

The Thermodynamic Projector and Model Reduction in Chemical Kinetics

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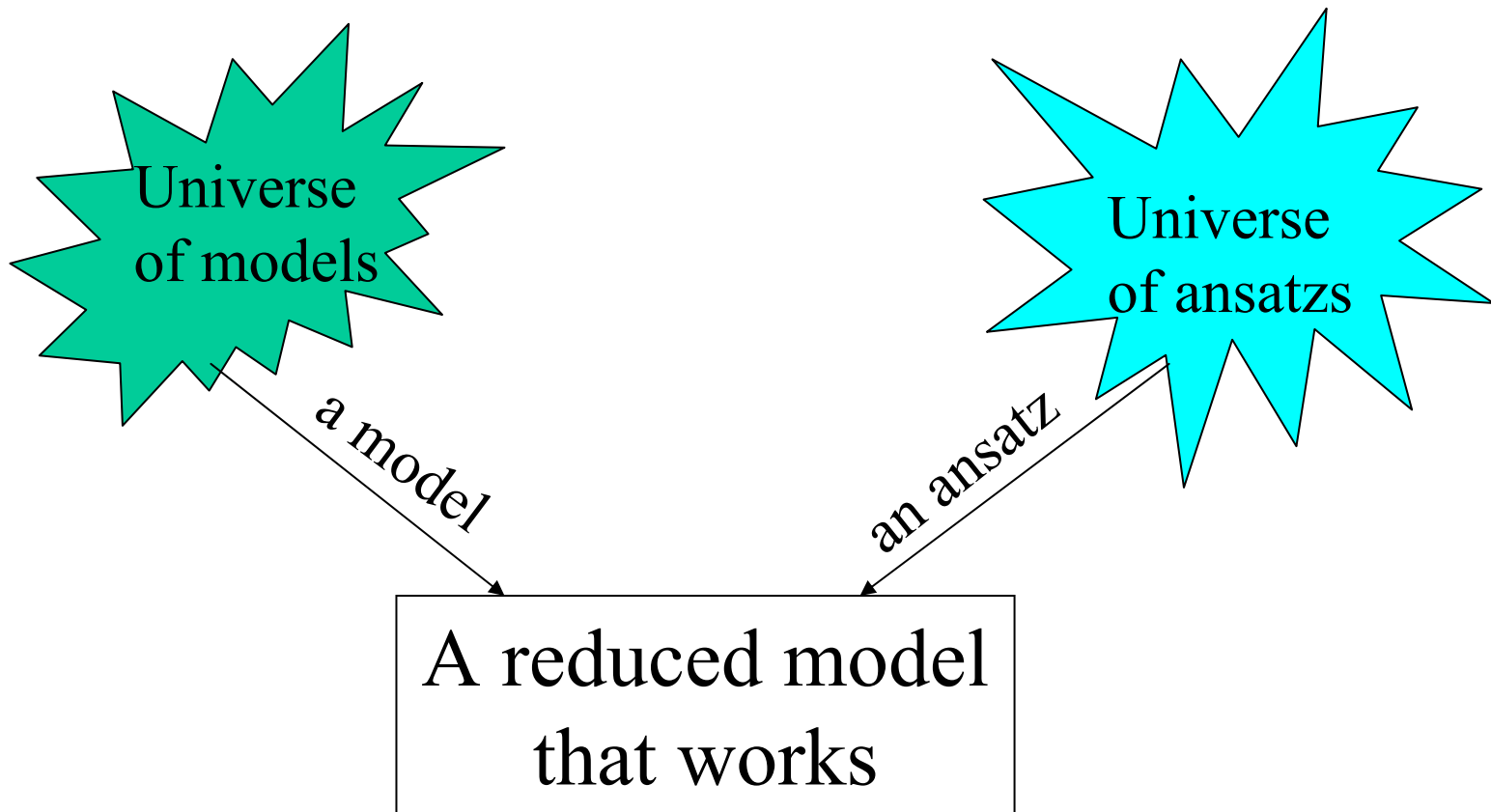
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Plan

- Chemical kinetics – source of ideas about temporal organization
- Model reduction or solution?
- The Second Law and model reduction
- Fast-slow decomposition
- QSS and QE
- Invariance equation
- Entropic inner product
- Entropy gradient in entropic inner product
- The thermodynamic projector
- Uniqueness theorem
- Conclusion

