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THE GOUY-STODOLA THEOREM AS A VARIATIONAL PRINCIPLE FOR OPEN SYSTEMS

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ABSTRACT. The variational method is very important in mathematical and theoretical physics because it allows us to describe the natural systems by physical quantities independently from the frame of reference. A global and statistical approach is introduced starting from irreversible thermodynamics to obtain the principle of maximum entropy generation for the open systems. The recent research in non equilibrium and far from equilibrium systems have been proved to be useful for their applications in different disciplines and many subjects. A general principle to analyse all these phenomena is required in science and engineering: a variational principle would have this fundamental role. Here, the Gouy-Stodola theorem is proposed to be this general variational principle, both proving that it satisfies the above requirements and relating it to a statistical results on entropy production. The result is a consequence of the Lagrangian approach to the open systems. Here it will be developed a general approach to obtain the thermodynamic Hamiltonian for the dynamical study of the open systems. Last the algebraic-geometrical structure for entropy generation is also introduced.

1. Introduction

The variational methods are very important in mathematics, physics, science and engineering because they allow us to describe the natural systems by physical quantities independently from the frame of reference used (Hahn and Özisik 2012). Moreover, Lagrangian formulation can be used in a variety of physical phenomena and a structural analogy between different physical phenomena has been pointed out (Truesdell 1984). The most important result of the variational principle consists in obtaining both local and global theories (Arnold 1989): global theory allows us to obtain information directly about the mean values of the physical quantities, while the local one about their distribution (Lucia 1995, 2013a,b,c; Lucia and Sciubba 2013).

Last, the notions of entropy and its production and generation are the fundamentals of modern thermodynamics and a lot of variational approaches has been proposed in thermodynamics (Lucia 2013b; Martyushev and Seleznev 2006). Today, the research in non equilibrium and far from equilibrium systems has been proved to be useful for their application in mathematical and theoretical biology, biotechnologies, nanotechnologies, ecology, climate changes, energy optimization, thermo-economy, phase separation, aging process, system theory and control, pattern formation, cancer pharmacology, DNA medicine, metabolic engineering, chaotic and dynamical systems, all summarized in non linear, dissipative and open systems.

A general principle to approach all these phenomena with a unique method of analysis is required in science and engineering: the variational principle would have this fundamental role. But, it has been proved that (Lebowitz 2011):

- a useful variational principle out of the use of work cannot be obtained;
- the entropy production for the system and the reservoir can be obtained if and only if only one heat bath (Lebowitz 2011) exists and its temperature is constant.

The different variational principle have never been related with these fundamental requirement for a general principle in thermodynamics of open system, and often they are related only to closed or isolated systems (Martyushev and Seleznev 2006).

Last, in engineering thermodynamics and thermal physics the open systems are analysed using entropy generation, but its statistical definition does not exist and this lack does not allow us to extend this powerful method to all the above discipline, where statistical approach is required. On the other hand, the statistical models are not so general to be used in any case with a unique approach; consequently, no of them represents a general principle of investigation.

In this paper, the Gouy-Stodola theorem (Duhem 1889; Gouy 1889a,b,c) is proposed to be this general variational principle, both proving that it satisfies the above requirements and relating it to a statistical results on entropy production and generation. Moreover, an algebraic-geometric approach is proposed in order to analyse irreversible systems in thermodynamics and to develop the application of the entropy generation to the study of these systems by the dynamical system approach.

2. The open systems

In this Section the thermodynamic system is defined. To do so, the definition of 'system with perfect accessibility', which allows us to define both the thermodynamic and the dynamical systems, must be considered.

An open N particles system is considered. Every $i-$th element of this system is located by a position vector $\mathbf{x}_i \in R^3$, it has a velocity $\dot{\mathbf{x}}_i \in R^3$, a mass $m_i \in R$ and a momentum $\mathbf{p} = m_i \dot{\mathbf{x}}_i$, with $i \in [1, N]$ and $\mathbf{p} \in R^3$ (Lucia 2008). The masses m_i must satisfy the condition:

$$\sum_{i=1}^{N} m_i = m \tag{1}$$

where m is the total mass which must be a conserved quantity, so it follows:

$$\dot{\rho} + \rho \nabla \cdot \dot{\mathbf{x}}_B = 0 \tag{2}$$

where $\rho = dm/dV$ is the total mass density, with V total volume of the system and $\dot{\mathbf{x}}_B \in R^3$, defined as $\dot{\mathbf{x}}_B = \sum_{i=1}^{N} \mathbf{p}_i/m$, velocity of the centre of mass. The mass density must satisfy the following conservation law (Lucia 1995):

$$\dot{\rho}_i + \rho_i \nabla \cdot \dot{\mathbf{x}}_i = \rho \Xi \tag{3}$$

where ρ_i is the density of the $i-$th elementary volume V_i, with $\sum_{i=1}^{N} V_i = V$, and Ξ is the source, generated by matter transfer, chemical reactions and thermodynamic transformations. This open system can be mathematical defined as follows.

