Maximum entropy generation in open systems: the Fourth Law?

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Abstract
This paper develops an analytical and rigorous formulation of the maximum entropy generation principle. The result is suggested as the Fourth Law of Thermodynamics.

Keywords: dynamical systems, entropy, entropy generation, ergodic theory, irreversibility, non-equilibrium thermodynamics

1 Introduction

Engineering and technical thermodynamics is the science which studies both energy and the best use of available energy resources: energy and energy transformations, including power production, refrigeration, and relationships among the properties of matter.

Energy is a thermodynamic property of systems, and that during an interaction, it can change from one form to another but the total amount of energy remains constant. The second law of thermodynamics states that energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy. Thermodynamics plays a key role in the analysis of systems and devices in which energy transfer and energy transformation take place. I. Dincer and Y.A. Cengel emphasize that Nature allows the conversion of work completely into heat, but heat is taxed when converted into work and, also, a careful study of this topic [energy] is required to improve the design and performance of energy-transfer systems. (Lucia 2010).

Stuart Kauffman has observed that since all free living systems are non-equilibrium systems indeed, since the biosphere itself is a non-equilibrium system driven by the flux of solar radiation it would be of the deepest importance, were it possible, to establish general laws predicting the behavior
of all non-equilibrium systems. Unfortunately, efforts to find such laws have not yet met with success. Kauffman notes that the systems whose behavior he wishes to predict are exceedingly complex. Microscopic models of such systems are so complex as to defy analysis (Morel and Fleck 2006).

It has been proved that entropy is the quantity which allows us to describe the progress of non-equilibrium dissipative process. By using the maximum entropy production principle, MEPP or MaxEP, it has been proved that a non-equilibrium system develops following the thermodynamic path which maximises its entropy generation under present constraints (Lucia 1995, Lucia 2008). Considering the statistical interpretation of entropy, entropy not only tends to increase, but it will increase to a maximum value. Consequently, MEPP may be viewed as the natural generalisation of the Clausius-Boltzmann-Gibbs formulation of the second law. Moreover, from 1995 to 2009 the principle of maximum entropy generation, elsewhere called maximum entropy variation due to irreversibility or maximum irreversible entropy $S_g$, has been proved for the open systems, and in 2008 it has introduced, for a general open system, also its statistical expression (Lucia 2008).

The principle of maximum for the variation of the entropy due to irreversibility represents a general principle of investigation for the stability of the open systems: this principle represents an important result in irreversible thermodynamics because it is a global theoretical principle for the analysis of the stability of open systems.

Moreover, it allows us to link the global approach to the statistical one when irreversible phenomena occur. The problem of irreversibility is difficult and part of the difficulty is due to dealing with the statistical mechanics of a large number of particles, but a global approach has been proved in 2008 (Lucia 2008). By entropy generation it has been introduced the global thermodynamic effect of the action of the forces finding a global expression which links the microscopical values to the macroscopical thermodynamic quantities (Lucia 2010).

The principle of maximum entropy generation represents the macroscopic effect of these theories, which, conversely, are its statistical interpretation. As a consequence of this principle it has been proved the irreversible ergodicity (Lucia 2008). As H. Primas has pointed out (Primas 1999): ‘The importance of the ergodic theorem lies in the fact that in most applications we see only a single individual trajectory that is a particular realization of the thermostatic process. The Kolmogorov’s theory of stochastic processes refers to equivalence classes of functions and the Birkoff’s ergodic theorem provides a crucial link between the ensemble description and the individual description of chaotic phenomena.’. The modern concept of subjective probabilities implies a behaviour based on the Boolean logic (Primas 1999). The result
obtained represents also the relation between the probability measurement in the probability space and real statistical facts. Following H. Primas (Primas 1999) the set-theoretical representation of the Boolean algebra in terms of a Kolmogorov probability space is useful because it allows to relate a dynamic in terms of a probabilistic density and all known context-independent physical laws are formulated in terms of pure states (Primas 1999).