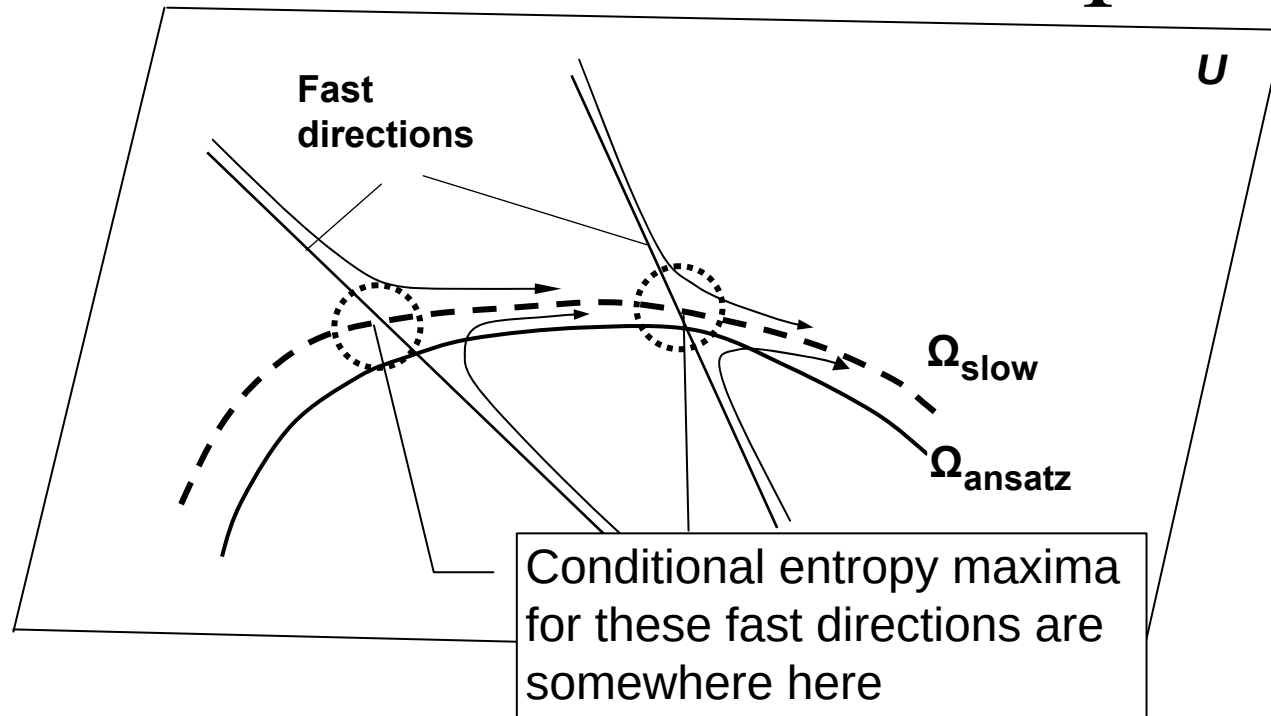
Two Universes of model reduction



The Second Law and model reduction

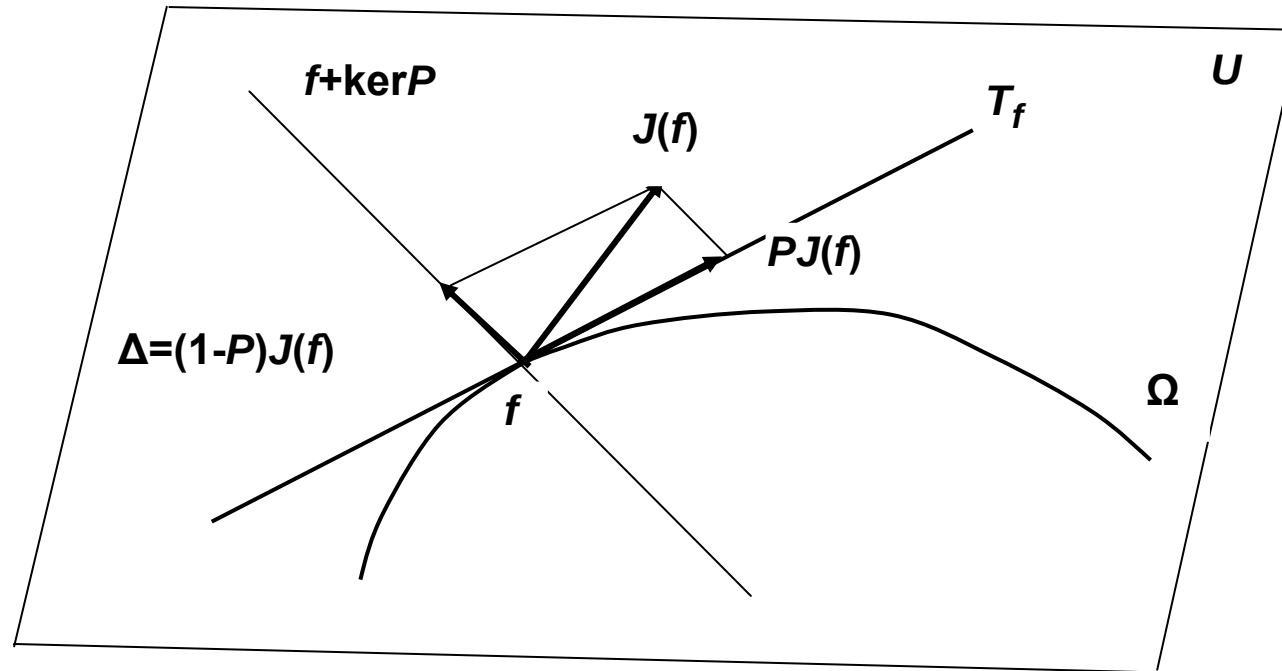
- Entropy of a closed system increases:
 $dS/dt \geq 0$;
- In a open system the entropy production is positive;
- These properties should hold for every model: **all the procedures of model reduction should preserve the sign of entropy production.**

