New universal Lyapunov functions for nonlinear kinetics

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Outline

1. Relative entropy and divergences
   - Classical relative entropy and H-theorems
   - f-divergences and Rényi–Csiszár–Morimoto H-theorems
   - The most popular examples of $H_h(P\|P^*)$
2. Maximum of quasiequilibrium relative entropies
   - Quasiequilibrium relative entropy
   - New Lyapunov functions
   - Forward–invariant peeling

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Boltzmann–Gibbs-Shannon relative entropy (1872-1948)

For a system with discrete space of states A_i

$$H_{\mathrm{BGS}}(P\|P^*) = \sum_i p_i \left(\ln\left(\frac{p_i}{p_i^*}\right) - 1 \right)$$

where $P = (p_i)$, $P^* = (p_i^*)$ are the positive probability distributions.

Kolmogorov's (master) equation

$q_{ij} = q_{i\leftarrow j} \geq 0$ for $i \neq j$ $(i,j = 1,\dots,n)$

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \sum_{j,j\neq i} (q_{ij}p_j - q_{ji}p_i)$$

With a known positive equilibrium P^*

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \sum_{j,j\neq i} q_{ij}p_j^* \left(\frac{p_j}{p_j^*} - \frac{p_i}{p_i^*}\right)$$

where p_i^* and q_{ij} are connected by the *balance equation*

$$\sum_{j,j\neq i} q_{ij}p_j^* = \left(\sum_{j,j\neq i} q_{ji}\right) p_i^* \quad \text{for all } i = 1,\dots,n$$

Information processing lemma (continuous time)

Information does not increase (in average) due to random manipulations (Shannon 1948).
For a system with positive equilibrium P^*

$$\frac{\mathrm{d}}{\mathrm{d}t}H_{\mathrm{BGS}}(P\|P^*) \leq 0$$

due to master equation

Mass action law

- A_i are components, c_i is concentration of A_i
- $\sum_i \alpha_{ri} A_i \rightleftharpoons \sum_i \beta_{ri} A_i$ – elementary reactions (reversible)
- $w_r^+ = k_r^+ \prod_i c_i^{\alpha_{ri}}$, $w_r^- = k_r^- \prod_i c_i^{\beta_{ri}}$;
- $w_r = w_r^+ - w_r^-$ – the reaction rate
- $\gamma_r = (\gamma_{ri}) = (\beta_{ri} - \alpha_{ri})$ – the stoichiometric vector
- $\dot{c} = \sum_r \gamma_r w_r$ – kinetic equations

Detailed balance and H-theorem (essentially, Boltzmann, 1872)

There exists a positive point of detailed balance:

$$c_i^* > 0, \forall r \;\; w_r^+(c^*) = w_r^-(c^*)$$

Then for all positive c

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_i c_i\left(\ln\left(\frac{c_i}{c_i^*}\right)-1\right)$$
$$= -\sum_r (w_r^+ - w_r^-)(\ln w_r^+ - \ln w_r^-) \le 0$$

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f-divergences

For any convex function $h(x)$ defined on the open ($x > 0$) or closed $x \geq 0$ semi-axis

$$\boxed{H_h(p) = H_h(P\|P^*) = \sum_i p_i^* h\left(\frac{p_i}{p_i^*}\right)}$$

where $P = (p_i)$ is a probability distribution, P^* is an equilibrium distribution.
Rényi (1960) Csiszár (1963), and Morimoto (1963) proved the information processing lemma (H-theorem) for these functions and Markov chains.

