8), the *real cause* of stability is represented by the contribution due to the Ordinality of "source terms", which must exceed the contribution due to the associated Exergy dissipation. In fact, as already shown in (Giannantoni 2001, 2002), the Maximum Em-Power Principle points out the contributions due to both *meta-mechanical* and *conjugated mechanical* causes, whereas Prigogine emphasizes only the mechanical aspects, which solely account for associated and concomitant conditions.

b) Condition (3.8) also shows how *instability necessarily* implies the violation of Eq. (3.4).

In fact, under such hypotheses, on the basis of the Maximum Em-Power Principle we have

$$\frac{\partial}{\partial t}[(\delta^2 Tr)]_{st} < 0 \qquad (3.12)$$

which, together with condition (3.8), consequently implies that

$$\frac{1}{2}\frac{\partial}{\partial t}[(\delta^2 Ex)]_{st} > 0 \qquad (3.13).$$

c) Condition (3.13), however, when verified (violation of Prigogine's condition (3.4)), does *not* represent a sufficient condition for *instability*, and the general criterion (3.8) is able to show why.

In fact condition (3.13) does not necessarily imply the violation of condition (3.8). When in fact (3.13) is introduced into condition (3.8), the latter only requires that

$$[Ex \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Tr)]_{st} \geq -[Tr \cdot \frac{1}{2}\frac{\partial}{\partial t}(\delta^2 Ex)]_{st} \qquad (3.14).$$

This condition simply asserts that the time variations of second order perturbations of Transformity must be *greater than* a prefixed *negative* quantity, but it does not absolutely imply that they *must be* negative. Consequently condition (3.9) is perfectly compatible with condition (3.14).
The general criterion (3.8) is thus also able to explain why the system can be stable even if Prigogine's stability condition (3.4) is violated.

JORGENSEN'S PRINCIPLE (ECOLOGICAL LAW OF THERMODYNAMICS)

This Principle asserts that: "*If a system receives a through-flow of exergy, it will utilize this exergy to move away from thermodynamic equilibrium. If the system is offered more than one pathway to move away from thermodynamic equilibrium, the one yielding most stored exergy, i.e. with the most organized structure, or the longest distance to thermodynamic equilibrium under the prevailing conditions, will have the propensity to be selected*." (Jorgensen 1992, 2000).

Such a "tentative Fourth Law" of Thermodynamics (ib.) is essentially based on the concept of Exergy which, because of its specific definition (see Szargut et al.,1988), is considered by the author as being an appropriate measure of the *information content* of a system as well as of its distance from equilibrium. For this reason Exergy seems to be, at the same time, a convenient "*indicator of the development of ecosystem structure and changes in species composition. Structural exergy, in particular, should be considered an appropriate measure of ecological integrity*." (ib.).

The essential characteristics of Jorgensen's Principle, seen in the light of the Maximum Em-Power Principle, clearly show that it hardly reaches the status of a Fourth Thermodynamic Principle. In fact: i) it has not been formulated in mathematical terms yet. This aspect represents a strong limitation on our ability to decide as to whether it is a Thermodynamic Principle or not; ii) it refers to an "organized" structure which is understood as being only based on "topological" ("mechanical") relationships. It does not consider any "excess" of meta-mechanical Ordinality; iii) the self-organizing criterion adopted (i.e. "most stored exergy") is too self-referent (with respect to the analyzed system). In fact it neglects the multiform coupling of the same with the surrounding habitat, i.e. those *bi-*directional contributions included in Odum's concept of "useful work"; iv) in addition, "structural exergy" cannot be considered as being "*an appropriate measure of ecological integrity*", because it is only the *conjugated* foundation of the same. "*Ecological integrity*", in fact, is expressed by the level of Ordinality (not considered by Jorgensen); v) its (verbal) formulation however suggests a sort a "tendency" Principle, even if the term *propensity* seems to indicate more a *potential trend* than an effective *tendency*; vi) it is formulated in terms of phenomenological effects by neglecting the subjacent "causes".

Derivation from the Maximum Em-Power Principle

The previous aspects enable us to show that Jorgensen's Principle can be seen as a reductive version of the Maximum Em-Power Principle. In fact:
i) by starting from the right side of Eq. (3.5) in its explicit form (3.6) (*phenomenological* aspects), we can equivalently write

$$[\frac{\partial}{\partial t}\int_{D^*(t)} C\cdot\rho\cdot ex^*\cdot d_3V - \int_{\partial D^*(t)} C\cdot\rho\cdot ex^*\cdot(-v_{rn})\cdot d_2S] \to Max \qquad (4.1),$$

where the second term on the first side of Eq. (4.1) represents the net Emergy inflow due to all the various contributions (mass, heat, work, etc.).
ii) In the case of a mere Exergy inflow ($v_{rn} < 0$), the coefficient C (which at a *local* level corresponds to the *global* concept of Transformity (see Giannantoni, 2000, 2002)) is identical to 1.