Definition 1. *(Huang 1987) - A dynamical state of N particles can be specified by the* $3N$ *canonical coordinates* $\left\{\mathbf{q}_i \in R^3, i \in [1,N]\right\}$ *and their conjugate momenta* $\left\{\mathbf{p}_i \in R^3, i \in [1,N]\right\}$*. The* $6N-$*dimensional space spanned by* $\{(\mathbf{p}_i, \mathbf{q}_i), i \in [1,N]\}$ *is called the phase space* Ω*. A point* $\sigma_i = (\mathbf{p}_i, \mathbf{q}_i)_{i\in[1,N]}$ *in the phase space* $\Omega := \left\{\sigma_i \in R^{6N} : \sigma_i = (\mathbf{p}_i, \mathbf{q}_i), i \in [1,N]\right\}$ *represents a state of the entire* $N-$*particle system.*

Definition 2. *(Lucia 2008) - A system with perfect accessibility* Ω_{PA} *is a pair* (Ω, Π)*, with* Π *a set whose elements* π *are called process generators, together with two functions:*

$$\pi \mapsto \mathscr{S} \tag{4}$$

$$\left(\pi', \pi''\right) \mapsto \pi''\pi' \tag{5}$$

where $\mathscr{S}$ *is the state transformation induced by* π*, whose domain* $\mathscr{D}(\pi)$ *and range* $\mathscr{R}(\pi)$ *are non-empty subset of* Ω*. This assignment of transformation to process generators is required to satisfy the following conditions of accessibility:*

(1) $\Pi\sigma := \{\mathscr{S}\sigma : \pi \in \Pi, \sigma \in \mathscr{D}(\pi)\} = \Omega$, $\forall\sigma \in \Omega$: *the set* $\Pi\sigma$ *is called the set of the states accessible from* σ *and, consequently, it is the entire* state space*, the phase spase* Ω*;*

(2) *if* $\mathscr{D}(\pi'') \cap \mathscr{R}(\pi') \neq 0 \Rightarrow \mathscr{D}(\pi''\pi') = \mathscr{S}_{\pi'}^{-1}(\mathscr{D}(\pi''))$ *and* $\mathscr{S}_{\pi''\pi'}\sigma = \mathscr{S}_{\pi''}\mathscr{S}_{\pi'}\sigma$ $\forall\sigma \in \mathscr{D}(\pi''\pi')$

Definition 3. *(Lucia 2008) - A process in* Ω_{PA} *is a pair* (π, σ)*, with* σ *a state and* π *a process generator such that* σ *is in* $\mathscr{D}(\pi)$*. The set of all processes of* Ω_{PA} *is denoted by:*

$$\Pi \diamond \Omega = \{(\pi, \sigma) : \pi \in \Pi, \sigma \in \mathscr{D}(\pi)\} \tag{6}$$

If (π, σ) *is a process, then* σ *is called the initial state for* (π, σ) *and* $\mathscr{S}\sigma$ *is called the final state for* (π, σ)*.*

Definition 4. *In an open system, there exists a characteristic time of any process, called lifetime* τ*, which represents the time of evolution of the system between two stationary states.*

Any observation of the open irreversible system, in order to evaluate its physical quantities related to stationary states, must be done only at the initial time of the process and at its lifetime. During this time range the system moves through a set of non-equilibrium states by fluctuations on its thermodynamic paths.

Definition 5. *(Lucia 1995) - A thermodynamic system is a system with perfect accessibility* Ω_{PA} *with two actions* $W(\pi, \sigma) \in R$ *and* $H(\pi, \sigma) \in R$*, called work done and heat gained by the system during the process* (π, σ)*, respectively.*

The set of all these stationary states of a system Ω_{PA} is called non-equilibrium ensemble (Lucia 2008).

Definition 6. *(Lucia 2008) - A thermodynamic path* γ *is an oriented piecewise continuously differentiable curve in* Ω_{PA}*.*

Definition 7. *(Lucia 2008) - A cycle $\mathscr{C}$ is a path whose endpoints coincide.*

Definition 8. *(Gallavotti 2005) - A smooth map $\mathscr{S}$ of a compact manifold $\mathscr{M}$ is a map with the property that around each point σ it can be established a system of coordinates based on smooth surfaces W_σ^s and W_σ^u, with s=stable and u=unstable, of complementary positive dimension which is:*

(1) *covariant: $\partial\mathscr{S}W_\sigma^i = W_{\mathscr{S}\sigma}^i, i = u, s$. This means that the tangent planes $\partial\mathscr{S}W_\sigma^i, i = u, s$ to the coordinates surface at σ are mapped over the corresponding planes at $\mathscr{S}\sigma$;*
(2) *continuous: $\partial\mathscr{S}W_\sigma^i$, with $i = u, s$, depends continuously on σ;*
(3) *transitivity: there is a point in a subsistem of Ω_{PA} of zero Liouville probability, called attractor, with a dense orbit.*

