

Extremal principles in non-equilibrium thermodynamics *(a nature inspiration)*

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me & myself

Context and motivations

- **Chemical engineering processes are controlled and operated at quasi steady state and with quasi equilibrium hypothesis**
 - long residence time, small driving forces, ...

- **Nature is inspiring:**
 - On one hand
 - Out-of-equilibrium, even far-from-equilibrium operation,
 - Bigger driving forces = bigger transfer flows, faster reactions
 - On the other hand, a dual injunction exist
 - Long time goal survival requires saving material and energy resources
 - Short time adaptation and resilience require quick and energy costly mechanisms

Context and motivations

- **Q1/ Should process evolution follow Nature?**

1. Process irreversibility / out-of-equilibrium ?

- What tells us the Thermodynamics' 2nd law?

» *For a closed isolated system, the process entropy change*

$$dS_i \geq 0$$

- reversible \Leftrightarrow no dissipation

\Leftrightarrow infinite time operation

\Leftrightarrow power $P = \frac{W}{t} \rightarrow 0 \Leftrightarrow$ no outcome

» *Process irreversibility is necessary!*

» *Some of the spent energy will be lost in inaccessible form*

Context and motivations

2. Process evolution

- Dynamic balances

$$\text{mass} \quad \frac{\partial \rho_i}{\partial t} = -\nabla \cdot (\rho_i \mathbf{v}) - \nabla \cdot \mathbf{j}_i + M_i \sum_{j=1}^l \nu_{ij} J_{\tau,j}$$

$$\text{motion} \quad \frac{\partial}{\partial t} (\rho \mathbf{v}) = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) - \nabla P - \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{F}$$

$$\text{energy} \quad \frac{\partial (\rho e)}{\partial t} = -\nabla \cdot (\rho e \mathbf{v}) - \nabla \cdot \mathbf{J}_e$$

$$\text{entropy} \quad \frac{\partial (\rho s)}{\partial t} = -\nabla \cdot (\rho s \mathbf{v}) - \nabla \cdot \mathbf{J}_s + \sigma$$

$$\frac{\partial \gamma}{\partial t} = -\nabla \cdot (J_\gamma + \gamma \mathbf{v}) + \mathcal{R}_{\gamma,t} + \sigma_\gamma$$

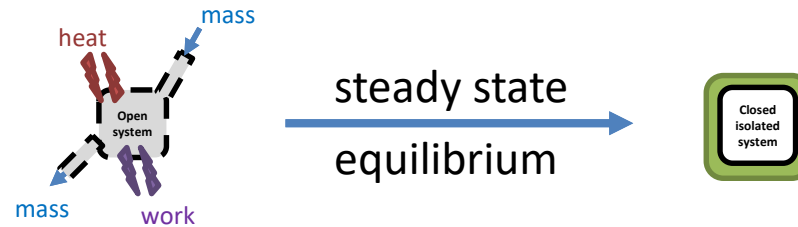
reversible

irreversible

- Q2/ Should σ_γ the irreversible dissipative contribution to dynamics follow a universal thermodynamic extremum principle?

Process at equilibrium

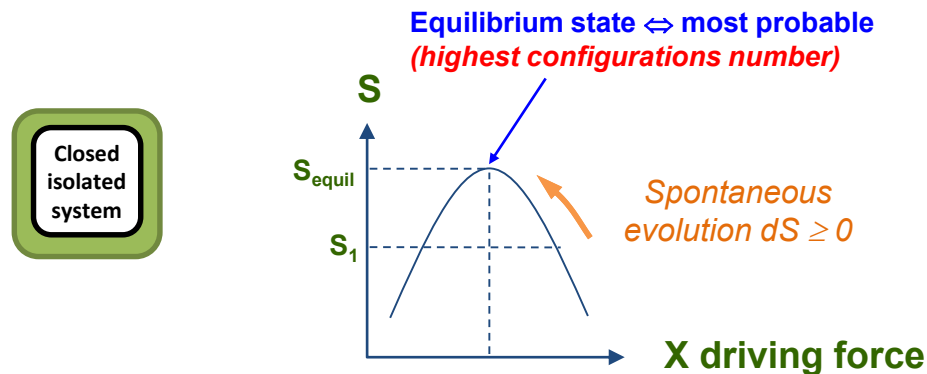
- Chemical engineering processes are controlled and operated at quasi steady state and with quasi equilibrium hypothesis