Idea of fast-slow decomposition



Bold dashed line – slow invariant manifold;
bold line – approximate invariant manifold;
several trajectories and correspondent directions
of fast motion are presented schematically.

Geometrical structures of model reduction



- U is the phase space,
- $J(f)$ is the vector field of the system under consideration: $\mathbf{df}/\mathbf{dt} = J(f)$,
- Ω is an ansatz manifold,
- T_f is the tangent space to the manifold Ω at the point f ,
- $PJ(f)$ is the projection of the vector $J(f)$ onto tangent space T_f ,
- $\Delta = (1-P)J(f)$ is the defect of invariance,
- the affine subspace $f + \ker P$ is the plain of fast motions, and Δ belongs to $\ker P$.

Example 1: QSS

R - concentrations of radicals,

C - concentrations of stable components

$$\frac{dR}{dt} = F_R(R, C), \frac{dC}{dt} = F_C(R, C)$$

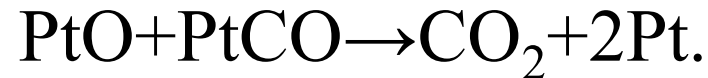
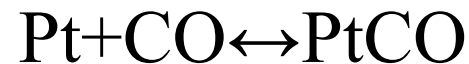
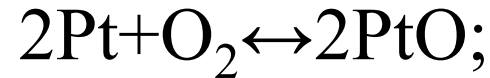
$$\sum_i R_i < B_R; \sum_i C_i < B_C; B_R \ll B_C$$

$$r = R / B_R; c = C / B_C; \tau = t / B_C; \varepsilon = B_R / B_C$$

$$\frac{dr}{d\tau} = \frac{1}{\varepsilon} F_R(B_R r, B_C c), \frac{dc}{d\tau} = F_C(B_R r, B_C c)$$

$$F_R(B_R r, B_C c) = 0 \Rightarrow r = r(c), \frac{dc}{d\tau} = F_C(B_R r(c), B_C c) \quad 7$$

QSS



$$2(k_1^+ [\text{Pt}]^2 [\text{O}_2] - k_1^- [\text{PtO}]^2) = k_3 [\text{PtO}] [\text{PtCO}];$$

$$k_2^+ [\text{Pt}] [\text{CO}] - k_2^- [\text{PtCO}] = k_3 [\text{PtO}] [\text{PtCO}];$$