In such conditions we always have

$$\int_{\partial D^*(t)} C \cdot \rho \cdot ex^* \cdot (-v_{rn}) \cdot d_2 S \geq \int_{\partial D^*(t)} \rho \cdot ex^* \cdot (-v_{rn}) \cdot d_2 S \qquad (4.2),$$

and thus, *a fortiori*, we can assert that

$$[\frac{\partial}{\partial t} \int_{D^*(t)} C \cdot \rho \cdot ex^* \cdot d_3 V - \int_{\partial D^*(t)} \rho \cdot ex^* \cdot (-v_{rn}) \cdot d_2 S] \to Max \qquad (4.3).$$

iii) In such a context, Jorgensen's Principles points out that

$$\frac{\partial}{\partial t} \int_{D^*(t)} \rho \cdot ex^* \cdot d_3 V \to Max \qquad (4.4)$$

that is *the propensity toward most stored exergy*, whereas the Maximum Em-Power Principle (more appropriately) indicates that the system tends to increase its organized structure *not only* in terms of "stored exergy", but also (and especially) in terms of *conjugated* meta-mechanical relationality expressed by Transformity (as clearly indicated by the explicit expression of first term of (4.1))

$$[\int_{D^*(t)} (\frac{\partial}{\partial t} C) \cdot (\rho \cdot ex^*) \cdot d_3 V + \int_{D^*(t)} C \cdot \frac{\partial}{\partial t} (\rho \cdot ex^*) \cdot d_3 V] \to Max \qquad (4.5)$$

while ever respecting the *tendency* condition (4.1), which *also* includes the "useful emergy" exchanged with the outside.

iv) This analysis shows that this attempt to overcome the limits of the well-known Thermodynamic Principles remains at a *virtual level*, because it does not free itself from that *cogent* and *necessary* perspective which is typical and intrinsic in the traditional Thermodynamic Principles.

v) Jorgensen in fact refers to a *necessary* Logic when he admits that "*it is hardly possible to make deterministic statements about the development of an ecosystem…*" and that "*it is absolutely necessary to test the tentative law with many more case studies before it can be recommended to use it more generally*." (Ulgiati and Bianciardi, 2004). In this respect he does not recognize that the emerging Quality[3] in living (and non-living) systems suggests the adoption of an "*adherent*" Logic (see Giannantoni, 2002).

vi) In addition, the research for "*deterministic statements*" not only confirms such a "necessary" approach, but also reveals that the "tendency Principle" proposed is not thought of as being the phenomenological result of internal "spring sources", but only a necessary consequential evolution of *constraining* conditions.

vii) In essence, after having attempted to take flight toward the formulation of a General Tendency Principle to explain the wide variability of ecological system dynamics, the "criterion of selection", based on a mere *quantitative* property (Exergy), together with the adoption of a *necessary* Logic and a strictly *efficient* causality, ended up by "clipping its wings".

[3] *Quality* is written with a capital "Q" because in this context is no more considered (as usually happens) as a simple "property" or a "characteristic" of a particular phenomenon, but it is understood (and recognized) as being any *emerging* "property" (from any physical process) *never reducible* to its phenomenological premises or to our traditional mental categories. This is also valid for the term *Ordinality* (with a capital "O"), because it is no more referred to as a (traditional) topological order (e.g. geometrical symmetries and so on, although not excluded), but it is understood as a *hierarchical order* based on the previous concept of *Quality*.

GEORGESCOU-ROEGEN'S PRINCIPLE (ENTROPY OF MATTER)

This Principle, proposed by the economist Nicholas Georgescou-Roegen in 1972, states that: "*In a closed system* (exchanging *energy* with the environment, but *not matter*) *a* "*material entropy*" *occurs and gradually reaches its maximum value* (*maximum disorder and mixture of matter*) *in such a manner that* "*all matter ultimately becomes unavailable*"" (Ulgiati and Bianciardi, 2004).

This statement, which is undoubtedly correct for an isolated system, was assumed by Georgescou-Roegen as being valid for the *biosphere*, considered as: i) a *closed system*; ii) with external exchanges too slow and therefore not very significant on the scale of the economy.