Moreover, it has been argued that the information of a complex system may be incomplete because the dynamics of the system can be only partially known consequently to its not complete accessibility (Wang 2004). In addition the $PA$-measure in the probability space is not yet univocally defined, and it is difficulty to develop a statistical thermodynamics for an irreversible system. In 2009 the integral expression of the $PA$-measure in the probability space, useful in statistical thermodynamics of the complex and irreversible systems, has been obtained (Lucia 2009). To do it the basis of the incomplete information on complex system was developed, underlying that in non-equilibrium transformation the volume of the phase space contracts; consequently, entropy generation were related to the incomplete information theory by using the Wang development of the Tsallis theory. This result underlines that the relevant physical quantities for the stochastic analysis of the irreversibility are the probability of the state in the phase space, the Hamiltonian valued at the end points of trajectory, and time (Lucia 2009).

But, the Hamiltonian valued at the end points of trajectory in the phase space is not easy to be evaluated. In recent years, the study of an increasing numbers of natural phenomena that appear to deviate from standard statistical distributions has kindled interest in alternative formulation of statistical mechanics (Kaniadakis 2005). The new formulations of statistical mechanics should preserve most of the mathematical and epistemological structure of the Boltzmann-Gibbs theory, while reproducing the phenomenology of the anomalous systems (Kaniadakis 2005). This $\kappa$-theory obtained a lot of results in the analysis of natural phenomena, but it was not extended to irreversible open systems. A modified $\kappa$-theory has been proposed to use it in irreversible open systems, in order to obtain the integral value of the Hamiltonian at the end points of trajectory in the phase space, obtaining a new statistical expressions for the entropy generation (Lucia 2010).

Here a summary of the maximum entropy generation principle is developed in a formal way: can this theory represent a Fourth Law of Thermodynamics as a general principle applicable to non-equilibrium, irreversible, open, complex and dynamical systems?
2 The open system

Definition 1 (Lucia 2008) - A system with perfect accessibility $\Omega_{PA}$ is a pair $(\Omega, \Pi)$, with $\Omega := \{\sigma_i \in \mathbb{R}^{6N} : \sigma_i = (p_i, q_i), i \in [1, N]\}$, being $N$ the number of particles, $q_i \in \mathbb{R}^{6N}$, $i \in [1, N]$ their canonical coordinates and $p_i \in \mathbb{R}^{6N}$, $i \in [1, N]$ their conjugate momenta, and $\Pi$ a set whose elements $\pi$ are called process generators, together with two functions:

$$\pi \mapsto S$$

$$\left(\pi', \pi''\right) \mapsto \pi'' \pi'$$

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

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

2. if $D(\pi'') \cap R(\pi') \neq \emptyset \Rightarrow D(\pi'' \pi') = S_{\pi''}^{-1}(D(\pi''))$ and $S_{\pi'' \pi'} \sigma = S_{\pi''} S_{\pi'} \sigma, \forall \sigma \in D(\pi'' \pi')$

Definition 2 (Lucia 2001) - A process in $\Omega_{PA}$ is a pair $(\pi, \sigma)$, with $\sigma$ a state and $\pi$ a process generator such that $\sigma$ is in $D(\pi)$. The set of all processes of $\Omega_{PA}$ is denoted by:

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

If $(\pi, \sigma)$ is a process, then $\sigma$ is called the initial state for $(\pi, \sigma)$ and $S\sigma$ is called the final state for $(\pi, \sigma)$.

Definition 3 (Lucia 2001) - A thermodynamic system is a system with perfect accessibility $\Omega_{PA}$ with two actions $W(\pi, \sigma) \in \mathbb{R}$ and $H(\pi, \sigma) \in \mathbb{R}$, called work done and heat gained by the system during the process $(\pi, \sigma)$, respectively.

