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Article

On the Problem of Formulating Principles in Nonequilibrium Thermodynamics

Paško Županović [1,*], Domagoj Kuić [1], Davor Juretić [1] and Andrej Dobovišek [2]

[1] Faculty of Science, University of Split, Teslina 12, 21000 Split, Croatia

[2] Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška cesta 160, SI-2000 Maribor, Slovenia

* Author to whom correspondence should be addressed; Tel.:+385 21 385 133; Fax: +385 21 384 086; E-Mail: pasko@pmfst.hr.

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Abstract: In this work, we consider the choice of a system suitable for the formulation of principles in nonequilibrium thermodynamics. It is argued that an isolated system is a much better candidate than a system in contact with a bath. In other words, relaxation processes rather than stationary processes are more appropriate for the formulation of principles in nonequilibrium thermodynamics. Arguing that slow varying relaxation can be described with quasi-stationary process, it is shown for two special cases, linear nonequilibrium thermodynamics and linearized Boltzmann equation, that solutions of these problems are in accordance with the maximum entropy production principle.

Keywords: relaxation; stationary process; entropy production

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1. Introduction

Physicists develop an axiomatic theory whenever possible. In the case of thermodynamics, the equilibrium properties of macroscopic systems can be well understood with three (or four) laws. The best known is the second law of thermodynamics, which defines the state of maximum entropy as the equilibrium state of an isolated system. If an isolated system is not in a state of maximum entropy, it changes spontaneously to the state of maximum entropy. Strictly speaking, an isolated system in equilibrium is not in a state of maximum but mean entropy. Because mean entropy is extremely close to maximum entropy, one can claim that the entropy of an isolated system is the maximum possible [1].

In contrast to the first law of thermodynamics, or other laws such as energy conservation or those provided by Maxwell equations, the second law is rooted in probability. The statistical nature of the second law was recognized already by Maxwell, who wrote that *"The second law of thermodynamics has as much truth as saying that, if you poured a glass of water into the ocean, it would not be possible to get the same glass back again"* [2].

In contrast to thermodynamics, which is the theory of the equilibrium properties of systems, the theory of irreversible processes is still not axiomatic. Already in 1912 Ehrenfest (Enzykl. Math. Wissensch, IV, 2(II) fasc.6, p82, note23, 1912) asked if there were some function which, like the entropy in the equilibrium state of an isolated system, achieves its extreme value in a stationary non-equilibrium state. Although there is no unique theory of nonequilibrium processes, the principles have been found in some special cases.

There are a lot of principles of stationary processes [3–11]. On the 2009 year workshop in Jena, the issue has been raised whether MEP result is a principle and how to use it. Some of the participants has put the minimum entropy production principles on equal foot as MEP principle.

We argue in this paper that in the case of stationary non-equilibrium processes there are different possibilities for maintaining external constraints and non-equilibrium stationarity, some leading to the definition of extremal principles seemingly opposite to each other. External constrains are usually fixed by the experimentalist. Thus, the subjective choice of constraints is what leads to the definition of physical principles in the case of non-equilibrium stationary state. In order to avoid such interference between a subject and a system being examined, we propose the use of relaxation processes for a formulation of physical principles in nonequilibrium thermodynamics. It is shown that MEP principle, under certain conditions, can be used to describe the irreversible processes close to equilibrium.

For the readers convenience, a list of relevant research is summarized below:

L. Onsager [12,13] has shown that linear nonequilibrium thermodynamics can be described by the principle of the least dissipation of energy. We have shown in paper I [14] that this principle is equivalent to the maximum entropy production (MEP) principle.

In the case of rarefied gas close to equilibrium, von Enskog [15,16] has shown that the solution of the linearized Boltzmann equation makes entropy production the maximum possible.

In a series of papers [17–19], E.T. Jaynes used information theory as the starting point for statistical mechanics. Having in mind that the macroscopic development of a system depends upon constraints rather than the initial microscopic state, he used such constraints as the pillars of his theory. Claiming that our knowledge of the initial state of a system is not a matter of physics but information theory, he introduced the concept of information entropy and proposed that the probabilities of states, under certain constraints, make information entropy the maximum possible. This procedure is known as the MaxEnt formalism [10,19,20]. Since the MaxEnt formalism can be equally applied to equilibrium as well as to nonequilibrium processes, it has been used as a starting point in the description of stationary processes [10,20,21].

Dewar [10,20] has introduced paths in phase space as elements of his microscopic theory and the mean value of fluxes as constraints. Under certain assumptions found that the maximum entropy production

(MEP) principle follows from the MaxEnt formalism. Several authors have expressed criticism in respect to his assumptions [22–24].

Niven [21] applied MaxEnt to stationary processes in a different manner than Dewar. Values of fluxes are considered as key elements in his approach in the sense that their mean values are constraints. Assuming local equilibrium he found, under certain conditions, that MaxEnt leads to maximum entropy production.

Some authors have proposed minimum entropy production as the basic property of irreversible processes. The best known result from this proposal comes from Prigogine [25] regarding linear relationships among fluxes, j_1, j_2 and conjugated forces X_1, X_2 (close to equilibrium). Prigogine's approach is characterized by the fact that in the presence of a constant driving force X_1 the experiment is designed in such a way that the driven flux must reach a zero value in the stationary state. The chosen variable is secondary thermodynamic force X_2 (the output force). By elementary algebra he has found that the induced value of the secondary force in the stationary state is associated with minimum entropy production.