Under such conditions he "pointed out that it would be impossible to completely recover the matter used in the production of mechanical work or wasted in friction. The disappearance of any qualitative difference between materials is a sort of "*material death*" of the system, which is similar to the famous "*thermal death*" dictated by the entropy law for isolated systems" (ib.).

Such a "possible" Fourth Law of Thermodynamics has received several criticisms by various scientists (among others, the same authors whom the previous quotations were taken from).

In this respect we can observe that: i) the "Principle" has never been formulated in mathematical terms. This represents a basic difficulty for the Principle to be thought of as being a new Thermodynamic Principle; ii) the basic reason for such a misleading "Principle" relies on the fact that it supposes a radical de-coupling between Entropy and matter. The Maximum Em-Principle Principle enables us to recognize that self-organization is based on Emergy, and its mathematical formulation shows that this is *one sole physical entity* combining together both "meta-mechanical relationality" (expressed by Transformity) and "mechanical relationality", expressed by Exergy, which is the "conjugated" *extensive* aspect of the former (see Eq. (2.4)). In such a context "matter" is exactly the *physical support* of the "mechanical relationality", in the sense that any (mechanical) relationality is a specific property of the matter. In this perspective any order or disorder of matter is nothing but the order or disorder of the mechanical relationality expressed by Entropy. Consequently "Entropy of matter" is a sort of a tautology. "Entropy of matter", in fact, is nothing but simple "Entropy"; iii) the second misleading assumption concerns the absence of two additional basic concepts such as *information* (vehicled by "Energy and matter flows") and *time* (Cleveland and Ruth, 1997).

Derivation from the Maximum Em-Power Principle

On the basis of the previous considerations, Georgescou-Roegen's Principle can be seen as a particular version of the Second Thermodynamic Principle which, in turn, is a "reductive" version of the Maximum Em-Power Principle according to a mere quantitative *phenomenological* perspective (Giannantoni, 2001). In fact:

i) by starting from Eq. (3.5) and by taking into account both the complete absence of any generative "source term" and the schematization of the biosphere as usually adopted (Cleveland and Ruth, 1997; Söllner, 1997), the second side of Eq. (3.5), under the additional above-mentioned hypotheses, becomes a particular version of the Second Thermodynamic Principle (see Giannantoni, 2002, p. 87):

$$\frac{\partial}{\partial t}\int_{D^*(t)} \rho \cdot (u - Ts) \cdot d_3V = \int_{\partial D^*(t)} \dot{q}_s^+\, \theta \cdot d_2S - \frac{\partial}{\partial t}\int_{D^*(t)} \rho \cdot ex_{irr}^* \cdot d_3V \qquad (5.1).$$

ii) The first term on the second side of Eq. (5.1) represents the net balance between the effective absorbed solar Exergy flow and the low grade Exergy re-emission flow. We may thus assume that this contribution is negligible with respect to normal Exergy flows in economic activities.

iii) Under such hypotheses Georgescou-Roegen's Principle points out that the contribution of irreversibilities is not limited to "thermal" ones, such as in traditional systems usually analyzed by Classical Thermodynamics (engines, turbines, and so on). In this respect the generation of irreversibilities can be expressed by considering all the "flows" per unit volume (j_k) and their associated generalized "forces" (X_k). Then the last term of Eq. (5.1) explicitly becomes (apart from the constant factor T_0)

$$\frac{\partial}{\partial t}\int_{D^*(t)} \rho \cdot s^*_{irr} \cdot d_3V = \sum_k \int_{D^*(t)} (\nabla X_k) \cdot j_k \cdot d_3V = \sum_k \int_{D^*(t)} (\nabla X_k) \cdot \frac{\partial y_k}{\partial t} \cdot d_3V \qquad (5.2)$$

where y_k = generic extensive physical property (per unit volume)

j_k = the corresponding flow defined by the time variation $\partial y_k / \partial t$.