A great number of systems satisfies also the hyperbolic condition: the lenght of a tangent vector $\mathbf{v}$ is amplified by a factor $C\lambda^k$ for $k > 0$ under the action of $\mathscr{S}^{-k}$ if $\sigma \in W_k^s$ with $C > 0$ and $\lambda < 1$. This means that if an observer moves with the point σ it sees the nearby points moving around it as if it was a hyperbolic fixed point. But, in a general approach this

The experimental observation allows us to obtain and measure the macroscopic quantities which are mathematically the consequence of a statistics μ_E describing the asymptotic behaviour of almost all initial data in perfect accessibility phase space Ω_{PA} such that, except for a volume zero set of initial data σ, it will be:

$$\lim_{T\longrightarrow\infty} \frac{1}{T} \sum_{j=1}^{T-1} \varphi\left(\mathscr{S}^j\sigma\right) = \int_\Omega \mu_E\left(d\sigma\right)\varphi\left(\sigma\right) \tag{7}$$

for all continuous functions φ on Ω_{PA} and for every transformation $\sigma \mapsto \mathscr{S}_t(\sigma)$. For hyperbolic systems the distribution μ_E is the Sinai-Ruelle-Bowen distribution, SRB-distribution or SRB-statistics. In particular, here, the statistics is referred to a finite time τ process, as every real process is, so it is considered a SRB-statistics for a finite time system, which exists even if it is not so easy to be evaluated.

The notation $\mu_E(d\sigma)$ expresses the possible fractal nature of the support of the distribution μ_E, and implies that the probability of finding the dynamical system in the infinitesimal volume $d\sigma$ around σ may not be proportional to $d\sigma$ (Lucia 2008). Consequently, it may not be written as $\mu_E(\sigma)d\sigma$, but it needs to be conventionally expressed as $\mu_E(d\sigma)$. The fractal nature of the phase space is an issue yet under debate (García-Morales and Pellicer 2006), but there are a lot of evidence on it in the low dimensional systems (Hoover 1998). Here this possibility is also considered.

Definition 9. *(Billingsley 2012) - The triple $(\Omega_{PA}, \mathscr{F}, \mu_E)$ is a measure space, the Kolmogorov probability space, Γ.*

Definition 10. *(Lucia 2008) - A dynamical law τ_d is a group of meausure-preserving automorphisms $\mathscr{S} : \Omega_{PA} \to \Omega_{PA}$ of the probability space Γ.*

Definition 11. *(Lucia 2008) - A dynamical system $\Gamma_d = (\Omega_{PA}, \mathscr{F}, \mu_E, \tau_d)$ consists of a dynamical law τ_d on the probability space Γ.*

3. The Gouy-Stodola theorem

Irreversibility occurs in all natural processes. In accordance with the second law of thermodynamics, irreversibility is the phenomenon which prevents from extracting the most possible work from various sources. Consequently, it prevents from doing the complete conversion of heat or energy in work; indeed, in all the natural processes a part of work, W_λ is lost due to irreversibility. This work can be related to the entropy generation. In this Section the entropy generation and its relation to the work lost due to irreversibility is developed for the open systems, introducing the Gouy-Stodola Theorem.

Definition 12. *(Bejan 2006) The work lost W_λ for irreversibility is defined as:*

$$W_\lambda = \int_0^\tau dt\, \dot{W}_\lambda \tag{8}$$

where $\dot{W}_\lambda$ is the power lost by irreversibility, defined as:

$$\dot{W}_\lambda = \dot{W}_{max} - \dot{W} \tag{9}$$

with $\dot{W}_{max}$ maximum work transfer rate (maximum power transferred), which exists only in the ideal limit of reversible operation, and $\dot{W}$ the effective work transfer rate (effective power transferred).

Definition 13. *(Bejan 2006) The entropy of the whole system, composed by the open system and the environment is defined as:*

$$S = \int \left(\frac{\delta Q}{T}\right)_{rev} = \Delta S_e + S_g \tag{10}$$

where S_g is the entropy generation, defined as:

$$S_g = \int_0^\tau dt\, \dot{S}_g \tag{11}$$

with $\dot{S}_g$ entropy generation rate defined as:

$$\dot{S}_g = \frac{\partial S}{\partial t} + \sum_{out} G_{out} s_{out} - \sum_{in} G_{in} s_{in} - \sum_{i=1}^{N} \frac{\dot{Q}_i}{T_i} \tag{12}$$

while ΔS_e is defined as the entropy variation that would be obtained exchanging reversibly the same heat and mass fluxes throughout the system boundaries, G in the mass flow, the terms out and in means the summation over all the inlet and outlet port, s is the specific entropy, S is the entropy, $\dot{Q}_i, i \in [1,N]$ is the heat power exchanged with the $i-$th heat bath and T_i its temperature, τ is the lifetime of the process which occurs in the open system.

Then the term due to irreversibility, the entropy generation S_g, measures how far the system is from the state that will be attained in a reversible way.