Rényi–Csiszár–Morimoto H-theorem

Due to Master equation with the positive equilibrium P^*

$$\frac{\mathrm{d}H_h(p)}{\mathrm{d}t} = \sum_{l,j,j\neq l} h'\left(\frac{p_j}{p_j^*}\right) q_{jl} p_l^* \left(\frac{p_l}{p_l^*} - \frac{p_j}{p_j^*}\right)$$

$$= \sum_{i,j,j\neq i} q_{ij} p_j^* \left[h\left(\frac{p_i}{p_i^*}\right) - h\left(\frac{p_j}{p_j^*}\right) + h'\left(\frac{p_i}{p_i^*}\right)\left(\frac{p_j}{p_j^*} - \frac{p_i}{p_i^*}\right)\right] \leq 0$$

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Hartley & BGS

- $h(x)$ is the step function, $h(x) = 0$ if $x = 0$ and $h(x) = -1$ if $x > 0$.

$$H_h(P\|P^*) = -\sum_{i,\ p_i>0} 1\,.$$

(the Hartley entropy);

- $h = |x - 1|$,

$$H_h(P\|P^*) = \sum_i |p_i - p_i^*|\,;$$

(the l_1-distance between P and P^*);

- $h = x \ln x$,

$$H_h(P\|P^*) = \sum_i p_i \ln\left(\frac{p_i}{p_i^*}\right) = D_{\mathrm{KL}}(P\|P^*)\,;$$

(the relative Boltzmann–Gibbs–Shannon (BGS) entropy);

Burg & Fisher

- $h = -\ln x$,

$$H_h(P\|P^*) = -\sum_i p_i^* \ln\left(\frac{p_i}{p_i^*}\right) = H_{\mathrm{BGS}}(P^*\|P)\,;$$

(the relative Burg entropy);

- $h = \frac{(x-1)^2}{2}$,

$$H_h(P\|P^*) = \frac{1}{2}\sum_i \frac{(p_i - p_i^*)^2}{p_i^*} = H_2(P\|P^*)\,;$$

(the quadratic approximation of the relative Botzmann–Gibbs-Shannon entropy);

Cressie–Read (CR) family

- $h = \frac{x(x^\lambda - 1)}{\lambda(\lambda+1)}$

$$H_h(P\|P^*) = \frac{1}{\lambda(\lambda+1)} \sum_i p_i \left[\left(\frac{p_i}{p_i^*} \right)^\lambda - 1 \right] ;$$

(the Cressie–Read (CR) family).
If $\lambda \to 0$ then $H_{\mathrm{CR}\ \lambda} \to H_{\mathrm{BGS}}$,
if $\lambda \to -1$ then $H_{\mathrm{CR}\ \lambda} \to H_{\mathrm{Burg}}$;

-

$$H_{\mathrm{CR}\ \infty}(P\|P^*) = \max_i \left\{ \frac{p_i}{p_i^*} \right\} - 1 ;$$

$$H_{\mathrm{CR}\ -\infty}(P\|P^*) = \max_i \left\{ \frac{p_i^*}{p_i} \right\} - 1 .$$

Tsallis

- $h = \frac{(x^\alpha - x)}{\alpha - 1}$, $\alpha > 0$,

$$H_h(P\|P^*) = \frac{1}{\alpha - 1} \sum_i p_i \left[\left(\frac{p_i}{p_i^*} \right)^{\alpha - 1} - 1 \right] .$$

(the Tsallis relative entropy).

The puzzle of nonlinear systems

- For the linear systems many Lyapunov functionals are known in the explicit form,
- On the contrary, for the nonlinear MAL systems with detailed balance we, typically, know the only Lyapunov function H_{BGS};
- The situation looks rather intriguing and challenging: for every finite reaction mechanism with detailed balance there **should be** many Lyapunov functionals, but we cannot construct them.
- We present a general procedure for the construction of a family of new Lyapunov functionals from H_{BGS} for nonlinear MAL kinetics and a given reaction mechanism.
- There is no chance to find many Lyapunov functions for *all* nonlinear mechanisms together.

