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Energy efficiency

Oral

EXTREMAL PRINCIPLES IN NON-EQUILIBRIUM THERMODYNAMICS

Sergio da Cunha¹, Vincent Gerbaud¹, Nataliya Shcherbakova¹,

¹ Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France

Corresponding author e-mail: vincent.gerbaud@ensiacet.fr

Along the years, a number of researchers have used variational principles to derive important results in thermodynamics for studying the general evolution of systems. In this contribution, we clarify the two entropy production extremisation principles and analyse their relation with the *least-action principle* and *fastest dissipation principle*.

Two of the most famous variational principles in non-equilibrium thermodynamics are Ziegler's maximization of entropy production (MaxEP) and Prigogine's minimization of entropy production (MinEP). Despite their apparent incompatibility, both principles coexist together. According to Martyushev, "If the time is short, the system maximizes entropy production at preset fixed forces at a given moment... If the time is long, the system changes free thermodynamic forces so as to decrease entropy production".¹

Consider flux-force couples $\{J, X\}$ like {heat flux, $1/T$ gradient} { i comp. diffusion flux, $-\mu_i/T$ gradient} {chemical reaction, $-\sum v_i \mu_i/T$ gradient}. The usage is to write transport laws as single linear relations flux and force, like Fourier's or Fick's law, but Onsager's linear non-equilibrium thermodynamics proves a more general multilinear expression $J_i = \sum_j L_{ij} X_j$.

Then, Ziegler's MaxEP states that fluxes J associated to forces X maximize the entropy production σ of the system under strict assumptions: (i) σ is a function of fluxes, $\sigma_a \equiv \sigma(\underline{J})$; (ii) σ 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, σ (see Figure). Assumption (i) is displayed by a surface (orange), and assumption (ii) is a plane (blue). Generally their intersection is a curve, and MaxEP postulates that the exact state of the system corresponds to the maximum of this curve with respect to coordinate σ .

MinEP principle states that, if a number of forces X_1, X_2, \dots, X_k is fixed and the rest of the forces $X_{k+1}, X_{k+2}, \dots, X_n$ is free to vary, then the system evolves in such a way that it reaches a minimum of entropy production at the steady state. In the figure, when X_1 is fixed, the change in the free force X_2 corresponds to a rotation of the plane $\sigma_b = \underline{J} \cdot \underline{X}$. The stationary state $J_2 = 0$ corresponds to a minimum of entropy production, as depicted by the red dot in the figure.

This allows us to refine Martyushev's statement, saying that the system maximizes entropy production at every *instant*, but its *evolution in time* decreases entropy production.

Some common conjectures in non-equilibrium thermodynamics claim that this evolution follows a *least-action principle* or a *fastest dissipation principle*.² However, these conjectures are mostly stated vaguely and without a consensus in academia.

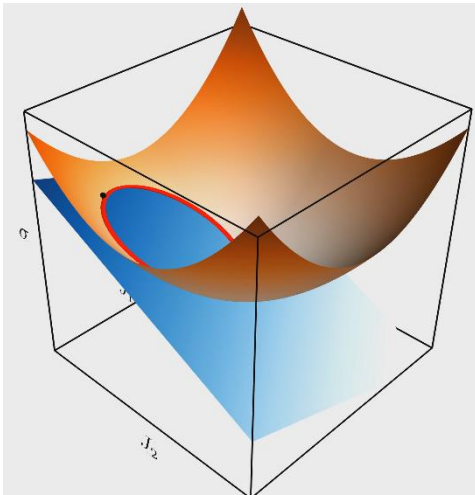
Here, we investigate whether the least-action principle refers to: 1) minimizing the arc length of a trajectory between an initial and a stationary point on the surface σ_a ; or 2) minimizing the amount of entropy produced during this evolution. We also question whether the fastest dissipation principle refers to minimizing the time necessary for a system to go from an initial state to a stationary state. These conjectures are tested for a near-equilibrium system with 2 coupled reactions, .

Références:

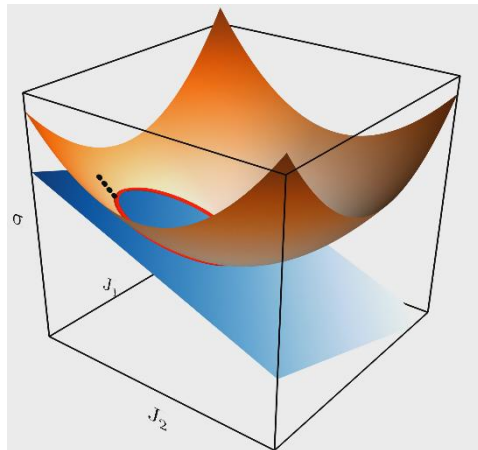
Martyushev, L.M.; Seleznev, V.D., 2006. Maximum entropy production principle in physics, chemistry and biology, Physics Reports 426, 1-45.

Moroz, A., 2008. On a variational formulation of the maximum energy dissipation principle for non-equilibrium chemical thermodynamics, Chemical Physics Letters 457, 448-452.

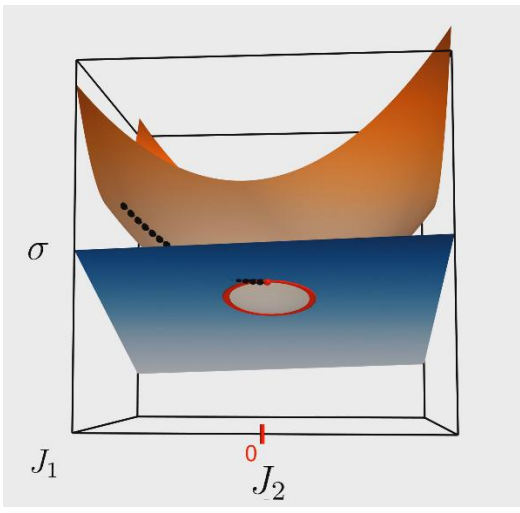




Ziegler's MaxEP principle defines the state of a system for given forces X_1 and X_2 .



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



At stationary state ($J_2 = 0$), the system satisfies MinEP. MinEP is a natural consequence of the application of MaxEP throughout the evolution of the system.