- Extremal principle at equilibrium

– Thermodynamics' 2nd law

- Either $dS_i \geq 0$ or $\sigma = \frac{dS_i}{dt} \geq 0$
- For a closed isolated system, entropy is maximal at equilibrium



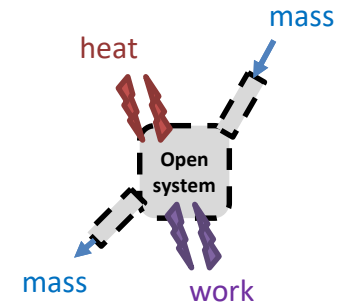
Process out of equilibrium

- **Non-equilibrium thermodynamics**

- Total entropy change,

$$\frac{dS_{total}}{dt} = \frac{dS_e}{dt} + \frac{dS_i}{dt}$$

Internal contribution: dS_i
External contribution: dS_e



- Entropy production $dS_i/dt = \sigma$,

- From balances:

$$\sigma = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) - \frac{1}{T} \sum_{i=1}^n \mathbf{j}_i \cdot \left[T \nabla \left(\frac{\mu_i}{T} \right) - \mathbf{F}_i \right] - \frac{1}{T} \boldsymbol{\tau} : (\nabla \mathbf{v}) + \frac{1}{T} \sum_{j=1}^l A_j J_{rj} \geq 0$$

$$\frac{dS_i}{dt} = \sum_k J_k X_k = \sigma$$

↗ Flux (extensive) e.g. heat transfer
↘ Driving force (intensive) e.g. $\Delta(1/T)$

- Thermodynamics' 2nd law,

$$\sigma \geq 0$$

Process out of equilibrium but near equilibrium

Onsager's phenomenological linear relations

- **e.g. thermodiffusion**

- heat & mass transfer coupling

Fourier \leftarrow $\overline{\quad}$ $\overline{\quad}$ \rightarrow Dufour

$$J_q = -\lambda \nabla T - DQ \nabla c$$
$$J_i = -D \nabla c - c D_T \nabla T$$

Fick \leftarrow $\overline{\quad}$ $\overline{\quad}$ \rightarrow Soret

λ = heat conduction coeff.

D = diffusion coeff.

D_T = thermal diffusion coeff.

- **e.g. membrane reverse osmosis**

- hydrostatic & osmotic pressure coupling

$$J_v = L_p (\nabla P - \sigma_r (\nabla \Pi))$$
$$J_s = c_{s,av} (1 - \sigma_r) J_v + \omega (\nabla \Pi)$$

σ_r = reflection coeff.

ω = solute permeability coeff.

L_p = mechanical filtration coeff.

Process out of equilibrium

Onsager's phenomenological linear relations

- **e.g. thermodiffusion**
 - heat & mass transfer coupling
- **e.g. membrane reverse osmosis**
 - hydrostatic & osmotic pressure