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Quasiequilibrium

Let

$$H(c) = H_{\mathrm{BGS}}(c) = \sum_i c_i \left(\ln \left(\frac{c_i}{c_i^*} \right) - 1 \right)$$

For every linear subspace $E \subset \mathbb{R}^n$ and a given concentration vector $c^0 \in \mathbb{R}^n_+$ the *quasiequilibrium composition* is the conditional minimizer of H:

$$c_E^*(c^0) = \operatorname*{argmin}_{c \in (c^0 + E) \cap \mathbb{R}^n_+} H(c)$$

The *quasiequilibrium divergence* is the value of H at the quasiequilibrium:

$$H_E^*(c^0) = \min_{c \in (c^0 + E) \cap \mathbb{R}^n_+} H(c)$$

Properties of quasiequilibria

- H is strongly convex and ∇H has logarithmic singularity at $c_i \to 0$.
- Therefore, for a positive vector $c^0 \in \mathbb{R}^n_+$ and a given subspace $E \subset \mathbb{R}^n$ the quasiequilibrium composition $c^*_E(c^0)$ is also positive.
- $$H^*_E(c^0) \leq H(c^0)$$

  and this inequality turns into the equality if and only if c^0 is the quasiequilibrium $c^0 = c^*_E(c^0)$.

- Such quasiequilibrium “entropies” were discussed by Jaynes (1965).
- He considered the quasiequilibrium H-function as the Boltzmann H-function H_{B} in contrast to the original Gibbs H-function, H_{G}.
- The Gibbs H-function is defined for the distributions on the phase space of the mechanical systems. The Boltzmann function is a conditional minimum of the Gibbs function, therefore the Jaynes inequality holds

$$H_{\mathrm{B}} \leq H_{\mathrm{G}}$$

- These functions are intensively used in the discussion of time arrow.
- In the theory of information, quasiequilibrium was studied in detail under the name *information projection*.

- Consider the reversible reaction mechanism with the set of the stoichiometric vectors Υ.
- For each $\Gamma \subset \Upsilon$ we can take $E = \mathrm{Span}(\Gamma)$ and define the quasiequilibrium.
- Let $\mathcal{E}_\Upsilon$ be the set of all subspaces of the form $E = \mathrm{Span}(\Gamma)$ ($\Gamma \subset \Upsilon$).
- $\mathcal{E}_\Upsilon^k$ is the set of k-dimensional subspaces from $\mathcal{E}_\Upsilon$ for each k.
- Define $H_\Upsilon^{k,\max}$ for each dimension $k = 0, \ldots, \mathrm{rank}(\Upsilon)$: $H_\Upsilon^{0,\max} = H$, and for $k > 0$

$$\boxed{H_\Upsilon^{k,\max}(c) = \max_{E \in \mathcal{E}_\Upsilon^k} H_E^*(c)}$$

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$H^{1,\max}$

$$H_{\Upsilon}^{1,\max}(c^0) = \max_{\gamma\in\Upsilon}\left\{\min_{c\in(c^0+\gamma\mathbb{R})\cap\mathbb{R}^n_+} H(c)\right\}$$

$H_{\Upsilon}^{1,\max}(c)$ is a Lyapunov function in $\mathbb{R}^n_+$ for all MAL systems with the given equilibrium c^* and detailed balance on the set of stoichiometric vectors $\Gamma \subseteq \Upsilon$.