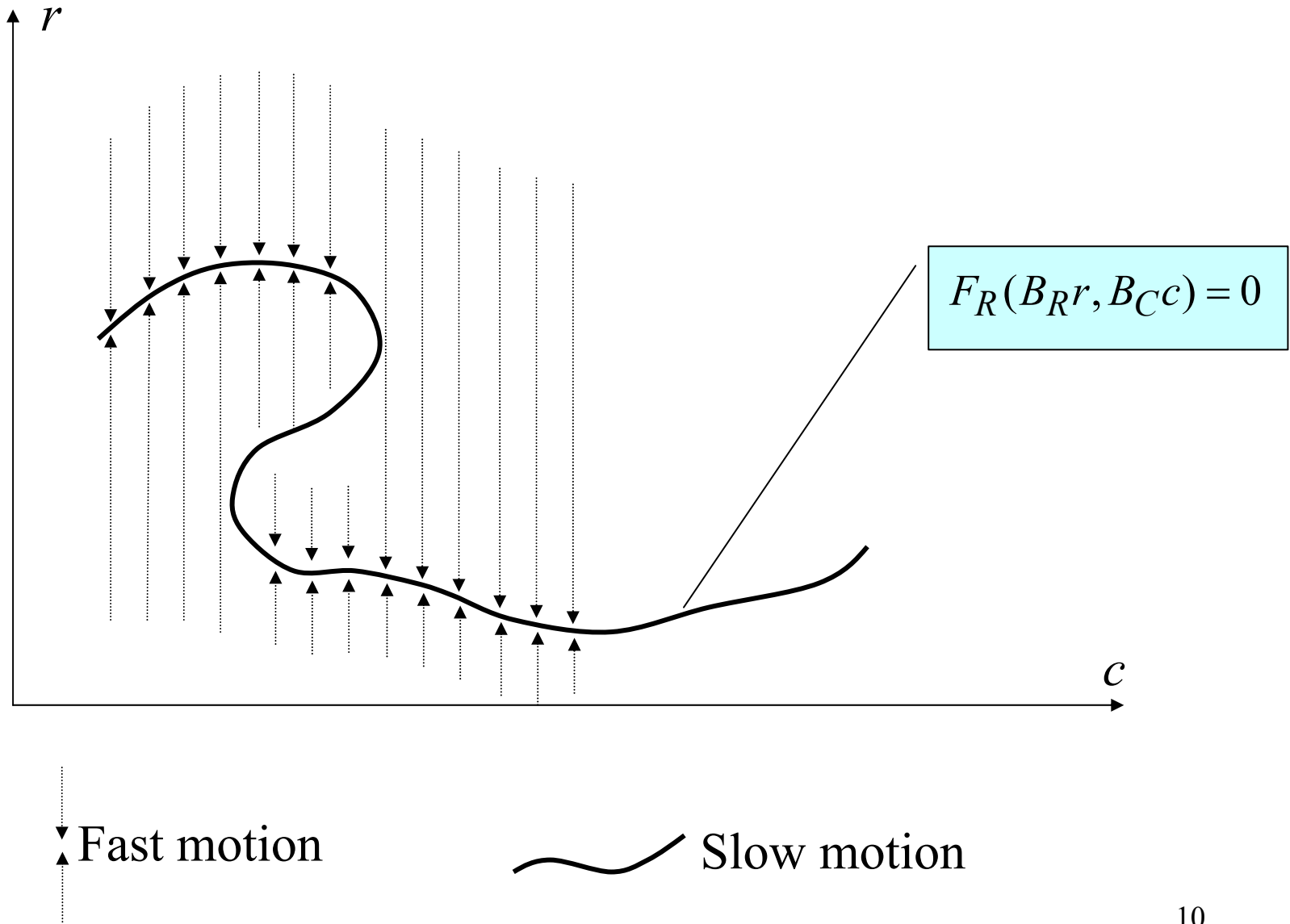
$$[\text{Pt}] + [\text{PtO}] + [\text{PtCO}] = b_{\text{Pt}}$$

A typical mistake

In QSS, dR/dt is not “small,” because in QSS

$$\frac{dR}{dt} = \frac{\partial F_R(R, c)}{\partial c} \frac{dc}{dt}$$

Geometry of QSS



Example 2: QE

$\alpha_{s1}A_1 + \dots + \alpha_{sn}A_n \leftrightarrow \beta_{s1}A_1 + \dots + \beta_{sn}A_n$ - fast reactions,

$\gamma_{si} = \beta_{si} - \alpha_{si}$ - stoichiometric vectors of fast reactions,

$L = \text{Lin}\{\gamma_{si}\}$ - the plain of fast motions,

$\Omega = \{c : \sum_i \mu_i(c) \gamma_{si} = 0 \text{ for all fast reactions}\}$ - QE manifold;

$\mu_i(c)$ - chemical potentials;

$\{m_j\}$ - a basis in orthogonal complement to L ;

$m_j(c) = (m_j, c)$ - slow variables;

$\dot{c} = F_{fast}(c) + F_{slow}(c)$ - kinetic equations;

$$c \in \Omega \left(\sum_i \mu_i(c) \gamma_{si} = 0 \quad \forall s \right), \quad \frac{dm_j(c)}{dt} = (m_j, F_{slow}(c))$$

QE

1. $A \leftrightarrow B$ fast; $\gamma = (-1, 1)$, $\Omega = \{c : c_A = Kc_B\}$, $m(c) = c_A + c_B$,

$$\text{on } \Omega, c_A(m) = \frac{Km}{1+K}, c_B(m) = \frac{m}{1+K},$$

If there are some additional reactions and components
and the initial eqs. for c_A, c_B are