Theorem 1 (Gouy-Stodola Theorem)**.** *In any open system, the work lost for irreversibility W_λ and the entropy generation S_g are related each another as:*

$$W_\lambda = T_a S_g \tag{13}$$

where T_a is the ambient temperature.

Proof. Considering the First and Second Law of Thermodynamics for the open systems, the maximum power transferred is:

$$\dot{W}_{max} = \sum_{in} G_{in}\left(h + \frac{v^2}{2} + gz + T_a s\right)_{in} - \sum_{out} G_{out}\left(h + \frac{v^2}{2} + gz + T_a s\right)_{out} - \frac{d}{dt}(E - T_a \dot{S}) \tag{14}$$

while the effective power transferred results:

$$\dot{W} = \sum_{in} G_{in}\left(h + \frac{v^2}{2} + gz + T_a s\right)_{in} - \sum_{out} G_{out}\left(h + \frac{v^2}{2} + gz + T_a s\right)_{out} - \frac{d}{dt}(E - T_a \dot{S}) - T_a \dot{S}_g \tag{15}$$

where h is the specific enthalpy, v the velocity, g the gravity constant, z the height and E is the instantaneous system energy integrated over the control volume.

Considering the definition of power lost, $\dot{W}_\lambda$, it follows that:

$$\dot{W}_\lambda = T_a \dot{S}_g \tag{16}$$

form which, integrating over the range of lifetime of the process, the Gouy-Stodola theorem is proven:

$$W_\lambda = \int_0^\tau dt\, \dot{W}_\lambda = T_a \int_0^\tau dt\, \dot{S}_g = T_a S_g \tag{17}$$

□

The Gouy-Stodola result on the entropy generation is expressed in a global way, without any statistical approach and expression. In order to extend the use the Gouy-Stodola theorem to any approach and context, a statistical expression of entropy generation is required. To do so the following definition can be introduced:

Definition 14. *(Gallavotti 2006) The entropy production Σ_{prod} is defined as:*

$$\Sigma_{prod} = \sum_{i=1}^{N} \frac{\dot{Q}}{k_B T_i} = \int_\Gamma \Sigma(\sigma)\mu_E(d\sigma) \tag{18}$$

with N number of heat baths, whose temperature is T_i, $i \in [1,N]$ in contact with the system, $\dot{Q}_i$, $i \in [1,N]$ heat power exchanged with each $i-th$ heat bath, k_B Boltzmann constant, $\Sigma(\sigma)$ phase space contraction and μ_E SRB-statistics.

Theorem 2. *In a stationary state, the entropy generation and the entropy production are related one another by the relation:*

$$S_g = -k_B \int_0^\tau dt\, \Sigma_{prod} \tag{19}$$

Proof. If the system is in a stationary state ($\partial S/\partial t = 0$) and if:

(1) the system is closed: $\sum_{out} G_{out} s_{out} = 0$ and $\sum_{in} G_{in} s_{in}$, or
(2) the system is open, but $\sum_{out} G_{out} s_{out} - \sum_{in} G_{in} s_{in} = 0$

and considering the relations (12) and (18), then it follows:

$$\dot{S}_g = -k_B \Sigma_{prod} \tag{20}$$

from which, integrating the statement is obtained. □

Theorem 3. *The thermodynamic Lagrangian is:*

$$\mathscr{L} = W_\lambda \tag{21}$$

Proof. Considering the entropy density per unit time and temperature ρ_S, the Lagrangian density per unit time and temperature $\rho_{\mathscr{L}}$, the power density per unit temperature ρ_π, and the dissipation function ϕ, the following relation has been proven (Lavenda 1978):

$$\rho_{\mathscr{L}} = \rho_S - \rho_\pi - \phi \tag{22}$$

and considering that $\rho_S - \rho_\pi = 2\phi$, it follows (Lucia 1995) that:

$$\rho_{\mathscr{L}} = \phi \tag{23}$$

consequently (Lucia 2008),

$$\mathscr{L} = \int_t dt \int_T dT \int V \rho_{\mathscr{L}}\, dV = \int_t dt \int_T dT \int V \rho_{\mathscr{L}}\, \phi\, dV = W_\lambda \tag{24}$$

□

Theorem 4. *At the stationary state, the work λ lost for irreversibility is an extremum.*

Proof. Considering the definition of action $\mathscr{A}$ it follows that:

$$\mathscr{A} = \int_0^\tau dt\, \mathscr{L} = \int_0^\tau dt\, W_\lambda \tag{25}$$

and considering the least action principle it follows:

$$\delta\mathscr{A} \le 0 \Rightarrow \delta W_\lambda \le 0 \tag{26}$$

which allow us to state that:

(1) W_λ is minimum if the work lost is evaluated inside the system
(2) W_λ is maximum if the work lost is evaluated outside the system, inside the environment

in accordance with the thermodynamic sign convention. □

Of course, this extremum is extended also the entropy generation, S_g, using the Gouy-Stodola Theorem $W_\lambda = T_a S_g$.