Hypothesis 1 (Lucia 2008) - There exists a statistics $\mu_{PA}$ describing the asymptotic behaviour of almost all initial data in perfect accessibility phase space $\Omega_{PA}$ such that, except for a volume zero set of initial data $\sigma$, it will be:

$$\lim_{T \to \infty} \frac{1}{T} \sum_{j=1}^{T-1} \varphi(S^j \sigma) = \int_{\Omega} \mu_{PA}(d\sigma) \varphi(\sigma)$$

for all continuous functions $\varphi$ on $\Omega_{PA}$ and for every transformation $\sigma \mapsto S(\sigma)$. 
Definition 4 - The triple \((\Omega_P, \mathcal{F}, \mu_P)\), with \(\mathcal{F}\) an algebra or a \(\sigma\)-algebra, is a measure space, the Kolmogorov probability space \(\Gamma\).

Definition 5 - A dynamical law \(\tau\) is a group of measure-preserving automorphisms \(S : \Omega_P \to \Omega_P\) of the probability space \(\Gamma\).

Definition 6 (Lucia 2008) - A dynamical system \(\Gamma_d = (\Omega_P, \mathcal{F}, \mu_P, \tau)\) consists of a dynamical law \(\tau\) on the probability space \(\Gamma\).

3 Entropy generation

In thermodynamics, the energy lost for irreversible processes is evaluated by the first and second law of thermodynamics for the open systems. So the following definition can be introduced:

Definition 7 (Lucia 2009) - The entropy generation \(S_g\) is defined as:

\[
\frac{W_{\text{lost}}}{T_{\text{ref}}} = S_g := \frac{Q_r}{T_a} \left(1 - \frac{T_a}{T_r}\right) + \frac{\Delta H}{T_a} - \Delta S + \frac{\Delta E_k + \Delta E_g - W}{T_a}
\]

(5)

where \(W_{\text{lost}}\) is the work lost for irreversibility, \(T_{\text{ref}}\) the temperature of the lower reservoir, \(Q_r\) is the heat source, \(T_r\) its temperature, \(T_a\) is the ambient temperature, \(H\) is the enthalpy, \(S\) is the entropy, \(E_k\) is the kinetic energy, \(E_g\) is the gravitational one and \(W\) is the work.

Following Truesdell (Truesdell 1970), for each continuum thermodynamic system (isolated or closed or open), in which it is possible to identify a thermodynamics subsystem with elementary mass \(dm\) and elementary volume \(dV = dm/\rho\), with \(\rho\) mass density (Truesdell 1970, Lucia 1995, Lucia 2001, Lucia 2008) the thermodynamic description can be developed by referring to the generalized coordinates \(\{\xi_i, \dot{\xi}_i, t\}_{i \in [1,N]}\), with \(\xi_i = \alpha_i - \alpha_i^{(0)}\), \(\alpha_i\) the extensive thermodynamic quantities and \(\alpha_i^{(0)}\) their values at the stable states.

Theorem 1 (Lucia 1995) - The thermodynamic Lagrangian can be obtained as:

\[
\mathcal{L} = -T_{\text{ref}} S_g
\]

(6)

Theorem 2 - The principle of maximum entropy generation (Lucia 1995, Lucia 2008): The condition of stability for the open system’s stationary states is that its entropy generation \(S_g\) reaches its maximum:
4 Irreversible ergodicity

A real-valued random variable $\pi : \Omega_{PA} \rightarrow \mathbb{R}$ on $\Gamma$ induces a probability measurement $\mu_{PA} : \mathcal{F} \rightarrow [0, 1]$ on the state space $(\mathcal{F}_\mathbb{R}, \mathbb{R})$. Considering the probability as a property of the generating conditions of a sequence, randomness can be related to predictability and retrodictability (Primas 1999). A family $\{\xi(t) : t \in \mathcal{R}\}$ is called a stochastic process, which can be represented by a family $\{\gamma(\sigma(t)) : t \in \mathbb{R}\}$ of equivalent classes of random variables $\xi(t)$ on $\Gamma$. The point function $\gamma(\sigma(t))$ is called trajectory of the stochastic process $\xi(t)$. The description of physical systems in terms of a trajectory of a stochastic process corresponds to a point dynamics, while its description in terms of equivalent classes of trajectories and an associated probability measure corresponds to an ensemble dynamics (Primas 1999).