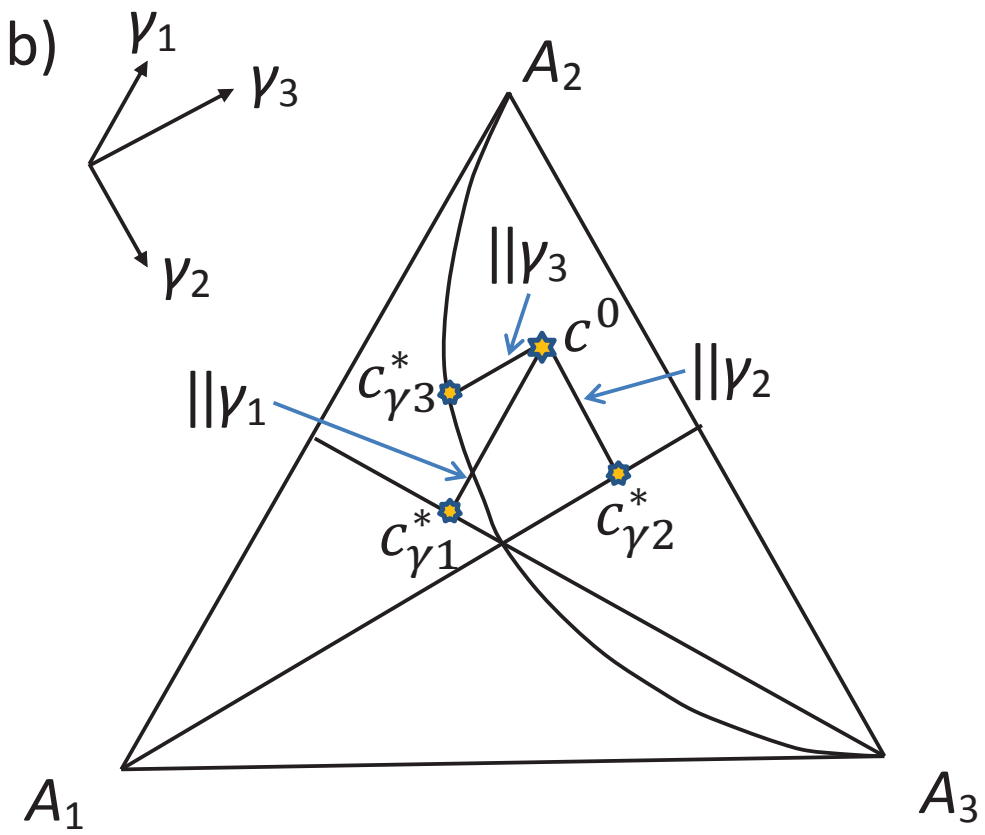
Simple reaction mechanism for example

Consider a simple reaction mechanism:

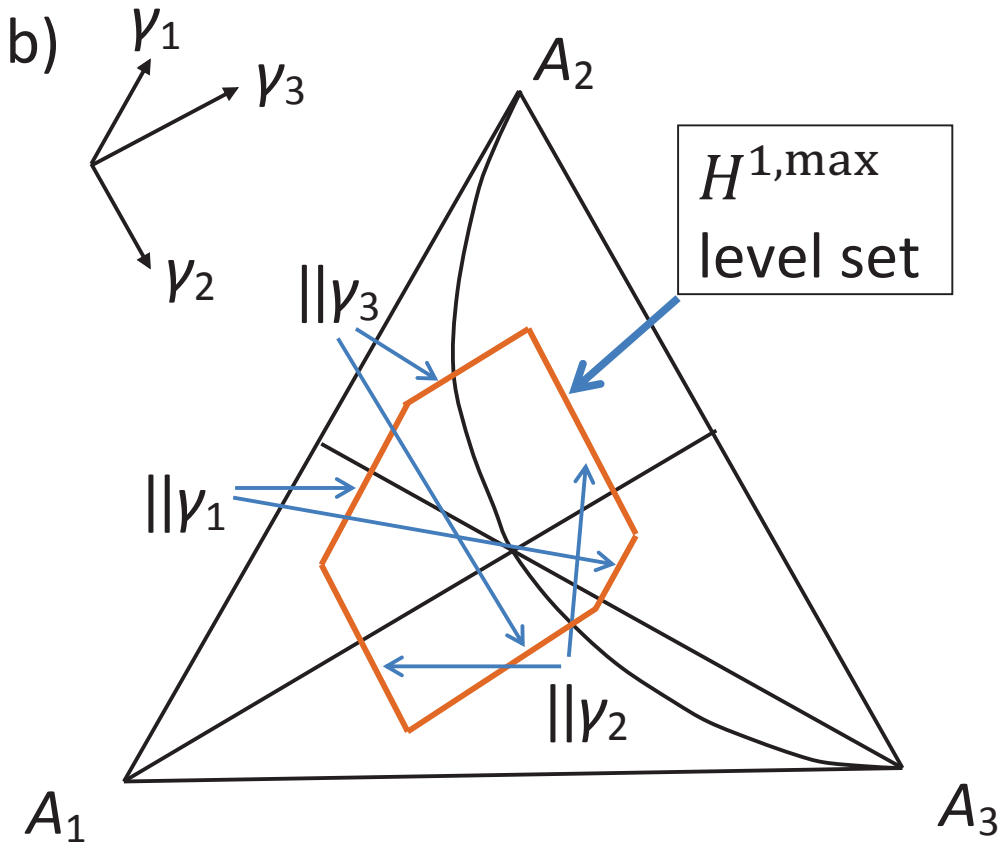
1. $A_1 \rightleftharpoons A_2$,
2. $A_2 \rightleftharpoons A_3$,
3. $2A_1 \rightleftharpoons A_2 + A_3$.