4. Thermodynamic Hamiltonian and entropy generation

Theorem 5. - ***The thermodynamic hamiltonian***: *For an open irreversible system, the thermodynamic Hamiltonian $\mathscr{H}$ is $T_a S_g$.*

Proof. . From the general relation (Arnold 1989):

$$\dot{\mathscr{H}} + \frac{\partial \mathscr{L}}{\partial t} = 0 \tag{27}$$

it follows that

$$\dot{\mathscr{H}} = -\frac{\partial \mathscr{L}}{\partial t} = T_a \frac{\partial S_g}{\partial t} \tag{28}$$

from which, integrating this last relation in the lifetime t of the process, it is possible to obtain:

$$\mathscr{H} = T_a S_g \tag{29}$$

□

So, for an open system, the thermodynamic Hamiltonian is related only to the entropy generation. Consequently, this quantity seems to be the basis of the analysis of these systems. Consequently, the irreversibility seems to be the fundamental phenomenon which drives the evolution of the states of the open systems.

From the relations (21) and (29) it follows that:

$$\dot{q}_i = \frac{\partial \mathscr{H}}{\partial p_i} = 0 \tag{30}$$

so:

$$q_i = constant \tag{31}$$

proving that the dissipation not varies the velocity of the points inside the phase space, but it varies the path, in agreement with the hypothesis of Jaynes (Dewar 2003).

5. The algebraic-geometric structure of entropy generation

In this Section the algebraic-geometric structure of the entropy generation. To do this, only the results of algebraic-geometric calculus (Hestenes 1986b; Hestenes and Sobczyk 1984) useful for the thermodynamic applications will be summarized without proofs.

The Hamilton's equations of motion can be expressed in configuration space as the pair of equations (Hestenes 1986b):

$$\begin{aligned} \dot{q} &= \partial_p \mathscr{H} \\ \dot{p} &= \partial_q \mathscr{H} \end{aligned} \tag{32}$$

Since p and q are independent variables this pair of coupled equations has been reduced to a single equation in a space of higher dimensions, preserving the essential structure of Hamilton's equation in a way which facilitates computation (Hestenes 1986b). To do so, the following definition has been introduced in Geometric Calculus (Hestenes 1986b):

Definition 15. *The configuration space $\mathbb{R}^{3N}$ is the space spanned by an orthonormal basis $\{e_k\}_{k\in[1,3N]}$ with*

$$e_i \cdot e_j = \frac{1}{2}(e_i e_j + e_j e_i) = \delta_{ij} \tag{33}$$

so the coordinate and the momentum result:

$$\begin{aligned} \mathbf{q} &= \textstyle\sum_{i=1}^{3N} q_i e_i \\ \mathbf{p} &= \textstyle\sum_{i=1}^{3N} p_i e_i \end{aligned} \tag{34}$$

The vectors in configuration space generate a real Geometric Algebra $\mathscr{R}_{3N} = \mathscr{G}(\mathbb{R}^{3N})$ with geometric product (Hestenes 1986b):

$$qp = \mathbf{q} \cdot \mathbf{p} + \mathbf{q} \wedge \mathbf{p} \tag{35}$$

Definition 16. (Hestenes 1986b) - *The momentum space $\tilde{\mathbb{R}}^{3N}$ is the space spanned by an orthonormal basis $\{\tilde{e}_k\}_{k\in[1,3N]}$ with*

$$\tilde{e}_i \cdot \tilde{e}_j = \frac{1}{2}(\tilde{e}_i \tilde{e}_j + \tilde{e}_j \tilde{e}_i) = \delta_{ij} \tag{36}$$

so the momentum results:

$$\tilde{\mathbf{p}} = \sum_{i=1}^{3N} p_i \tilde{e}_i \tag{37}$$

Definition 17. (Hestenes 1986b) - *The phase space, described in* Definition 1 *can be obtained as the direct sum:*

$$\mathbb{R}^{6N} = \mathbb{R}^{3N} \oplus \tilde{\mathbb{R}}^{3N} \tag{38}$$

In this paper the phase space described in *Definition (1)* will be called only phase space, while its algebraic-geometric description, obtained by the *relation (38)* will be called geometric phase space.

The vectors in geometric phase space generate a real Geometric Algebra $\mathscr{R}_{6N} = \mathscr{G}(\mathbb{R}^{6N})$ with the orthogonality relation (Hestenes 1986b):

$$e_i \cdot \tilde{e}_j = \frac{1}{2}(e_i \tilde{e}_j + \tilde{e}_j e_i) = \delta_{ij} \tag{39}$$

The geometric phase space can be represented also by a $2m-$dimensional vector manifold $\mathscr{M}^{2m}$, with m degrees of freedom (Hestenes 1986b).

Each point in the phase space manifold represents an allowable stationary state of the open system.