Already in 1848, Kirchhoff [11], taking into account the charge conservation law, has shown that currents, within a volume with a given electric potential on its surface, distribute within the volume in accordance to the minimum entropy production principle. In addition, Jeans has shown [26] that in linear electric networks with no electromotive force, currents distribute in accordance with the principle of minimum entropy production.

Additional examples of the application of this principle are the solutions of the linearized Boltzmann equation [16].

In this paper, we ask which system is the best one to use when one aims for the definition of principles in nonequilibrium thermodynamics.

2. Interference of Subject and Object in Stationary Processes

All the above applications of maximum entropy or minimum entropy production relate to stationary processes. At first glance, stationary processes seem appealing for the formulation of such principles since all physical quantities, including probabilities, do not depend on time. But one has to have in mind that in a stationary process the system is in contact with an energy bath. The subject controls the baths and can strongly affect the development of a system. For example, take into consideration the distribution of electric currents. In the case of a volume with a fixed potential on its surface, or a linear network with no sources of electromotive forces, the currents are distributed in such a way so as to produce the minimum possible entropy [11,26]. If one considers a planar linear network, that consists of sources of electromotive forces and resistors, and takes into account both conservation laws (charge and energy) one finds that currents are distributed according to the MEP principle [27].

A similar conclusion is valid for Prigogine's result of minimum entropy production. Here too a system is in contact with an energy bath and the energy exchange between system and bath can be controlled by an observer who has designed an experiment in such a way so as to ensure that zero secondary flux is achieved.

3. Relaxation as A Quasi-Stationary Process. Maximum or Minimum Entropy Production?

It stems from the foregoing analysis that we have to resort to relaxation processes in order to exclude the interference of the subject. We can pose a question: Is it possible to approximate the relaxation process with a stationary one, and, if the answer is yes, under which conditions is it possible? Then the relaxation process must be slow enough to be approximated with stationary one. If the process is slow enough, one can calculated fluxes as the instantaneous functions of thermodynamic forces. Using material properties of the system one can self-consistently calculate the decrease of the thermodynamic forces and fluxes, respectively. Equations that describes relaxation must take into account the conservation laws constraints.

A linear planar electric network is a good example of this. The relaxation time of sources of electromotive forces (several hours in the case of mobile or laptop batteries) is much larger than the relaxation time of electric currents (order of μs for ordinary networks). Therefore, we can describe the relaxation of the planar electric network as a quasi-stationary process. Let us point out that if one takes into account that both energy and charge are conserved the distribution of current is described by the MEP principle [27].

In the paper I [14] we have considered solutions of the linearized Boltzmann equation. Using Boltzmann's equation, Kohler has found the expression that relates entropy production to the collision integral [16]. In other words, the source of entropy production are the collisions of molecules in a nonequilibrium state. One can replace the distribution function that is the solution of the linearized Boltzmann equation with some other distribution function. The variation of such a trial distribution function, under stationary constraint, leads to the conclusion that the solution of the Boltzmann equation is associated with extremal entropy production. If one takes into account that entropy production, due to molecular collisions, is equal to the sum of the products of thermodynamic forces and conjugated fluxes, one finds that the solution of the Boltzmann equation is the distribution that produces the maximum possible entropy.

Kohler has replaced the constraint that requires equality between entropy production due to the molecular collisions and macroscopic entropy production, calculated as the product of the heat flux and corresponding thermodynamic force, with the one that keeps heat flux constant. Then he has found that solutions of the Boltzmann equation are those that produce the minimum possible entropy [16].

The Boltzmann equation incorporates the conservation laws (mass, energy, momentum and angular momentum). The linearized Boltzmann equation means that the system is close to equilibrium and the relaxation process can be approximated with a quasi-stationary one. So it seems that both principles (MEP and minimum entropy production) are equivalent in this case. However, it is just not the case. As we have noted in paper I [14], Kohler's assumption of fixed fluxes suffers from inconsistency. In his approach thermodynamic forces are constant from the outset of the problem. If, in addition, one fixes the fluxes, entropy production is fixed then also, so the very procedure of variations is put into question. More precisely, Kohler varied the distribution function without taking into account that entropy production associated with the collision integral should be equal to the sum of the products of thermodynamic forces and conjugated fluxes. In this way the consistency of his approach is put into question, since the process can be stationary only if the entropy produced due to molecular collisions is equal to the measured entropy production (the sum of the products of thermodynamic forces and conjugated fluxes). Otherwise, the entropy delivered by rarefied gas to the bath would not be equal to the entropy generated by molecular collisions.

4. Conclusions

In contrast to relaxation processes, stationary processes are not free of interference between subject and system. Therefore, we argue that relaxation processes are more suitable than stationary processes for the formulation of principles in nonequilibrium thermodynamics.

Slow relaxation process can be approximated with quasi-stationary process. For quasi-stationary process in an isolated system one can take advantage of well-known characteristics of an isolated system (conservation laws) to formulate a principle or principles guiding such processes. We argue in this short paper that, assuming that the stationary process is not put in question, the MEP principle rather than the minimum entropy production principle correctly describes the distribution of electric currents in a linear network and the distribution function of the linearized Boltzmann equation. In other words, we can say that the MEP principle is valid in the case of slow varying relaxation processes.

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