iv) If we now assume that irreversibility due to heat flows associated with thermal differences represent one of the contributions indicated in Eq. (5.2), let's say the first one

$$\int_{D^*(t)} (\nabla X_1) \cdot j_1 \cdot d_3V = \int_{D^*(t)} (\nabla T) \cdot j_{q,v} \cdot d_3V = \int_{D^*(t)} (\nabla T) \cdot \frac{\partial q_v}{\partial t} \cdot d_3V \qquad (5.3),$$

where $\partial q_v / \partial t$ is the flow (per unit volume) derivable form Fourier's Equation, the mathematical formulation of Georgescou-Roegen's Principle could be given as follows

$$\sum_{k \neq 1} \int_{D^*(t)} (\nabla X_k) \cdot \frac{\partial y_k}{\partial t} \cdot d_3V \to 0 \qquad (5.4)$$

or, alternatively, on the basis of Eq. (5.1) (and associated assumptions on the system)

$$\frac{\partial}{\partial t}\int_{D^*(t)} \rho \cdot (Ts) \cdot d_3V = \frac{\partial}{\partial t}\int_{D^*(t)} \rho \cdot ex^*_{irr} \cdot d_3V = = -T_0 \sum_k \int_{D^*(t)} (\nabla X_k) \cdot \frac{\partial y_k}{\partial t} \cdot d_3V \to 0 \qquad (5.5).$$

v) In this form the Principle asserts a general tendency toward a *progressive levelling* of the mechanical relationality, expressed by Exergy, but it *does not imply* any *levelling* of its associated Transformity which, on the contrary, tends progressively to increase (Giannantoni, 2001, 2002).

CONCLUSIONS

The four Principles here considered represent different attempts at "catching" (and describing) the *excess of Quality* clearly pointed out by the Maximum Em-Power Principle. However, they do not achieve such an important result because of their intrinsic and specific limitations:

i) Onsager's Principle is undoubtedly the nearest one to the concept of "emerging Quality". Firstly because its validity is independent from any particular molecular model. This makes the discovery of *Reciprocal Relations* surely a new Thermodynamic result (Prigogine, 1980). Secondly, because it brings out the *reciprocity of processes*, even if only in quantitative terms, without succeeding in expressing their *cooperative* behavior in terms of a unique process (think of a "binary" system (Giannantoni, 2002)). In fact its formulation can be simply obtained as a particular case of Prigogine's *Minimum Entropy Production Principle*, which only expresses a sort of inertia of any system in a stationary non-equilibrium state (Prigogine, 1980);

ii) Prigogine's *Excess Entropy Production Principle* aims at extending non-equilibrium stability conditions, but in so doing it does not consider the *cooperative* characteristic of the phenomena involved, in favor of the mere quantitative aspects. In other terms, if seen in the light of Maximum Em-Power Principle, Prigogine's Principle reduces, once again, the perspective timidly opened by Onsager, because Prigogine's approach still refers to the global system, without considering any *intrinsic* form of simple cooperation nor even of a more sophisticated "binarity", that is that special form of "reciprocity" describable by means of "binary" functions (Giannantoni, 2002).

iii) Jorgensen's Principle represents an attempt at establishing a *tendency* Principle in the field of Biological Systems, even if, in the end, a (desired) deterministic approach seems again to prevail. In addition, it only considers phenomenological effects, without any mention of their pertinent causes. In this respect Jorgensen's Principle does not consider any *excess of Quality* (specific to the Maximum Em-Power Principle), which is never completely reducible to physical phenomena;

iv) Finally, Georgescou-Roegen's "*Matter Entropy*" *Principle* has its basic merit in having stressed the importance of more correct relationships between Man and Environment. Though it cannot be recognized as being a new Thermodynamic Principle, it emphasizes that the concept of Entropy, in the case of very complex systems (such as ecological systems) is much more articulated than the one from Classical Thermodynamics.

Consequently, if we take into account that: i) on the one hand, none of the above-mentioned Principles has the same generality as the Maximum Em-Power Principle; ii) on the other hand, the mathematical formulation of the latter first led us to clearly define in what sense it can be considered as a *Thermodynamic* Principle; iii) and now it has enabled us to show that all the other Principles (proposed as a possible Fourth Thermodynamic Principle) are nothing but four different *reductive quantitative* versions of the Maximum Em-Power Principle, we can conclude that: the Maximum Em-Power Principle is the candidate most adequate to be recognized as the *Fourth* Thermodynamic Principle.

The whole logical demonstrative process adopted is synthesized in Fig. 1, where the axis t ideally represents the "last century" and the vertical axis points out the *irreducible discontinuity* of the "jump" from *quantity* to *Quality*. This would also indicate that, when *obtaining* the four above-mentioned Principles from the Maximum Em-Power Principle, there is a specific stage of the demonstrative process at which we have to *deny* (or, at least, to *neglect*) all the *Quality* characteristics pertaining to this Principle. In other words, the four Principles *cannot* be considered as being *particular cases* of the Maximum Em-Power Principle, but only *reductive cases*, because they correspond to four different *quantitative versions* of the same. This also means that the term "derivation" (previously adopted) rigorously applies only to this specific phase of the demonstrative process. In fact, from a general point of view, it is more appropriate to say that the four considered Principles are "obtained" (rather than "derived") from the Maximum Em-Power Principle.