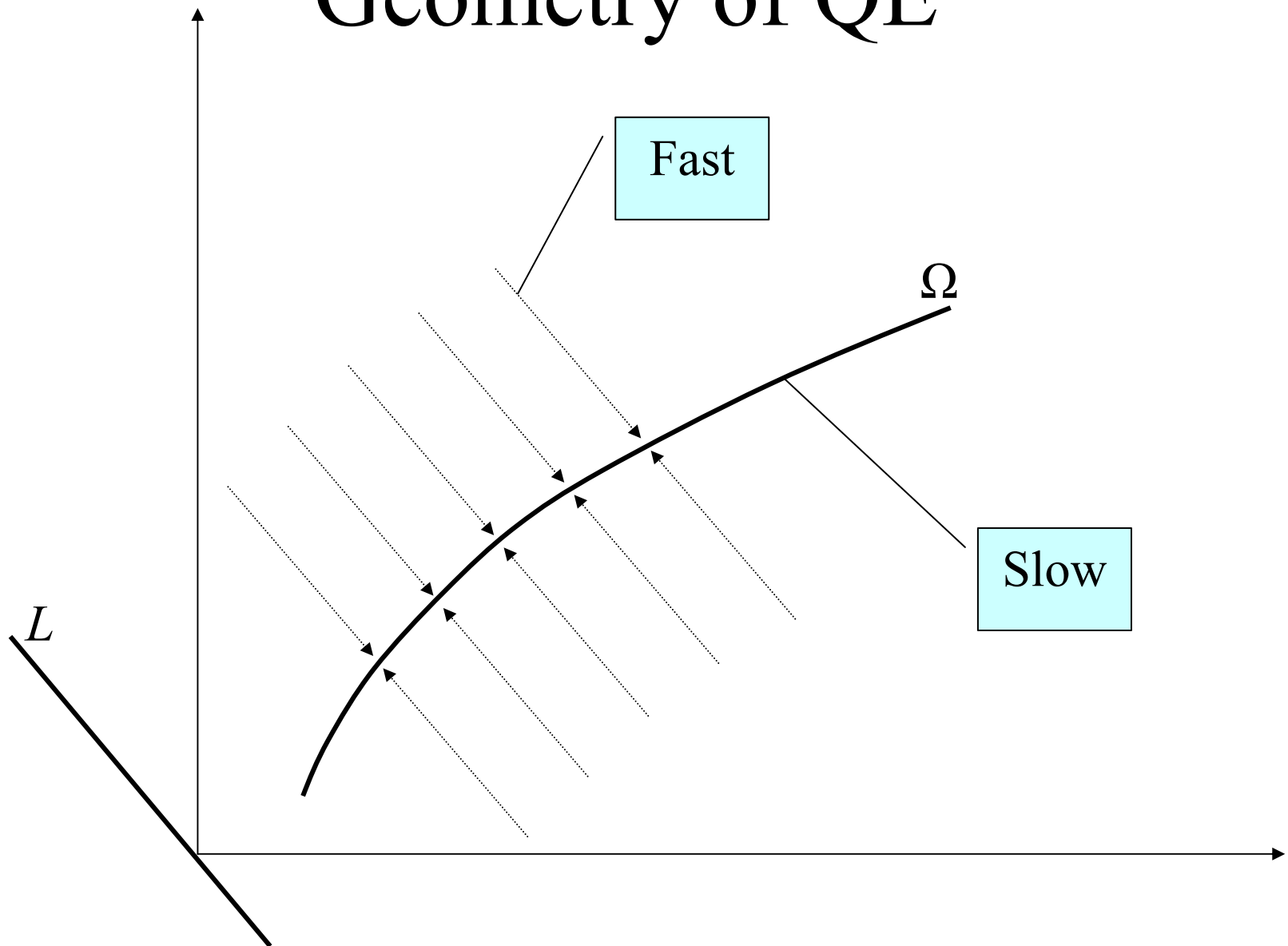
$$\dot{c}_A = F_{A \text{ fast}}(c) + F_{A \text{ slow}}(c), \dot{c}_B = F_{B \text{ fast}}(c) + F_{B \text{ slow}}(c),$$

then the QE eq. is $\dot{m} = F_{A \text{ slow}}(c(m)) + F_{B \text{ slow}}(c(m))$.

2. $A + B \leftrightarrow C$ fast; $\gamma = (-1, -1, 1)$, $\Omega = \{c : c_A c_B = Kc_C\}$,