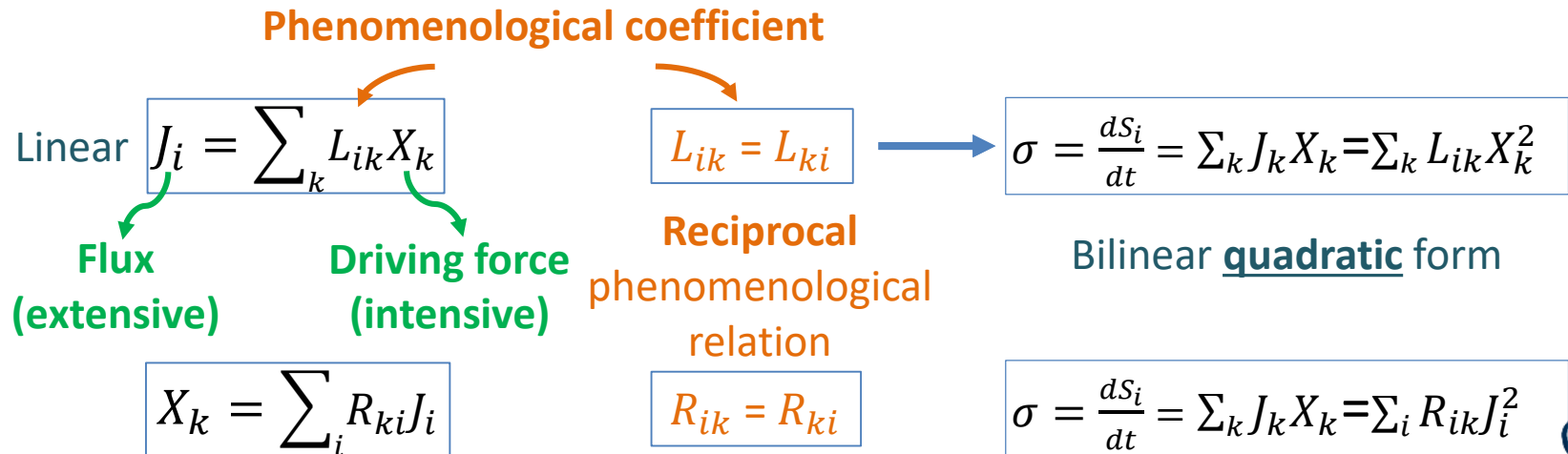
$$\begin{aligned} J_q &= -\lambda \nabla T - DQ \nabla c \\ J_i &= -D \nabla c - c D_T \nabla T \end{aligned}$$

$$\begin{aligned} J_q &= L_{qq} \nabla(1/T) + L_{qi} \nabla(-\mu_i/T) \\ J_i &= L_{iq} \nabla(1/T) + L_{ii} \nabla(-\mu_i/T) \end{aligned}$$

$$\begin{aligned} J_v &= L_{pp} (\nabla P - \nabla \Pi) + L_{pd} (\nabla \Pi / c_s) \\ J_s &= L_{dp} (\nabla P - \nabla \Pi) + L_{dd} (\nabla \Pi / c_s) \end{aligned}$$

• Onsager's relations in 1931

- Linear non-equilibrium thermodynamics



Process out-of-equilibrium

Entropy Production: Prigogine's minEP

- **Prigogine's minEP (1947, 1962)**

- 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 stationary state.

- stationary state \Rightarrow null fluxes

$$J_m = 0 \Leftrightarrow \frac{\partial \sigma}{\partial X_m} = 0, \quad m = k + 1, k + 2, \dots, n$$

- Since the bilinear quadratic entropy production $\sigma = \sum_i \sum_j L_{ij} X_i X_j$ is definite positive, the extremum is a minimum

- NB: stationary state does not mean equilibrium state:

- if at least one of the given fixed forces is at a value different from 0, then the system will always be out of equilibrium.

Process out-of-equilibrium

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- **Minimizing work in processes \Leftrightarrow MinEP under constraints**

- See Kjelstrup et al., Non-equilibrium thermodynamics for engineers. World scientific 2017

Process out-of-equilibrium

Entropy Production: Ziegler's maxEP

- Ziegler proposed a generalization of Onsager's reciprocal relations for far-from-equilibrium systems (1958, 1968).

- Solution

- From $\sigma = \sum_k J_k X_k(\underline{J})$, solve for \underline{J} orthogonality relations at fixed forces using Lagrange maximization

$$\frac{X_i^*(\underline{J})}{\sigma(\underline{J})} \sum_k \frac{\partial \sigma(\underline{J})}{\partial J_k} J_k = \frac{\partial \sigma(\underline{J})}{\partial J_i}$$

- Limitations (Martyushev, 2013, 2014)

- (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, $\sigma_b \equiv \sigma = \underline{J} \cdot \underline{X}$

- NB. Onsager's relations are a consequence of the maxEP principle.

