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THEORETICAL ARGUMENTS ON EXERGY METHOD  
AND NON-EQUILIBRIUM IN NUCLEAR PROCESSES

Argomentazioni teoriche sul metodo exergetico  
e non equilibrio nei processi nucleari

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*A Gabriella e Giampiero Palazzo*

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## ABSTRACT

The present Ph.D. thesis aims at discussing theoretical aspects and arguments concerning thermodynamic methods and applications to fission and fusion nuclear plants. All parts of the thesis are rooted in the ground of the scientific literature, and all outcomes and conclusions corroborate the conceptual building with no disprove of any foundations constituting the framework accepted and shared by the whole scientific community. Though, clarifications, extensions, generalizations and applications of concepts and definitions represent primary outcomes deemed by the author beneficial for a rational and systematic perspective of Physics and Thermodynamics in the research and applications to technological and industrial developments. This abstract attempt to summarize state-of-the-art and references, methods, achievements, original results, future perspectives and is followed by an index breaking down all sections to enable an overview on the way the thesis is organized.

The mechanical aspect of the entropy-exergy relationship, together with the thermal aspect usually considered, represents the outset of the research and one of the central topics. This very aspect leads to a formulation of physical exergy and chemical exergy based on both useful work and useful heat, or useful work and useful mass, representing first outcomes based on the concept of available energy of a thermodynamic system interacting with a reservoir. By virtue of the entropy-exergy relationship, this approach suggests that a mechanical entropy contribution can be defined, in addition to the already used thermal entropy contribution, for work interaction due to pressure and volume variations. The mechanical entropy is related to energy transfer through work interaction, and it is complementary to the thermal entropy that accounts energy transfer by means of heat interaction. Then, the logical sequence to get mechanical exergy expression to evaluate useful work withdrawn from available energy is demonstrated. Based on mechanical exergy expression, the mechanical entropy set forth is deduced in a general form valid for any process. Finally, the formulation of physical exergy is proposed that summarizes the contribution of either heat or work interactions and related thermal exergy as well as mechanical exergy that both result as the outcome from the available energy of the composite of the system interacting with a reservoir. This formulation contains an additional term that takes into account the volume and, consequently, the pressure that allow to evaluate exergy with respect to the reservoir characterized by constant pressure other than constant temperature. The basis and related conclusions of this paper are not in contrast with principles and theoretical framework of thermodynamics and highlight a more extended approach to exergy definitions already reported in literature that remain the reference ground of present analysis.

The literature reports that equality of temperature, equality of potential and equality of pressure between a system and a reservoir are necessary conditions for the stable equilibrium of the system-reservoir composite or, in the opposite and equivalent logical inference, that stable equilibrium is a sufficient condition for equality. A novelty of the present study is to prove that equality of temperature, potential and pressure is also a sufficient condition for stable equilibrium, in addition to necessity, implying that stable equilibrium is a condition also necessary, in addition to sufficiency, for equality. A subsequent implication is that the proof of the sufficiency of equality (or the necessity of stable equilibrium) is attained by means of the generalization of the entropy

property, derived from the generalization of exergy property, which is used to demonstrate that stable equilibrium is a logical consequence of equality of generalized potential. This proof is underpinned by the Second Law statement and the Maximum-Entropy Principle based on the generalized entropy which depends on temperature, potential and pressure of the reservoir. The conclusion, based on these two novel concepts, consists of the theorem of necessity and sufficiency of stable equilibrium for equality of generalized potentials within a composite constituted by a system and a reservoir.

Among all statements of Second Law, the existence and uniqueness of stable equilibrium, for each given value of energy content and composition of constituents of any system, has been adopted to define thermodynamic entropy by means of the impossibility of Perpetual Motion Machine of the Second Kind (PMM2) which is a consequence of the Second Law. Equality of temperature, chemical potential and pressure in many-particle systems are proved to be necessary conditions for the stable equilibrium. The proofs assume the stable equilibrium and derive, through the Highest-Entropy Principle, equality of temperature, chemical potential and pressure as a consequence. In this regard, a first novelty of the present research is to demonstrate that equality is also a sufficient condition, in addition to necessity, for stable equilibrium implying that stable equilibrium is a condition also necessary, in addition to sufficiency, for equality of temperature potential and pressure addressed to as generalized potential. The second novelty is that the proof of sufficiency of equality, or necessity of stable equilibrium, is achieved by means of a generalization of entropy property, derived from a generalized definition of exergy, both being state and additive properties accounting for heat, mass and work interactions of the system underpinning the definition of Highest-Generalized-Entropy Principle adopted in the proof.

To complement the physical meaning and the reasons behind the need of a generalized definition of thermodynamic entropy, it is proposed a logical relation of its formulation on the base of Gibbs equation expressing the First Law. Moreover, a step forward is the extension of the canonical Equation of State in the perspective of thermal and chemical aspect of microscopic configurations of a system related to inter-particle kinetic energy and inter-particle potential energy determining macroscopic parameters. As a consequence, a generalized State Equation is formulated accounting for thermal, chemical and mechanical thermodynamic potentials characterizing any system in any state.