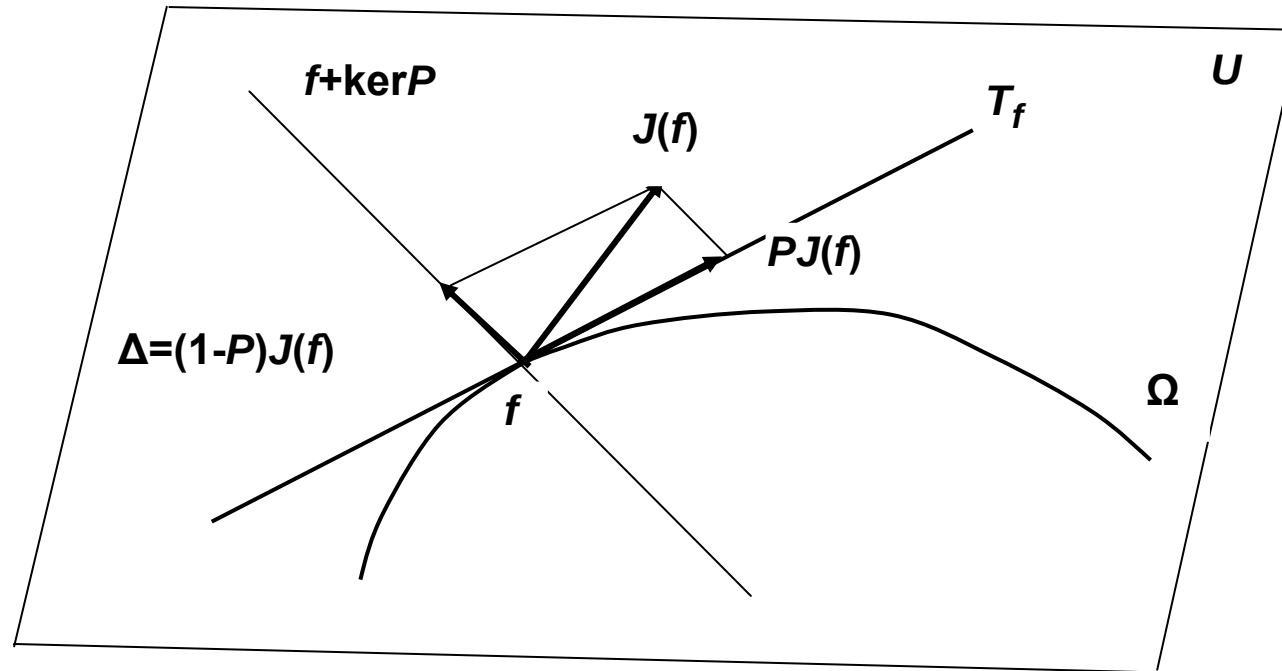
$$m_1(c) = c_A - c_B, m_2(c) = c_A + c_B + 2c_C$$

Geometry of QE



No “fast components,” but some “fast directions”

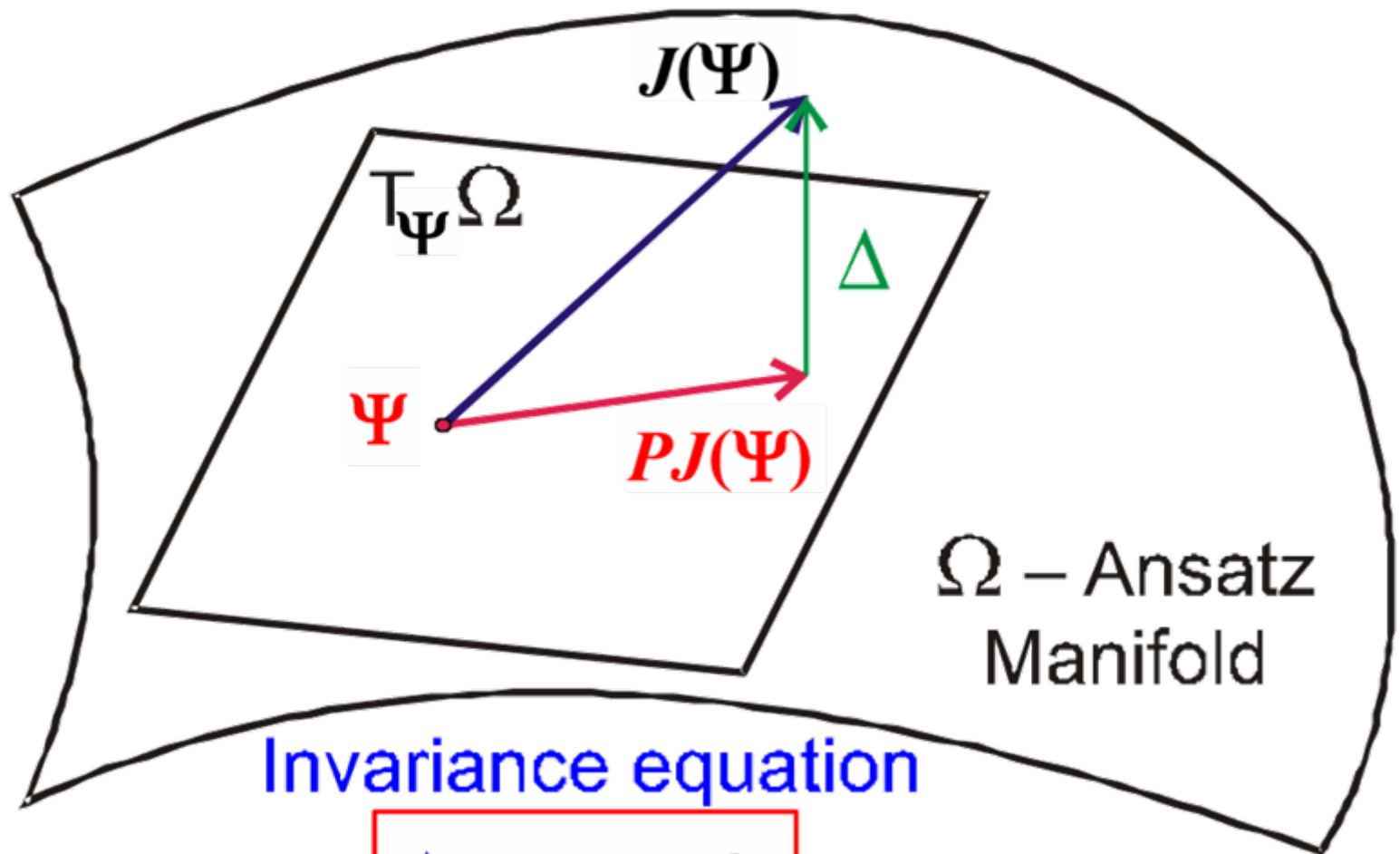
Geometrical structures of model reduction



