

ABOUT SOME EXTREMAL PRINCIPLES IN NON-EQUILIBRIUM THERMODYNAMICS

Sergio da Cunha^{1*}, Vincent Gerbaud^{1*}, Nataliya Shcherbakova¹

¹ Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France
* sergio.dacunha@ensiacet.fr, vincent.gerbaud@ensiacet.fr

ABSTRACT

We revisit some extremum principles in non-equilibrium thermodynamics (NET), highlighting their limitations. The key idea is that system dynamics and phenomenological laws cope with the minimization or maximization of a relevant function or functional.

An early variation principle in NET was proposed by Onsager in 1931,¹ being another formulation of the reciprocal laws for coupled phenomena. Onsager's law is rigorously derived for continuous thermodynamic systems close to equilibrium, based on the principle of microscopic reversibility, and is valid for linear flux-forces relationships and when local equilibrium holds.¹ Prigogine used Onsager's law to derive his "Principle of Minimum Entropy Production" (minEP). It states that, if some thermodynamic forces are fixed in a system, and others are free to change, the system evolves in such a way that it reaches a minimum of entropy production at steady state.¹ Later, Ziegler proposed his "Orthogonality Principle" as a generalization of Onsager's law for nonlinear flux-force relationships,^{1,2} and attempted to demonstrate it in the particular case of homogeneous rheological bodies. He also proposed an equivalent formulation for the orthogonality principle called "Principle of Maximum Dissipation Rate" (maxEP),^{1,2} and postulated its validity for continuous system under certain conditions.³ Despite them seeming contradictory, minEP can be deduced from maxEP (Figure 1): the system maximizes entropy production at every instant, but its evolution in time decreases entropy production.²

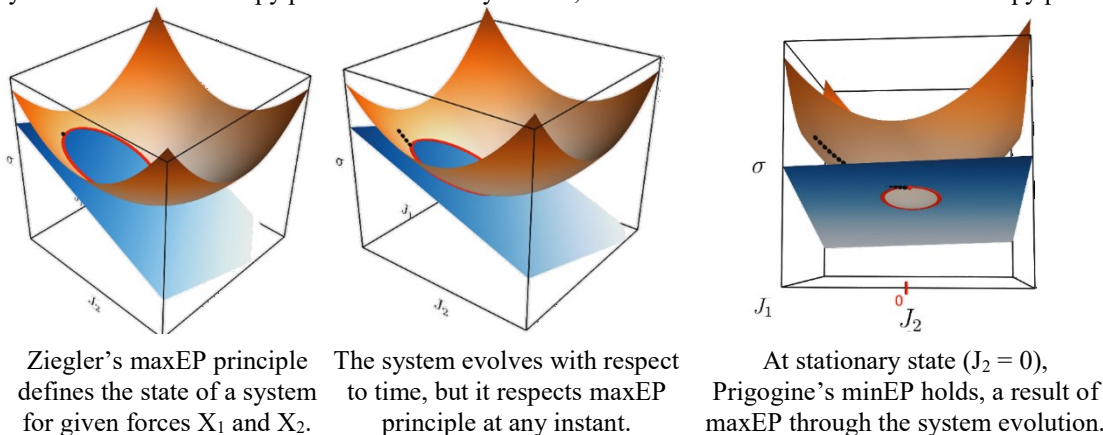


Figure 1: Stationary Prigogine's minEP principle as a consequence of instantaneous Ziegler's maxEP principle.

An extremum principle that remains valid outside of linear NET would be a powerful tool in the study of coupled phenomena. That is the reason Ziegler's work is commonly praised in the literature. But it turns out that maxEP is inaccurate for a system with coupled reactions far from equilibrium.⁴ Many of the arguments in favour of Ziegler's principle are based on the fact that it yields Onsager's reciprocal relations in the linear domain. However, Ziegler conceived his principle as a generalization of Onsager's law, i.e., maxEP was designed so it would coincide with Onsager's law near equilibrium.

Later works kept looking for general extremum principles in NET. A variational formulation was proposed by Moroz following the least-action principle, and applied to reactive systems.⁵ He used as a Lagrangian a sum of a positive-defined thermodynamic potential Ψ - seen as a penalty for being out of equilibrium - and of some dissipation function Φ . But his example relies on a linear approximation of the chemical affinity with respect to the reaction extent; and we can also point out some unit inconsistency of Ψ and Φ and the lack of a clear definition of Φ .

None of the extremum formulations seems to be general: exploring the landscape of NET principles, several restrictions are pointed out for each of them. We shall discuss these restrictions for a number of principles, including the aforementioned ones.

REFERENCES

- [1] R.C. Dewar, C.H. Lineweaver, R.K. Niven and K. Regenauer-Lieb, Beyond the Second Law. An overview. in R.C. Dewar et al. (eds.), *Beyond the Second Law - Entropy Production and Non-Equilibrium Systems*, chap. 1, Springer: Berlin/Heidelberg, Germany, 2014.
- [2] L.M. Martyushev and V.D. Seleznev, Maximum Entropy Production Principle in Physics, Chemistry and Biology, *Physics Reports*, vol. 426, pp. 1-45, 2006.
- [3] L.M. Martyushev and V.D. Seleznev. The restrictions of the maximum entropy production principle. *Physica A* 410, pp. 17-21, 2014.
- [4] J. Bataille, D.G.B. Edelen and J. Kestin, Nonequilibrium Thermodynamics of the Nonlinear Equations of Chemical Kinetics, *J. Non-Equilib. Thermodyn.*, vol. 3, pp. 153-168, 1978.
- [5] A. Moroz, On a Variational Formulation of the Maximum Energy Dissipation Principle for Non-equilibrium Chemical Thermodynamics, *Chemical Physics Letters*, vol. 457, pp. 448-452, 2008.