Martyushev L.M. Entropy and Entropy Production: Old Misconceptions and New Breakthroughs *Entropy* 15, 1152-1170, 2013
Martyushev L.M., Seleznev V.D. The restrictions of the maximum entropy production principle. *Physica A* 410, 17-21, 2014

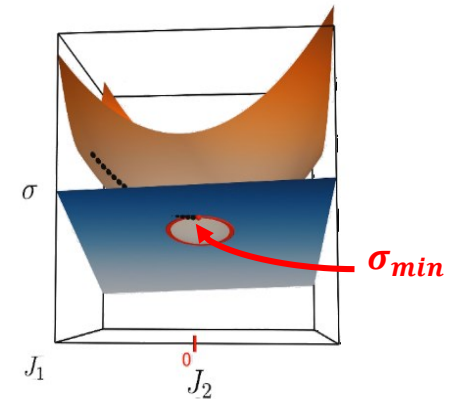
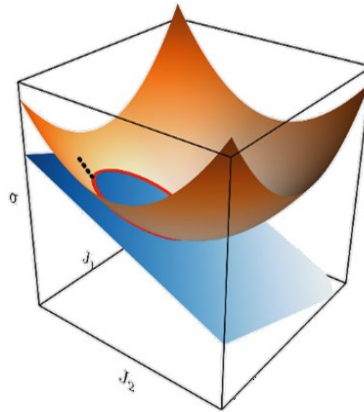
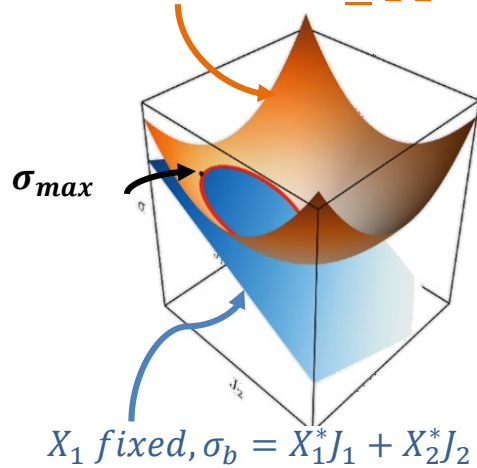
Process out-of-equilibrium

Entropy Production: Prigogine's minEP vs Ziegler's maxEP

- Prigogine's minEP can be deduced from Ziegler's maxEP

» Extra hypothesis: we choose a linear relationship $\underline{X} = \underline{R} \cdot \underline{J}$

$$\sigma_a = \sigma(J_1, J_2) = \underline{R} \cdot \underline{J} \cdot \underline{J}$$



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, as a result of maxEP through system evolution.

- The system maximizes *local* entropy production at every instant (Ziegler), but its evolution in time decreases total entropy production (Prigogine)

More limitations exist!

- **Despite the claim for Ziegler's applicability 'far from equilibrium', $\sigma_a \equiv \sigma(\underline{J})$, one must stay in Onsager's Linear NET framework**
 - e.g. coupled reactions $A \rightleftharpoons B$ and $B \rightleftharpoons C$ (also Bataille et al.(1978))
 - Affinity (reaction driving force $A_r = X_r = -\sum \nu_i \mu_i$):
 - » $A_1 = \mu_A - \mu_B = RT \ln \left[K_1(T) \frac{C_A}{C_B} \right]$ $A_2 = \mu_B - \mu_C = RT \ln \left[K_2(T) \frac{C_B}{C_C} \right]$
 - Reaction rate (flux J_r) is non linear w.r.t. force
 - » $v_1 = k_1^f C_A \left[1 - e\left(-\frac{A_1}{RT}\right) \right]$ $v_2 = k_2^f C_B \left[1 - e\left(-\frac{A_2}{RT}\right) \right]$

Bataille, J., D.G.B. Edelen and J. Kestin, Nonequilibrium Thermodynamics of the Nonlinear Equations of Chemical Kinetics, J. Non-Equilib. Thermodyn., vol. 3, 153-168, 1978.

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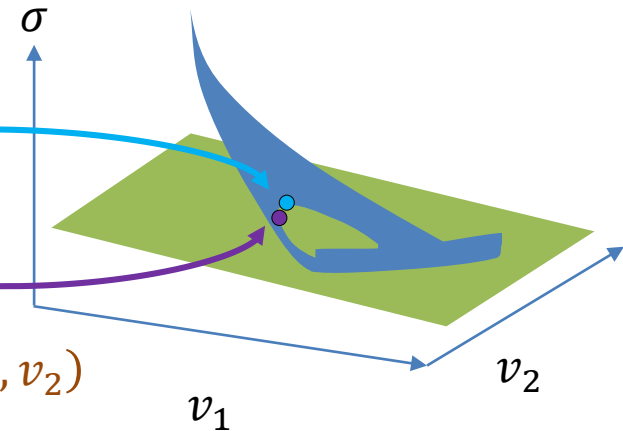
$$A_1 = \mu_A - \mu_B = RT \ln \left[K_1(T) \frac{C_A}{C_B} \right] \quad A_2 = \mu_B - \mu_C = RT \ln \left[K_2(T) \frac{C_B}{C_C} \right]$$