Definition 18. (Hestenes 1986b) - *There exists a symplectic bivector J, which describes the symplectic structure of the geometric phase space, defined as:*

$$J = \sum_k J_k \tag{40}$$

with component 2-blades:

$$J_k = e_k \tilde{e}_k = e_k \wedge \tilde{e}_k \tag{41}$$

The bivector J determines a unique pairing of directions in configuration space with directions in momentum space, expressed as (Hestenes 1986b):

$$\begin{aligned} \tilde{e}_k &= e_k \cdot J = e_k \cdot J_k = e_k J_k = -J_k e_k \\ e_k &= J \cdot \tilde{e}_k = J_k \cdot \tilde{e}_k = J_k \tilde{e}_k = -\tilde{e}_k J_k \end{aligned} \tag{42}$$

Each blade J_k pairs a coordinate q_k with its corresponding momentum p_k.

Each J_k satisfies $J_k^2 = -1$. Consequently, it functions as a unit imaginary relating q_k to p_k. The bivector J determines a unique complex structure for the geometric phase space (Hestenes 1986b).

Definition 19. *A state of the open thermodynamic system can be described by a single point x in the geometric phase space, defined as:*

$$x = \tilde{q} + p = p + q \cdot J \tag{43}$$

Definition 20. (Hestenes 1986b) - *The derivative with respect to the geometric phase space point is given by:*

$$\begin{aligned} \partial &= \partial_x = \partial_{\tilde{q}} + \partial_p = \tilde{\partial}_p \\ \tilde{\partial} &= \tilde{\partial}_x = -J \cdot \partial_x = -\partial_q + \tilde{\partial}_p \end{aligned} \tag{44}$$

Definition 21. *The Hamiltonian of the open thermodynamic system is a scalar-valued function $\mathscr{H}$, defined as:*

$$
\begin{aligned}
&\mathscr{H} = \mathscr{H}(x) \textit{ on the geometric phase space}\\
&\mathscr{H} = \mathscr{H}(\mathbf{p}, \mathbf{q}) \textit{ on the phase space}\\
&\mathscr{H} = T_a S_g \textit{ using global quantities}\\
&\mathscr{H}(x) = \mathscr{H}(\mathbf{p}, \mathbf{q}) = T_a S_g
\end{aligned}
\tag{45}
$$

Consequently, the Hamilton's equations for a phase space trajectory of the system assume the form:

$$\dot{x} = \tilde{\partial}\mathscr{H} \tag{46}$$

From the previous relations it follows that the open thermodynamic system evolves from the initial to the final stationary states of a process following a path in a geometric phase space described by the equivalent Hamilton's equation:

$$\dot{x} = t_a \tilde{\partial} S_g \tag{47}$$

This result is interesting because it represents the link between the global thermodynamic and the algebraic-geometric description of the evolution between two stationary states of a process for an open thermodynamic irreversible system.

Hamiltonian $\mathscr{H}$(x) determines a vector field $\tilde{h} = \tilde{h}(x)$ on $\mathscr{M}^{2m}$, given by:

$$\tilde{h} = \tilde{\partial}\mathscr{H} = (\partial\mathscr{H}) \cdot J \tag{48}$$

Consequently, the Hamilton's equations become:

$$\dot{x}(t) = \tilde{h}\big(x(t)\big) \tag{49}$$

and they determine integral curves of the vector field. Moreover, it is possible to introduce a bivector field $\Omega = HJ$ such that:

$$\tilde{h} = (\partial H) \cdot J = \nabla \cdot (HJ) = \nabla \cdot \Omega \tag{50}$$

Consequently, the Hamilton's equations become:

$$\dot{x} = \nabla \cdot \Omega \tag{51}$$

The last relation can be written as:

$$\dot{x} = \nabla \cdot \Omega = \nabla \cdot (HJ) = T_a \nabla \cdot (S_g J) \tag{52}$$

and S_g plays the role of an integrating factor for the bivector field Ω. Last, from the Liouvilles Theorem:

$$\nabla \cdot \tilde{h} = \partial \cdot \tilde{h} = T_a \nabla (S_g J) = 0 \tag{53}$$

it follows that these curves describe an incompressible flow for the entropy generation inside the geometric phase space, during the evolution between two stationary states of the open irreversible system.

6. Discussion

In this section some consideration are developed and an application is suggested.

Carnot general conclusion about heat engines is that there exists a certain limit for the conversion rate of the heat energy into the kinetic energy and that this limit is inevitable for any natural system: the cold space is the ultimate dump for heat below which no heat engine can operate. In 1889, Gouy proved that the lost energy in a process is proportional to the entropy generation, which resulted the quantity useful to describe the progress of dissipative and irreversible processes; indeed, an open system develop towards the stationary states following the thermodynamic path such that the entropy generation reaches its extremum.

So, the use of the entropy generation, as proved independently by Gouy and Stodola, is a useful quantity because it allows us to evaluate all the energy lost, due to:

- mechanical effects as friction, viscosity, etc.;
- electromagnetic interactions;
- chemical reactions;
- interactions with external heat sources as thermostats, etc..