Definition 8 - A stochastic process is said weakly stationary if:

1. $[\xi^2(t)]_{ev}, \forall t \in \mathbb{R}$
2. $\xi_{ev}(t + \tau) = \xi_{ev}(t), \forall t, \tau \in \mathbb{R}$
3. $[\xi(t_\alpha + \tau) \xi(t_\beta + \tau)]_{ev} = [\xi(t_\alpha) \xi(t_\beta)]_{ev}, \forall t_\alpha, t_\beta, \tau \in \mathbb{R}$.

Following Wiener and Akutowics, we can assume the following:

Hypothesis 2 (Primas 1999) Every stationary process with absolutely continuous spectral function (= regular process) is ergodic.

The mathematical foundation of ergodic theory is to establish a connection between phase average and time average (van Lith 2001). It follows an association between ergodic theory and objective interpretation of probability because the ergodic theory establishes a connection between probability measures and objective features of real word (van Lith 2001). A probability distribution is stationary if it is constant at all fixed points in $\Gamma$, and it reflects the fact that the system is in a steady state. Modern ergodicity is founded on the concept of measure preserving dynamical systems $\Gamma_d$ and on the Birkhoff’s ergodic theorem (van Lith 2001). Here, considering the previous Section, we introduce the stochastic processes. To do so, we state that:

Theorem 3 - If $\mu_{PA}(\Omega_{PA})$ is finite, then for any integrable function $\varphi : \Omega_{PA} \rightarrow \mathbb{R}$, the time average $\langle \varphi \rangle_t$ on $\gamma$ is defined for all orbits $\gamma$ outside of a set $\mathcal{N}_\varphi$ of measure $\mu(\mathcal{N}_\varphi) = 0$. Furthermore $\langle \varphi \rangle_t$ is integrable, with $\langle \varphi \rangle_t \circ \gamma = \langle \varphi \rangle_t$ wherever it is defined, and with

$$
\int_{\Omega_{PA}} \langle \varphi \rangle_t d\Omega_{PA} = \int_{\Omega_{PA}} \varphi d\Omega_{PA}
$$

(7)
Corollary 1 - **Birkoff’s ergodic theorem.** A measure preserving transformation \( S : \Omega_{PA} \to \Omega_{PA} \) is ergodic if and only if, for every integrable function \( \varphi : \Omega_{PA} \to \mathbb{R} \), the time average \( \langle \varphi \rangle_t \) on \( \gamma \) is equal to the space average \( \int_{\Omega_{PA}} \varphi(\sigma) \mu_{PA}(d\sigma) \) for all points \( \sigma \) outside of some subset \( N_\varphi \) of measure \( \mu_{PA}(N_\varphi) = 0 \).

Consequently, measurements results as the infinite time averages of phase functions because they take a long time compared to the microscopic relaxation time and, for metrically transitive (= ergodic) systems, measurement results are almost always equal to microcanonical averages (van Lith 2001). Moreover, the initial states lead to different paths in phase space, so the averages depend on the initial state.

**Definition 9 - \( \varepsilon \)-steady state.** Let \( \Gamma_d \) be a dynamical system and \( \varepsilon = \{ \varepsilon_S \} \) be fixed and non zero. An open system is in \( \varepsilon \)-steady state during the time interval \( \mathcal{T} \) if and only if for all \( S \in \Omega_{PA} \) there exists \( \zeta_S \in \mathbb{R} \) such that for all \( t \in \mathcal{T} \) it follows:

\[
|\langle S \rangle_T - \zeta_S| \leq \varepsilon_S \tag{8}
\]