Finally, it is worth noting that *Quality* (different from quantity) is represented (in Fig. 1) as being "measured" by hierarchical levels of *Ordinality*, as better illustrated in the companion paper titled "*Differential Bases of Emergy Algebra*".

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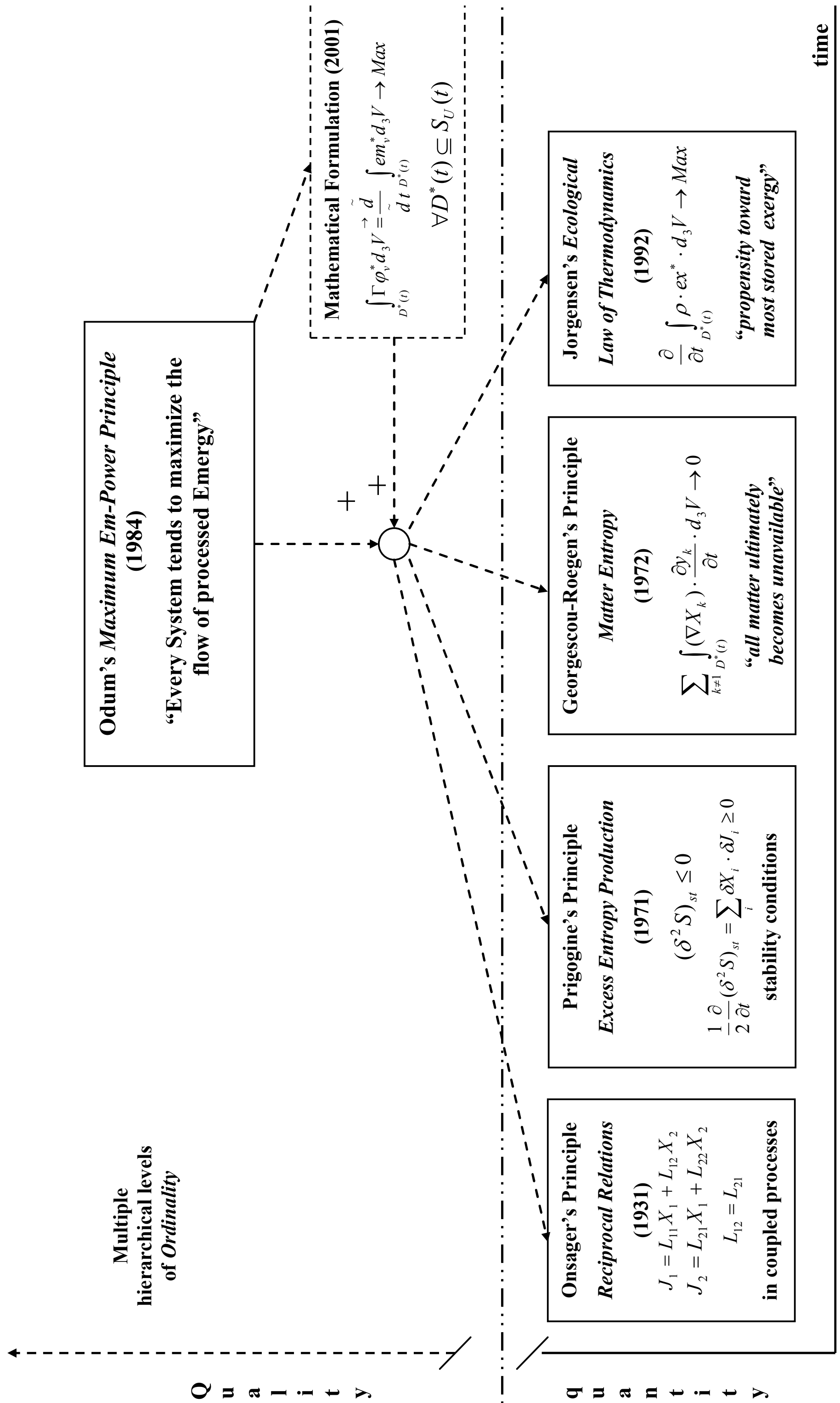

Figure 1. *Historical-Logical Synthetic Scheme*