Consequently, a system, capable of assuming many conformations, will tend to assume the one, or frequently return to the one, that maximizes the rate of dissipation of the powering energy gradients: consequently, the principle of entropy growth is not only about increasing, but increasing as fast as possible. The energy gradients are the motive forces of the physical processes and the entropy quantifies the system's evolution toward increasingly more probable states, while entropy generation describes its irreversibility.

In relation to universe (system and environment) the entropy increases, being it an isolated system. It represents a general principle of investigation for the stability of the open systems. The basis of this approach is the interaction between the open systems and their environments. The consequence of this interaction is the entropy generation variation which is determined by mass, energy, ions and chemical flows across the boundary of the system and the processes inside the system. But, the flows represents also the communications between system and environment. It is easy to develop observations of the environment, so the analysis of the entropy generation of the system can be evaluated by the environment.

This last consideration represents the difference between this approach, elsewhere named bioengineering thermodynamics, and the Glansdorff-Prigogine's one. Indeed, Glansdorff-Prigogine approach is based on the analysis of the system, while the bioengineering thermodynamic approach consider the interaction between the system and its environments. Indeed, the bases of our approach can be summarized as follows:

- The energy lost by a system is gained by the environment, consequently, the information lost by the system is gained by the environment: the problem is to codify this information;
- The environment is completely accessible by any observer, so it is easy to collect data on the lost energy of any system;
- The flows cause entropy generation variations, consequently we can evaluate the entropy generation to obtain information to the flows, even when we are unable to evaluate the flows themselves;
- The entropy generation is a global quantity, so we can obtain global information on the open system, the useful information on the result on any process in the system.

So, the entropy generation results only an objective function useful to describe this interaction, under the condition of the Le Chatelier's principle, for which any change in concentration, temperature, volume, or pressure generates a readjustment of the system in opposition to the effects of the applied changes in order to establish a new equilibrium, or stationary state.

Consequently, it follows that the fundamental imperative of Nature is to consume free energy in least time. Any readjustment of the state of the system can be obtained only by generating fluxes of free energy which entail any process where the system evolves from one state to another. The free energy "fuels" evolutionary processes so that the basic building blocks of Nature, the quanta of energy, are either absorbed from the surroundings to the system's in the form bound energy or emitted from the system to its surroundings as freely propagating photons.

Transport phenomena (transfer both of mass and of energy) play a fundamental role in systems out of equilibrium. Here we discuss an application to mass transfer. Mass transfer can be obtained by the applicaton of directional force on the mass. When a selected portion of a bistable potential is heated, the relative stability of the two wells differs as a result of which some proportion of mass is transferred from the heated well to the other: this phenomenon is known as Landauer's blowtorch effect (M. Das, D. Das, and Ray 2015). We must highlight that, in the Landauer's blowtorch effect, the difference in temperature between two parts of a body causes a mass transfer. Consequently, the difference in temperature gives rise to transport of mass. The origin of this phenomenon lies on the extra kinetic energy gained by the particles at the high temperature region, which supplies the energy required to cross a potential barrier.

To model this effect, we consider N Brownian particles, each of mass m in a bistable potential $V(x)$, where x is a position variable. The potential is completely symmetric, which means that $V(-x) = V(x)$ and it has a maximum in $x = x_{max} = 0$ and two minima, one in $x = -x_{min}$ and the other in $x = x_{min}$. The temperature of the system is T. We heat at temperature T_h only the left part of the potential $x \in [-x_1, -x_2]$, such that $-x_{min} \leq -x_1 \leq -x_2 \leq 0$. The maximum represents a potential barrier. Consequently, the heat transfer from the high to the low bath can be evaluated as:

$$Q = \int_{-x_1}^{-x_2} V(x)dx \tag{54}$$

Consequently, the entropy variation becomes:

$$S_g = \Delta S = \left(\frac{1}{T_h} - \frac{1}{T}\right)\left[V(-x_2) - V(-x_1)\right] \tag{55}$$

As a consequence, the two relative population density in the steady state is modified as:

$$\frac{P_R}{P_L} = \frac{P_{R,eq}}{P_{L,eq}} exp\left\{\left(\frac{1}{T_h} - \frac{1}{T}\right)\left[V(-x_2) - V(-x_1)\right]\right\} \tag{56}$$

where P is the integrated probability of residence of the particle in the state L or R, while L and R means left and right respectively, and eq means equilibrium. So, in this effect the entropy increases as a consequence of flows of Brownian particles across a barrier, with a variation of the relative population density inthe two wells (M. Das, D. Das, and Ray 2015).