The concentration triangle $c_1 + c_2 + c_3 = b$ is split by the partial equilibria lines into six compartments.

Example: QE states



Example: $H^{1,\max}$ level set



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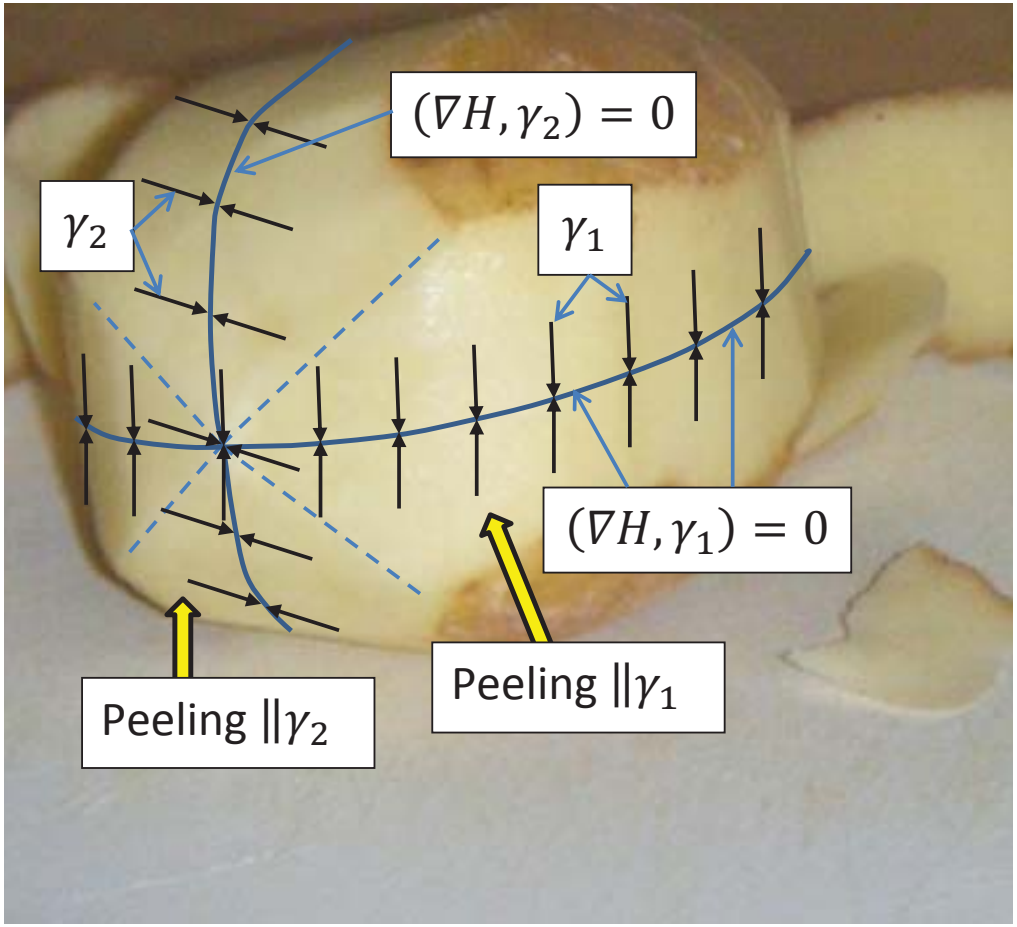
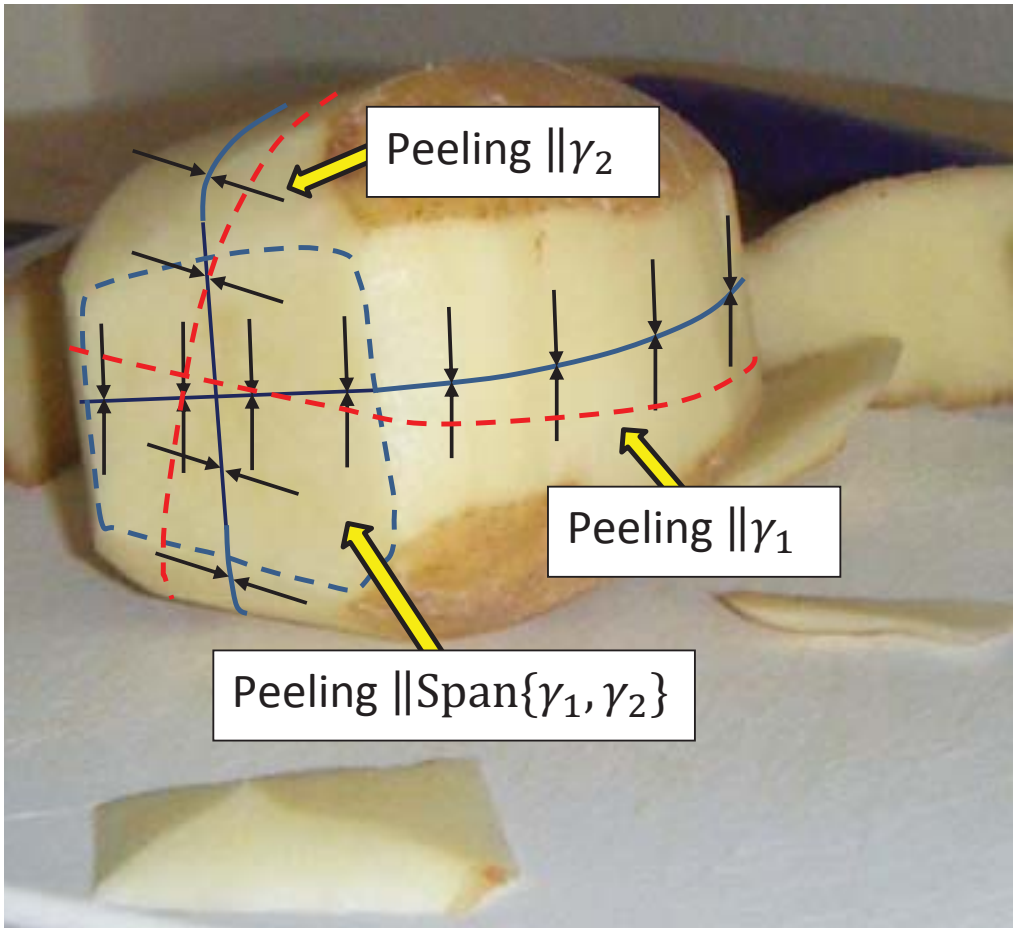
- Let U be a convex compact set of non-negative n-dimensional vectors c and for some $\eta > \min H$ the η-sublevel set of H belongs to U: $\{N \,|\, H(N) \leq \eta\} \subset U$.
- Let $h > \min H$ be the maximal value of such η.
- Select $\varepsilon > 0$. The $\varepsilon > 0$-*peeled* set U is

$$U^{\varepsilon}_{\Upsilon} = U \cap \{N \in \overline{R^{n}_{+}} \,|\, H^{1,max}_{\Upsilon}(N) \leq h - \varepsilon\}$$

- For sufficiently small $\varepsilon > 0$ ($\varepsilon < h - \min H$) this set is non-empty and forward–invariant.

Illustration: forward-invariant peeling





The additional peeling $\|\mathrm{Span}\{\gamma_1, \gamma_2\}$ makes the peeled set forward–invariant with respect to the set of systems with interval reaction rate constants.

Main message

- For every reaction mechanism there exists an infinite family of Lyapunov functions for reaction kinetics that depend on the equilibrium but not in the rate constants.
- These functions are produced by the operations of conditional minimization and maximization from the BGS relative entropy.

References

Just look Gorban in arXiv and references there.