Consequently, the probability may fluctuate within small bounds and, consequently, dynamical evolution towards steady states is allowed. Every statistical observable is induced by a random variable, while an observable, that is a \( \sigma \)-homomorphism, defines only an equivalence class of random variables which induce this homomorphism. For a statistical description it is not necessary to know the point function \( \sigma \mapsto S(\sigma) \), but it is sufficient to know the observable \( \xi \). The description of a physical system in terms of an individual function \( \pi : \sigma \mapsto S(\sigma) \) distinguishes between different points \( \sigma \in \Omega_{PA} \) and corresponds to an individual description of equivalence classes of random variables does not distinguishes between different points and corresponds to a statistical ensemble description.

**Definition 10 -** Let it be \( \pi : \Omega_{PA} \to \mathbb{R} \) a real-valued Borel function such that \( \sigma \mapsto S(\sigma) \) is integrable over \( \Omega_{PA} \) with respect to \( \mu_{PA} \), the expectation value \( \pi_{ev} \) of \( S(\sigma) \) with respect to \( \mu_{PA} \) is:

\[
\pi_{ev} := \int_{\Omega} S(\sigma) \mu_{PA}(d\sigma) \tag{9}
\]

As a consequence of the theorem (2) and the relation (12), it follows that:

**Theorem 4 - Irreversible ergodicity** (Lucia 2008) - In non equilibrium transformation the volume of the phase space \( \Omega_{PA} \) contracts indefinitely.
5 Entropy generation and its statistics

If the system is ergodic, the time-averages over infinite times coincide with
the Gibbs phase-averages, but there remains open the problem that noth-
ing is known concerning the time-averages for large but finite times. It was
shown that the use of time-averages amounts to introducing a measure in
phase space, suitably defined by the dynamics of the system. One can imag-
ine that, if one has to deal with a metastable state ergodic behaviour is
granted only on a times-scale much larger than the available one, then the
orbits could exhibit some strange features, such as a non integer fractal di-
mension on the observed time-scale, which may prevent the use of the Gibbs
measure. It has been suggested that in some problems where meta stable
states show up, one has to replace the Gibbs measure by the Tsallis one.
In the present paper we show that, if a system has dynamical time-averages
compatible with a Tsallis ensemble, then, on a certain time-scale, the orbits
have a definite non integer fractal dimension. We also show that the diffusion
process of the orbits in phase space is, in some sense, slower than in the full
chaotic case corresponding to Gibbs measure. In order to establish a cor-
respondence between dynamics and Tsallis distribution one has to solve an
analytical problem by an exact correspondence between dynamics and Tsallis
distribution, given only for continuous-time dynamical systems and not for
mappings. In the case of a mapping, such a correspondence is obtained by
introducing a suitable limiting procedure (Carati 2008).

In 1988 Tsallis postulated the physical relevance of one-parameter gener-
alization of the entropy (Tsallis 1988), introducing a generalization of stan-
ard thermodynamics and of Boltzmann-Gibbs statistical mechanics. In
2002, Kaniadakis proved some properties for the generalized logarithm, so
that we can introduce the following:

**Definition 11** (Kaniadakis 2003, Pistone 2009) The generalized exponential
\( \exp_{\kappa} \) is defined as follows:

\[
\exp_{\kappa}(\tau) = \exp \left( \int_0^\tau \frac{dt}{\sqrt{1 + \kappa^2 t^2}} \right) = \begin{cases} 
(\kappa \tau + \sqrt{1 + \kappa^2 \tau^2})^{1/\kappa} & \text{if } \kappa \neq 0 \\
\exp(\tau) & \text{if } \kappa = 0 
\end{cases}
\]

\[(10)\]

**Definition 12** (Kaniadakis 2003, Pistone 2009) The generalized logarithm
\( \ln_{\kappa} \) is defined as follows:

\[
\ln_{\kappa}(\tau) = \frac{\tau^\kappa - \tau^{-\kappa}}{2 \kappa}
\]

\[(11)\]
Definition 13 (Lucia 2010) The statistical expression, for the irreversible-entropy variation, results:

\[ S_g = - \sum_{\gamma} p_{\gamma} \ln_{\{\kappa\}}(p_{\gamma}) \]  