Now, considering that:

$$\frac{P_R}{P_L} - \frac{P_{R,eq}}{P_{L,eq}} = \frac{P_{R,eq}}{P_{L,eq}} \left(exp\left\{ \left(\frac{1}{T_h} - \frac{1}{T} \right) \left[V(-x_2) - V(-x_1) \right] \right\} - 1 \right) \tag{57}$$

the flow of mass results:

$$\dot{m} = m \int_{-x_1}^{-x_2} n \frac{P_{R,eq}}{P_{L,eq}} \left(exp\left\{ \left(\frac{1}{T_h} - \frac{1}{T} \right) \left[V(-x_2) - V(-x_1) \right] \right\} - 1 \right) dx \tag{58}$$

where n is the linear density of particles. Now, if $T_h - T << T$, then the mass flows becomes:

$$\dot{m} = m \frac{P_{R,eq}}{P_{L,eq}} \left[\frac{T_h - T}{T^2} \left(V(-x_2) - V(-x_1) \right) \right] \int_{-x_1}^{-x_2} ndx \tag{59}$$

This approach can be useful also for explaining the macroscopic effect of the diffusion in a temperature gradient, the non completely understood Soret's effect. This effect is very important in civil engineering because it is the basis of the water motion when termal bridge occurs.

This applications shows how the flows thermodynamics is useful in applications. Indeed, the microscopic effects allow us to obtain a formal approach to describe the motion of masses due to energy (temperature) differences. This microscopic approach allows us to explain the global effect used in macroscopic physics, the bases of the engineering. This example shows how the bioengineering thermodynamics could be a powerful approach for application. The formal approach allows us to highlight how a mathematical physical approach could improve this thermodynamic approach.

7. Conclusions

A general principle to approach the stability of the stationary states of the open systems is required in science and engineering because it would represent a new approach to the analysis of these systems, with the result of improving their applications in mathematical and theoretical biology, biotechnologies, nanotechnologies, ecology, climate changes, energy optimization, thermo-economy, phase separation, aging process, system theory and control, pattern formation, cancer pharmacology, DNA medicine, metabolic engineering, chaotic and dynamical systems, etc..

Here, the Gouy-Stodola theorem has been proved to be the searched variational principle, which satisfies the two fundamental request:

(1) to be a work principle, because a useful variational principle out of the use of work has been proved not to be obtained (Lebowitz 2011)
(2) to use only one temperature which remains constant (because the environmental temperature is always considered constant in the usual applications), because for the open systems, the entropy production for the system and the reservoir has been proved to be obtained if and only if only one heat bath (Lebowitz 2011) exists and its temperature is constant (Lebowitz 2011).

Consequently, a link between the global thermodynamic and the algebraic-geometric approach has been introduced in order to develop a general analysis of the open irreversible systems.

Indeed, in phenomena out of equilibrium irreversibility manifests itself because the fluctuations of the physical quantities, which bring the system apparently out of stationarity, occur symmetrically about their average values (Gallavotti 2006). The notions of entropy and its production in equilibrium and non-equilibrium processes form the basis of modern thermodynamics and statistical physics (Dewar 2003; Maes and Tasaki 2007).

Entropy has been proved to be a quantity describing the progress of non-equilibrium dissipative process. Great contribution has been done in this by Clausius, who in 1854-1862 introduced the notion of entropy in physics and by Prigogine who in 1947 proved the minimum entropy production principle (Lucia 2013b). A Lagrangian approach to this subject allowed us to obtain the mathematical consequences on the behaviour of the entropy generation, S_g (Lucia 1995, 2008). The ε-steady state definition allowed us to obtain that for certain fluctuations the probability of occurrence follows a universal law and the frequency of occurrence is controlled by a quantity that has been related to the entropy generation (Lucia 2008). Moreover, this last quantity has a purely mechanical interpretation which is related to the the ergodic hypothesis which proposed that an isolated system evolves in time visiting all possible microscopic states. Moreover, considering that the open system is a system with perfect accessibility represented as a probability space in which is defined a *PA*-measure and a statistical approach has been developed (Lucia 2008). To link this statistical approach to the dynamical one it is needed to obtain the thermodynamic Hamiltonian for the open systems. It follows that this last quantity is related only to the entropy generation. Consequently, entropy generation seems to be the basis of the analysis of these systems.

Moreover, the irreversibility seems to be the fundamental phenomenon which drives the evolution of the states of the open systems, and that irreversibility and dissipation have a completely non-linear behaviour inside the phase space where the points of the open system' states move at constant velocity, but on particular path, not equal to the reversible systems, as proving the hypothesis introduced by Jaynes (Dewar 2003).

Last, the algebraic-geometry is a powerful mathematical approach to physical system (Hestenes 1986a). Consequently, the use of this approach results interesting also in the thermodynamic analysis of the open systems. The result obtained in this paper is just a link between the mathematical and the physical theories. The quantity, which allows one to link the two approaches, is the entropy generation. This quantity seem to be the fundamental of the description of the open irreversible systems.

The result obtained consists in the new role for the entropy generation:

(1) operator which allowed us to obtain the evolution of the open irreversible system in the geometric phase space between two stationary states;
(2) integrating factor in the Hamilton's equations;
(3) fundamental quantity to foresee the stationary states for the open irreversible states.

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