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Thermodynamic paths and stochastic order in open systems

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HIGHLIGHTS

- The open systems can evolve following many paths.
- The path followed is the most probable.
- The entropy generation theorem describes the behavior of the open systems.
- The paths are statistically ordered as a consequence of the entropy generation principle.

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ABSTRACT

The theorem of extremum entropy generation is related to the stochastic order of the paths inside the phase space; indeed, the system evolves, from an indistinguishable configuration to another one, on the most probable path in relation to the paths stochastic order. The result is that, at the stationary state, the entropy generation is maximal and, this maximum value is a consequence of the stochastic order of the paths in the phase space. Conversely, the stochastic order of the paths in the phase space is a consequence of the maximum of the entropy generation for the open systems at the stationary states.

1. Introduction

The variational methods are very important in physics in order to describe natural systems by means of physical quantities independently from the frame of reference used. The approach of Maupertuis is not restricted to a stationary-state description, but customarily in thermodynamics variational principle is restricted to satisfy two fundamental requests [1]: being a work principle and using only one temperature which remains constant.

Moreover, following Wang [2–5], any effect in Nature is the consequence of the interplay and dynamic balance between pairs of opposite elements of the interaction between the systems and the environment.

Annila [6–10] pointed out that the aim of the formalism for the open systems is to give an accurate description of evolving nature. The analysis of the equation of motion reveals that the two principle of maximum of entropy generation and least action can be recognized as the only single fundamental law of nature. Quanta are exchanged between a system and its surroundings. Each quantum carries energy. Mass is a measure of how much energy there is associated with the quanta in relation to the energy density of the free space.

The natural behavior of the open systems is ascribed to the decrease of free energy in the least time, which can be calculated by the extremum (maximum) entropy generation theorem here reviewed.

Since 1995, a theoretical and phenomenological approach to irreversibility has been developed [11–21]: it is based on the entropy generation (better defined as entropy due to irreversibility, called also irreversible entropy), with the aim both

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of introducing a principle of analysis for irreversibility in engineering and science and of obtaining an approach related to the 'natural' behavior of the phenomena. The mathematical basis of this approach is the variational calculus [22], while its physical bases are the principle of least action [4,9,23–25], the Noether's theorem and the Gouy–Stodola theorem [26–31], with the following phenomenological hypothesis [20]: an open irreversible real linear or non-linear system is considered; each process has a finite lifetime τ; what happens in each instant in the range $[0, \tau]$ cannot be known, but what has happened after the time τ is well; the local equilibrium is not required; the entropy balance equation is a balance of fluxes both of entropy and of exergy. The result is the extremum entropy generation approach [20], which satisfies the previous requests for the variational calculus in thermodynamics because this principle involves only:

1. the work lost for irreversibility
2. the environment temperature, always considered constant during any process.

The principle of entropy generation is interesting in science, engineering and medicine because it allows us to obtain a condition in which the open systems persists in a stationary state and, consequently, to obtain a range when it is not in a stationary state. In order to extend this principle in economics, statistical physics and the analysis of the chaotic systems it is important to develop a statistical approach to this theorem. To do so in Section 2 the open systems and its statistical approach is introduced, in Section 3 the stochastic order is developed and its link to the extremum theorem for the entropy generation of open systems is proven and in Section 4 an application to a chemical reaction will be developed.