(12)

with

\[ p_{\gamma} = \alpha \exp_{\{\kappa\}} \left( - \frac{E_{\gamma} - \mu}{\lambda T} \right) \]  

(13)

\[ p_{\gamma} \] is the probability of the path \( \gamma \), and \( \alpha = \left[ \sum_{\gamma} \exp \left( - \frac{1}{2} \int_{V} H_{\gamma}(0) + \frac{\tau}{k_B T} dV + \frac{\tau \sigma}{2 k_B} \right) \right]^{-1} \), with \( H = u - \sum_i \mu_i \rho_i \) the non-equilibrium generalisation of the grand-canonical Hamiltonian, \( H_{\gamma}(0) \) and \( H_{\gamma}(\tau) \) the values of \( H \) at the end points of trajectory \( \gamma \) in \( \tau = 0 \) and \( \tau \), and \( \sigma_{\gamma} \) the time-averaged rate entropy production of \( \gamma \), and \( \lambda = 2 k_B \) are two arbitrary, real and positive parameters, \( \mu = \beta_1 / \beta_2 \), with \( \beta_1 \) and \( \beta_2 \) Lagrange multipliers in the entropic functional

\[ \mathcal{F} = S_{\kappa} - \beta_1 \left( \sum_{\gamma} p_{\gamma} - 1 \right) - \beta_2 \left( \sum_{\gamma} p_{\gamma} E_{\gamma} - U \right) \]  

(14)

which must be stationary for variations of \( \beta_1 \) and \( \beta_2 \), and where \( E_{\gamma} \) is the energy of the \( \gamma \)-th path and \( U \) is the total energy, \( \ln_{\{\kappa\}}(x) \) is an arbitrary function, a generalization of the logarithm function, whose properties have been studied by Csiszar (Csiszar 1967) and when \( \ln_{\{\kappa\}}(x) = \ln(x) \) the generalized entropy reduces to the Boltzmann-Gibbs-Shannon entropy (Wada and Scarfone 2009).

6 Conclusions

Ergodicity is the mechanism that allows us to pass from a mechanical description of the system to a statistical one. A fundamental question is what happens if the system is not ergodic. If the system is not ergodic, we can still have a relatively simple statistical description of it if the trajectory is a fractal curve embedded in the smooth energy surface of \( \Omega \) cells. If the reduced box-counting dimension of such a curve is \( 0 \leq d \leq 1 \) then the available phase space is a fractal object embedded in the Boltzmann 6\( N \)-dimensional smooth phase space: when \( d = 1 \) we regain completely the ergodicity (García-Morales and Pellicer 2006).

The unifying principle of the maximum entropy generation allows to build a generalized thermodynamic formalism analogously to that of Hamiltonian
mechanics. This is clearly seen in the definition of the entropy (6) and (12). Many experiments in various fields of nuclear and condensed matter physics suggest the inadequacy of the Boltzmann-Gibbs statistics and the need for the introduction of new statistics (Kaniadakis and Lissia 2003). In particular a large class of phenomena show power-law distributions with asymptotic long tails. Typically, these phenomena arise in presence of long-range forces, long-range memory, in chaotic systems, in opens systems or when dynamics evolves in a non-euclidean multi-fractal space-time. In the last decade many authors pursued new statistical mechanics theories that mimic the structure of the Boltzmann-Gibbs theory, while capturing the emerging experimental anomalous behaviors (Kaniadakis and Lissia 2003). In the last ten years, an intense activity has been modifying and improving our understanding of contemporary Statistical Mechanics and Thermodynamics.

The result is proposed as the Second Law of Thermodynamics for the open systems, but, better, as the Fourth Law of Thermodynamics.

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