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► **To cite this version:**

Sergio da Cunha, Nataliya Shcherbakova, Vincent Gerbaud. ABOUT SOME EXTREMAL PRINCIPLES IN NON-EQUILIBRIUM THERMODYNAMICS. Joint European Thermodynamic Conference, Jun 2021, Prague, Czech Republic. hal-03374390

**HAL Id: hal-03374390**

**<https://hal.science/hal-03374390>**

Submitted on 12 Oct 2021

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# ABOUT SOME EXTREMAL PRINCIPLES IN NON-EQUILIBRIUM THERMODYNAMICS

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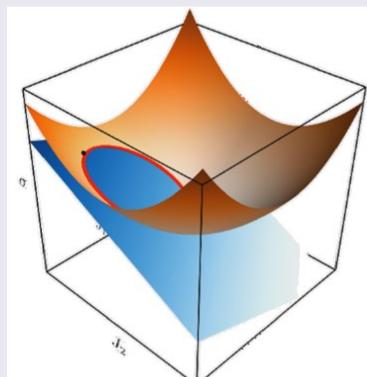
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## Context and motivations

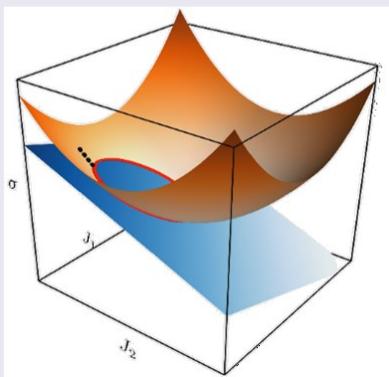
- A very large literature has been devoted to extremum principles in non-equilibrium thermodynamics (NET), like Prigogine's minEP or Ziegler's maxEP (EP = entropy production)
- An extremum principle that remains valid outside of linear NET would be a powerful tool in the study of coupled phenomena and of dynamics.
- But does such a principle exist? Any restrictions and limitations? This is what we are examining. Honestly, our results are timid but in progress.

## Extremum principles in non-equilibrium thermodynamics

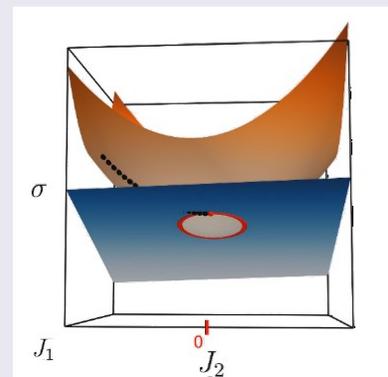
- 1931 : Onsager's early variation principle in NET [1] is another formulation of its famous reciprocal laws for coupled phenomena.
  - Limitations: Onsager's law is rigorously derived for continuous thermodynamic systems close to equilibrium, based on the principle of microscopic reversibility, and is valid for linear flux-forces relationships  $\underline{J} = \underline{L} \cdot \underline{X}$  or  $\underline{X} = \underline{R} \cdot \underline{J}$  and when local equilibrium holds [1]
- **Among popular principles, Prigogine's minEP in the 40's can be deduced from Ziegler's maxEP in the 60's [2]** : The system maximizes entropy production at every instant, but its evolution in time decreases entropy production. This is illustrated in Figure 1.
  - Prigogine used Onsager's law to derive minEP. It states that, given fixed  $X_1, X_2, \dots, X_k$  forces and forces  $X_{k+1}, X_{k+2}, \dots, X_n$  free to vary, the system reaches a minimum of entropy production at the steady state.
  - Martyushev et al. discussed strict restrictions on Ziegler's principle [3] : (i)  $\sigma$  is a function of fluxes,  $\sigma_a \equiv \sigma(\underline{J})$ ; (ii)  $\sigma$  equals the sum of fluxes times forces in the system,  $\sigma_b \equiv \sigma = \underline{J} \cdot \underline{X}$ .
    - With 2 forces  $X_1, X_2$  and 2 fluxes  $J_1, J_2$  only in the system, Ziegler's principle is easily represented with the 3-D coordinates  $J_1, J_2, \sigma$ . Assumption (i) is displayed by a surface (orange)  $\sigma_a = \underline{J} \cdot \underline{X} = \underline{R} \cdot \underline{J} \cdot \underline{J}$ , and assumption (ii) is a plane (blue). Generally their intersection is a curve, and maxEP postulates that the system state is at every instant the maximum of this curve w.r.t coordinate  $\sigma$  (black dot curve).
    - For minEP, when  $X_1$  is fixed, the free force  $X_2$  change corresponds to the blue plane rotation,  $\sigma_b = \underline{J} \cdot \underline{X}$ . The stationary state  $J_2 = 0$  corresponds to a minimum of entropy production (red dot in figure 1 far right)



Ziegler's maxEP principle defines the state of a system for given forces  $X_1$  and  $X_2$ .



The system evolves with respect to time, but it respects maxEP principle at any instant.



At stationary state ( $J_2 = 0$ ), Prigogine's minEP holds, a result of maxEP through the system evolution.

- 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. Ziegler 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.
- **So, is Ziegler's principle the superior one? answer is NO.**
  - Despite strong arguments that have ruled out several critics, restrictions apply [see 2, 3],
  - [2,3] has also overlooked that maxEP is inaccurate for a system with coupled reactions far from equilibrium [see for ex. 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 designed his maxEP principle so that it would coincide with Onsager's law near equilibrium. Hence, this argument is not valid.
- **Beretta's Steepest Entropy Ascent (SEA) law, would be a stronger candidate [5]** : "every non-equilibrium state of a system or local subsystem for which entropy is well defined must be equipped with a metric in state space with respect to which the irreversible component of its time evolution is in the direction of steepest entropy ascent compatible with the conservation constraints."
  - It was shown to be coherent with many advanced nonequilibrium frameworks [6]
  - It was shown to give an extension of Onsager's reciprocal laws as a non-linear relation valid far from equilibrium within the framework of quasi-equilibrium approximation.
  - A key point is that the metric operator defines the direction of SEA and the characteristic time driving the dynamic evolution of the system defines the evolution rate in such direction.

Future work: investigation is in progress, e.g. to decipher whether the black dot trajectory has special properties (geodesic? shortest time?) in the metric proposed by Beretta ; e.g. apply Beretta's proposal to chemical kinetics as in [4]

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