$$v_1 = k_1^f C_A \left[1 - e\left(-\frac{A_1}{RT}\right) \right] \quad v_2 = k_2^f C_B \left[1 - e\left(-\frac{A_2}{RT}\right) \right]$$

- We can apply Ziegler's max EP, \Rightarrow blue point $\max(\sigma)$

$$A_1^* \times \frac{1}{\sigma(v_1, v_2)} \sum_k \frac{\partial \sigma(v_1, v_2)}{\partial J_k} J_k = \frac{\partial \sigma(v_1, v_2)}{\partial J_1}$$

$$A_2^* \times \frac{1}{\sigma(v_1, v_2)} \sum_k \frac{\partial \sigma(v_1, v_2)}{\partial J_k} J_k = \frac{\partial \sigma(v_1, v_2)}{\partial J_2}$$



- We can also compute directly σ , \Rightarrow violet point $\sigma(v_1, v_2)$

1° by expressing $C_A(A_1, A_2)$ and $C_B(A_1, A_2) \Rightarrow v_1(A_1, A_2)$ and $v_2(A_1, A_2)$

2° and we can also get $A_1(v_1, v_2)$ and $A_2(v_1, v_2) \Rightarrow \sigma = v_1 A_1 + v_2 A_2 = \sigma(v_1, v_2)$

- maxEP is inappropriate for a coupled reactions system far from equilibrium

Perspective to be explored

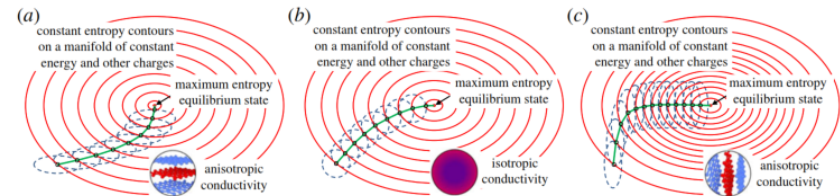
- Beretta's Steepest Entropy Ascent framework from the 80's is a promising generalization far-from-equilibrium

*“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.”*

- Coherent with many advanced nonequilibrium frameworks
- Extension of Onsager's reciprocal laws $L_{ik}=L_{ki}$ and $J_i = \sum_k L_{ik}X_k$ as a non-linear relation valid far from equilibrium within the framework of quasi-equilibrium approximation.

$$J_k = \sum_j L_{jk}(\gamma) X_k$$

$$L_{jk}(\gamma) = \frac{1}{\tau_\gamma} \left(\frac{\delta \hat{a}_j}{\delta \gamma} \Big|_C \Big| G_\gamma^{-1} \Big| \frac{\delta \hat{a}_k}{\delta \gamma} \Big|_C \right)$$



- The metric operator G_γ defines the direction of SEA
- The characteristic time τ_γ defines the evolution rate in such direction.

G.P. Beretta The fourth law of thermodynamics: steepest entropy ascent Philosophical Transactions of the Royal Society A, 378, 20190168, 2020.

G.P. Beretta GP. Steepest entropy ascent model for far-non-equilibrium thermodynamics. Unified implementation of the maximum entropy production principle. Phys. Rev. E 90, 042113, 2014.

Conclusion

- **Prigogine's minEP can be deduced from Ziegler's maxEP (see Martyushev)**
 - The system maximizes *local* entropy production at every instant (Ziegler), but its evolution in time decreases total entropy production (Prigogine)
- **But Ziegler's maxEP principle is not one superior to all others**
 - In addition to limits already discussed in the literature (Martyushev's papers), it is limited to non-equilibrium domain ... near equilibrium
- **In the quest for a thermodynamic driver of system dynamics, we learn that principles apply locally and globally, but are subjected to constraints**

Thank you