The maximum entropy production principle: two basic questions

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The overwhelming majority of maximum entropy production applications to ecological and environmental systems are based on thermodynamics and statistical physics. Here, we discuss briefly maximum entropy production principle and raises two questions: (i) can this principle be used as the basis for non-equilibrium thermodynamics and statistical mechanics and (ii) is it possible to 'prove' the principle? We adduce one more proof which is most concise today.

Keywords: entropy production; second law of thermodynamics; variational principle

Nature takes the easiest and most accessible paths and, hence, processes are accomplished very quickly in a minimum time. In 1962, Fermat used this principle to work out the refraction law. This was one of the first known attempts at successful deductive description of a physical phenomenon involving the variational principle. Presently, researchers concerned with non-equilibrium processes have turned back to Fermat's idea in the form of the maximum entropy production principle (MEPP) (see recent reviews Kleidon & Lorenz 2004; Martyushev & Seleznev 2006). In brief, a non-equilibrium system will most probably take the line of development when it maximizes the entropy production σ at some assigned external constraints. The following relationship with Fermat's principle can be pointed out. It is known that the entropy production equals the product of the thermodynamic force X by the flow $\mathcal{J}$. Therefore, if for example X is fixed, the maximum entropy production leads to maximum $\mathcal{J}$, i.e. selection of fastest processes. MEPP has proved to be good for understanding and description of diverse non-equilibrium processes in physics, biology and environmental science (Ozawa *et al.* 2003; Kleidon & Lorenz 2004; Martyushev & Seleznev 2006). This raises two questions: (i) can this principle claim to be the basis of all non-equilibrium physics? and (ii) is it possible to prove MEPP?

— Recall the following points before we answer the first question. MEPP can be used to derive the whole apparatus of linear and, probably, nonlinear thermodynamics as it was shown by H. Ziegler (Martyushev & Seleznev 2006). If the principle is used in the nonlinear region, the symmetry transformation imposes considerable constraints on the possible form of the entropy production (the scalar) as a function of flows, which can have an arbitrary tensor dimensionality. In the kinetic

theory of gases, MEPP can be used to derive the velocity distribution function for particles which satisfies the linearized Boltzmann equation and allows determination of experimentally verified kinetic coefficients for gaseous, electron and phonon systems. Sufficiently fundamental studies can be found in the literature showing the relation of this principle to the Fokker–Planck equation, the method of non-equilibrium statistical operator, relaxation laws, etc. These studies are reviewed by Martyushev & Seleznev (2006). Note that in the literature, MEPP is used for both deduction of master equations and selection of the solution out of several possible solutions (e.g. if the initially posed problem refers to the class of ill-posed problems). This, on the one hand, argues for the universality of the principle and the intention of investigators to use it as widely as possible, and on the other hand probably reflects the lack of sufficient rigour in its applications today. It should also be mentioned that the possibility of a local equilibrium interpretation of a non-equilibrium system and the representation of the entropy production as a bilinear form of flows and forces are so far a mandatory condition for the use of MEPP. Thus, considering the above discussion, the answer to the first question is 'yes' today.

— The second question is most interesting as follows from some recent studies (Dewar 2003, 2005; Martyushev & Seleznev 2006). Note first that a principle like MEPP cannot be proved. Examples of its successful applications for description of observed phenomena just support this principle, while experimental results (if they appear) contradicting the principle will just point to the region of its actual applicability. The balance of the positive and negative experience will eventually lead to the consensus of opinion on the true versatility or a limited nature of MEPP. Other principles, such as laws of thermodynamics and Newton's law, developed along similar lines. At the same time, there is always a temptation to relate the principle to other existing principles and, in this way,

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'prove' it. MEPP is traditionally related in the literature to the second law of thermodynamics (Dewar 2003; Ozawa *et al.* 2003; Martyushev & Seleznev 2006). However, investigators always have to use additional assumptions in their deductions and these assumptions prove to be less obvious than MEPP (of course, this opinion is subjective, but an argument in favour may be the fact that MEPP is formulated independently by investigators working in different domains of science, from biology to physics (Kleidon & Lorenz 2004; Martyushev & Seleznev 2006), while specific mathematical or physical evidence in support of MEPP is not apprehended by outsiders). Therefore, these proofs can hardly be viewed as fully successful. Still such efforts provide a deeper insight into the beginnings of MEPP and, for this reason, are always interesting and important. Let us adduce one more 'proof' which, in our opinion, is most concise today.

There is the classical variational formulation of non-equilibrium thermodynamics (e.g. according to Ziegler) (Martyushev & Seleznev 2006): $X = \text{const} > 0$ (an external thermodynamic force is preset); entropy production is known as a function of flows; $\sigma = X\mathcal{J}$ and the relation between thermodynamic flows and forces needs to be established (whether the relation is linear or nonlinear is wanted yet). We have to demonstrate that the system selects $\mathcal{J}$ (and, consequently, σ) as large as possible.

Assume that the second law of thermodynamics holds ($\sigma \geq 0$) and suppose several different flows are possible $\{\mathcal{J}_i, i \in \mathbb{N}\}$. All of them should be larger than zero because $\sigma \geq 0$ (the flows are directed towards the decrease of the thermodynamic force). It is at the observer's discretion to select the reference point of flows from $\{\mathcal{J}_i\}$, and this is not inconsistent under the problem statement in hand. So, we shall assume that the maximum flow is taken as the zero flow (or the maximum flow is equal to a positive infinitesimal and we have a quasi-equilibrium state). After this transformation (in practice, this can be realized, e.g. by time/space scaling), all the other flows are negative relative to the selected system and $\sigma < 0$ for those flows. As the second law of thermodynamics is a universal law of the nature and should not depend on such transformations (in principle, this invariance

may also be viewed as the main axiom (or hypothesis) of the proof), we prove that the maximum possible flow is realized at a given force and, hence, the entropy production is a maximum too. The above considerations can be generalized to the case when several thermodynamic forces are present in a system.

Why is it MEPP that can be nominated for the general law describing non-equilibrium processes? Along with the above arguments, we shall point out two more factors which are important in P. Dirac's opinion for the 'success' of a theory. They are simplicity and elegance. Both are rather obvious here. Many centuries ago, researchers (for example, P. Fermat) turned to ideas similar to MEPP and these ideas appeared to them so obvious that were taken as axioms in development of a theory. The elegance of the theory follows from the fact that all equilibrium physics of many particles are based on maximization of the entropy (the method of potentials developed by Gibbs in thermodynamics and, for example, the well-known Jaynes' approach in statistical physics). Therefore, the possibility that all non-equilibrium thermodynamics and statistical physics can be constructed on the basis of the entropy production (actually the time derivative of the entropy) maximization appears to be very intriguing.

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