2. The open system and its statistical approach

The open system was explicitly described in Ref. [20]. Here it is summarized in order to introduce also its description by using the phase space. The system considered is irreversible and open. It is composed by N elementary volumes. Every i-th element of this system is located by a position vector $\mathbf{x}_i$, it has a velocity $\dot{\mathbf{x}}_i$, a mass m_i and a momentum $\mathbf{p}_i = m_i\dot{\mathbf{x}}_i$. The total mass of the system is $m = \sum_i m_i$ and its density is $\rho = m/V$ with $V = \sum_i V_i$ total volume. The position of the center of mass is $\mathbf{x}_B$ and its velocity results $\dot{\mathbf{x}}_B = \sum_i m_i\dot{\mathbf{x}}_i/m$, while the diffusion velocity is $\mathbf{u}_i = \dot{\mathbf{x}}_i - \dot{\mathbf{x}}_B$. The total mass of the system is conserved, so the following relation $\dot{\rho} + \rho\nabla\cdot\dot{\mathbf{x}}_B = 0$ is satisfied together with its local expression $\dot{\rho}_i + \rho\nabla\cdot\dot{\mathbf{x}}_i = \rho\Xi_i$, related to the density of the i-th elementary volume of density ρ_i and a source Ξ generated by matter transfer, chemical reactions or thermodynamic transformations. For an open system, as just described in macroscopic way, the equation of the entropy balance is [20]:

$$\begin{aligned}&\frac{\partial s}{\partial t} + v\nabla\cdot\mathbf{J}_S = \dot{s}\\&\dot{s} = v\sigma\end{aligned}\tag{1}$$

where $s = S/m$, is the specific entropy, S entropy, σ the entropy production, v the specific volume and $\mathbf{J}_S$ is the entropic flux defined as:

$$\mathbf{J}_S = \frac{\mathbf{Q}}{T} + \sum_i \rho_i s_i\left(\dot{\mathbf{x}}_i - \dot{\mathbf{x}}_B\right)\tag{2}$$

with $\mathbf{Q}$ heat flux.

Any dynamical state of this system can be described by the $3N$ canonical coordinates $\{\mathbf{x}_i \in R^3, i \in [1, N]\}$ and their conjugate momenta $\{\mathbf{p}_i \in R^3, i \in [1, N]\}$. The $6N$-dimensional space spanned by $\{(\mathbf{p}_i, \mathbf{x}_i), i \in [1, N]\}$ is the phase space Ω of the open system considered. Any point $\mathbf{q}_i = (\mathbf{p}_i, \mathbf{x}_i)$, $\mathbf{q}_i \in R^{6N}$ in the phase space Ω, represents a state of the entire N-elements system [15].

Any family $\{\xi(t), t \in R\}$ is called a stochastic process in the phase space Ω and it can be represented by a family of equivalent classes of random variables $\xi(t)$ on Ω, $\{\gamma(\sigma(t)) : t \in R\}$. The point function $\gamma(\mathbf{q}(t))$ is called the trajectory of the stochastic process $\xi(t)$: a description of a physical system 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 their associated probability measure corresponds to an ensemble dynamics [32].

In this paper the approach introduced by Wang is followed [2–5,33,34]. So it is considered a non-equilibrium system moving in the Ω-space between two states, which are in two elementary cells of a given partition of the phase space. We use the concept of path of classical mechanics: if the motion of the system is regular, or if the phase manifold has positive or zero Riemannian curvature, there will be only a fine bundle of paths which track each other between the initial and the final cells [2–5,33,34]. For a system in chaotic motion, or when the Riemannian curvature of the phase manifold is negative, two points indistinguishable in the initial cell can separate from each other exponentially [2–5,33,34]. Then, between two given phase cells, there may be many possible paths γ_k, $k \in [1, \omega]$ with ω number of all the paths, with different traveling time $t_{\gamma k}$ of the system and different probability $p_{\gamma k}$ for the system to take the path k, called path probability distribution [2–5,33,34]. It is considered an ensemble of a large number L of identical systems, all moving in the phase space from two cells with ω possible paths, and L_k systems traveling on the path γ_k. The probability $p_{\gamma k}$ that the system take the path γ_k is defined as usual by $p_{\gamma k} = L_k/L$. If $\omega_k = 1$ then $p_{\gamma k} = 1$. By definition, $p_{\gamma k}$ is the transition probability from the two states considered [2–5,33,34]. Wang supposed that the different paths of the non-equilibrium systems moving between the