As far as the Non-Equilibrium Thermodynamic is concerned, the present research aims at discussing the hierarchical structure of so-called mesoscopic systems configuration. In this regard, thermodynamic and informational aspects of entropy concept are highlighted to propose a unitary perspective of its definitions as an inherent property of any system in any state, both physical and informational. The dualism and the relation between physical nature of information and the informational content of physical states of matter and phenomena play a fundamental role in the description of multi-scale systems characterized by hierarchical configurations. A method is proposed to generalize thermodynamic and informational entropy property and characterize the hierarchical structure of its canonical definition at macroscopic and microscopic levels of a system described in the domain of classical and quantum physics. The conceptual schema is based on dualisms and symmetries inherent to the geometric and kinematic configurations and interactions occurring in many-particle and few-particle thermodynamic systems. The hierarchical configuration of particles and sub-particles,

representing the constitutive elements of physical systems, breaks down into levels characterized by particle masses subdivision, implying positions and velocities degrees of freedom multiplication. This hierarchy accommodates the allocation of phenomena and processes from higher to lower levels in the respect of the equipartition theorem of energy. However, the opposite and reversible process, from lower to higher level, is impossible by virtue of the Second Law, expressed as impossibility of Perpetual Motion Machine of the Second Kind (PMM2) remaining valid at all hierarchical levels, and the non-existence of Maxwell's demon. Based on the generalized definition of entropy property, the hierarchical structure of entropy contribution and production balance, determined by degrees of freedom and constraints of systems configuration, is established. Moreover, as a consequence of the Second Law, the non-equipartition theorem of entropy is enunciated, which would be complementary to the equipartition theorem of energy derived from the First Law.

A section is specifically dedicated to specialize Second Law analyses to characterize balances of properties, and efficiencies of processes, occurring in elemental fission and fusion nuclear reactions. The conceptual schema is underpinned by the paradigm of microscopic few-particle systems and the inter-particle kinetic energy and binding potential energy determined by interactions among atomic nuclei and subatomic particles in non-equilibrium states along irreversible phenomena. The definition here proposed for thermodynamic entropy calculation is based on energy and exergy both being measurable properties by means of those values calculated from particles mass defect and used to directly derive entropy balances along nuclear processes occurring in operating industrial plants.

Finally, it is proposed a preliminary exergy analysis of EU DEMO pulsed fusion power plant considering the Primary Heat Transfer Systems, the Intermediate Heat Transfer System (IHTS) including the Energy Storage System (ESS) as a first option to ensure the continuity of electric power released to the grid. A second option here considered is a methane fired auxiliary boiler replacing the ESS. The Power Conversion System (PCS) performance is evaluated as well in the overall balance. The performance analysis is based on the exergy method to correctly assess the amount of exergy destruction determined by irreversible phenomena along the whole cyclic process. The pulse and dwell phases of the reactor operation are evaluated considering the state of the art of the ESS adopting molten salts alternate heating and storage in a hot tank followed by a cooling and recovery of molten salt in a cold tank to ensure the continuity of power release to the electrical grid. An alternative plant configuration is evaluated on the basis of an auxiliary boiler replacing the ESS with a 10% of the power produced by the reactor during pulse mode.

The conclusive summary of main achievements and original outcomes is followed by proposals of future developments in different fields of theoretical and applied research and technology. These themes represent an outlook on the opportunities and initiatives originating from the passionate dedication effort spent along the here ended Doctorate.

## MAIN ACHIEVEMENTS AND ORIGINAL OUTCOMES

- Definition of generalized thermodynamic exergy and thermodynamic entropy properties;
- Theorem of necessity and sufficiency of stable equilibrium and Highest-Generalized-Entropy principle for stable equilibrium and non-equilibrium
- Perspective of the State Equation extended to both thermal aspect and chemical aspect; relationship of State Equation with generalized thermodynamic entropy property; analysis of Gibbs equation incoherence and demonstration of units of measure equivalence; generalization of ideal state equation taking into account kinetic and potential energy due to inter-particle kinematic and geometric configurations;
- Hierarchical structure of thermodynamic entropy defined for mesoscopic systems: non-equipartition theorem on entropy, complementary to the equipartition theorem of energy for microscopic systems;
- Fission and fusion elemental reactions second law analyses based on exergy method: thermodynamic and informational aspect accounted for in nuclear physics;
- Simplified exergy balances and efficiencies calculations of ABWR and AP1000 fission nuclear reactors considering nuclear core and conventional plant;
- Preliminary exergy analysis of EU DEMO pulsed fusion reactor with molten salts energy storage system and auxiliary boiler configurations.

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