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Invariance equation

$$d\Psi/dt = J(\Psi)$$



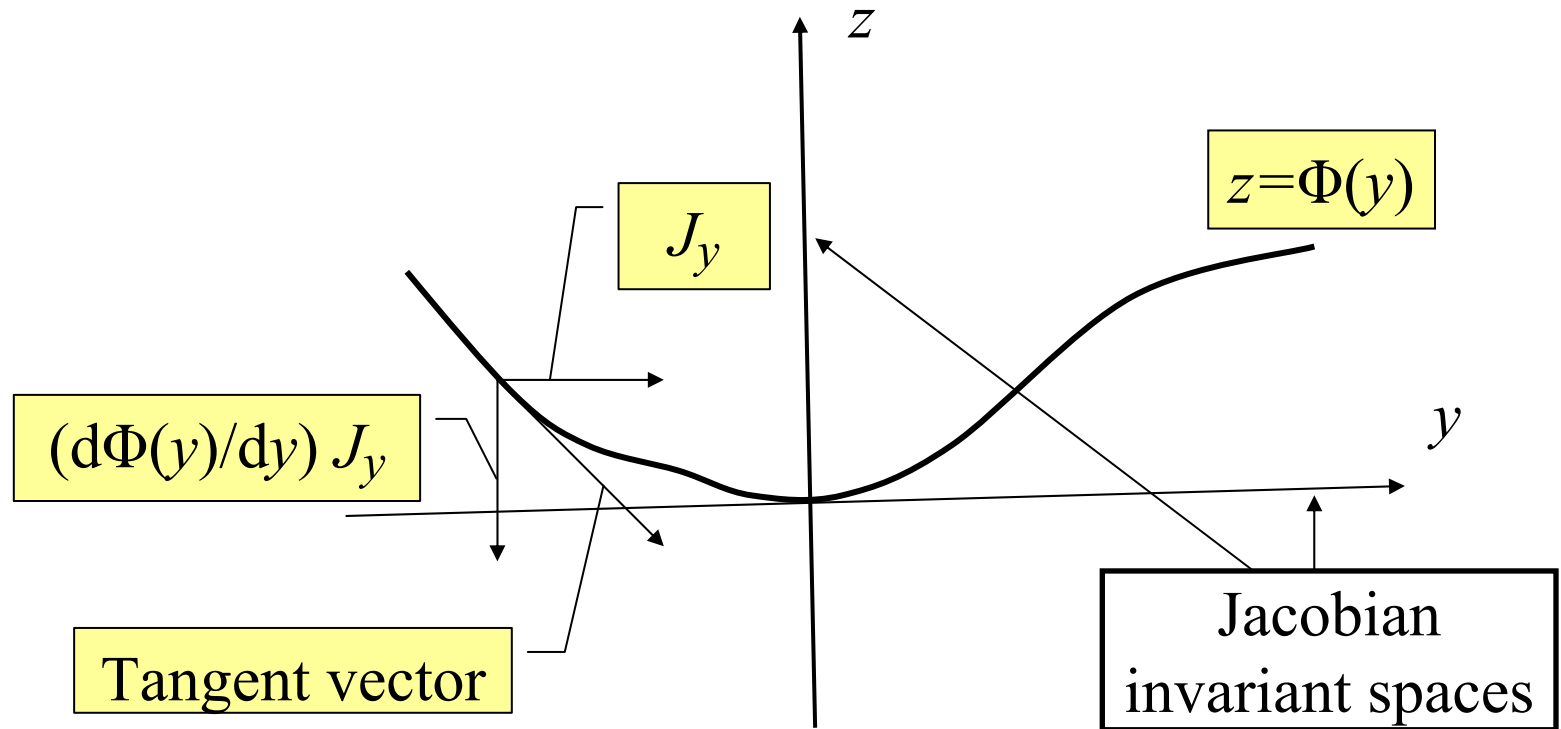
Invariance equation

$$\Delta = J - PJ = 0$$

Methods for Solution

- Taylor expansion near equilibrium (Lyapunov,...)
- Singular perturbation expansion (small parameter) (Chapman-Enskog, Fenichel,...)
- The Newton method (Kolmogorov-Arnold for Hamiltonian systems, Fraser-Roussel, Gorban-Karlin,...)
- Relaxation methods (Foias-Jolly-Kevrekidis-Sell-Titi; Gorban-Karlin,...)

The Lyapunov auxiliary theorem



Invariance equation: on the manifold,
 $(d\Phi(y)/dy) J_y = J_z$

Newton method with incomplete linearization

$$\Delta = 0 \text{ i.e. } (1 - P)J(f) = 0$$

$$\begin{aligned} J(f_{k+1}) &= J(f_k + \delta f_{k+1}) = \\ J(f_k) &+ DJ|_{f_k}(\delta f_{k+1}) + o(\delta f_k) \end{aligned}$$

The equation for one iteration :

$$(1 - P)DJ|_{f_k}(\delta f_{k+1}) = -\Delta_k$$

$$\text{under condition } P\delta f_{k+1} = 0$$

It converges to the **slowest manifold**
(under some technical conditions)

Relaxation method

The equation of motion for immersed manifolds is

$$\frac{d(F(x))}{dt} = (1 - P_{F(x)})J(F(X)) = \Delta(F(X))$$

We are looking for a stable fixed point

The invariance equation is

$$\Delta = 0 \text{ i.e. } (1 - P)J(f) = 0$$

The relaxation method:

$$f_{k+1} = f_k + h\Delta(f_k)$$

The choice of step h : we can project the motion on Δ_k and go ahead until the projection of current Δ on Δ_k becomes 0 (in the linear approximation) – it is the Newton method projected on Δ .

The problem of thermodynamic projector

For any given:

- concave entropy function (functional) S ;
- ansatz manifold Ω which is not tangent to the levels of S

Find a projector $\mathbf{P}$ that projects any vector field $\mathbf{J}$ with $dS/dt \geq 0$ in a vector field on Ω with the same inequality.

Thermodynamic Lyapunov functions for classical conditions

$$U, V = \text{const}, \quad G_{U,V} = -S/k_{\text{B}};$$

$$H, P = \text{const}, \quad G_{H,P} = -S/k_{\text{B}};$$

$$V, T = \text{const}, \quad G_{V,T} = F/k_{\text{B}}T = U/k_{\text{B}}T - S/k_{\text{B}} ;$$

$$P, T = \text{const}, \quad G_{P,T} = G/T = H/k_{\text{B}}T - S/k_{\text{B}} ,$$

where $F = U - TS$ is the free energy

$G = H - TS$ is the free enthalpy

Entropic inner product

$$\langle x, y \rangle_f = - \sum_{i,j} x_i \frac{\partial^2 S(f)}{\partial f_i \partial f_j} y_j$$

$$S(f) = - \sum_i f_i \ln(f_i / f_i^*)$$

$$\langle x, y \rangle_f = \sum_i \frac{x_i y_i}{f_i}$$

Shahshahani metric

$$S(f) = - \int f(z) \ln f(z) dz$$

$$\langle \varphi(z), \psi(z) \rangle_f = \int \frac{\varphi(z) \psi(z)}{f(z)} dz$$

Differential and gradient

Differential (Gato) of a function $S(f)$ at point f is a linear functional $D_f S$ that gives the best approximation of S near f : $S(f+\varepsilon x)=S(f)+\varepsilon D_f S(x)+o(\varepsilon)$ for any vector x .
Definition of differential does not depend on an inner product.

Gradient is a vector that represents the differential by the inner product

$$g = (\text{grad} S)_f \Leftrightarrow (D_f S)(x) = \langle g, x \rangle_f$$

$$\text{or } S(f + \varepsilon x) = S(f) + \varepsilon \langle g, x \rangle_f + o(\varepsilon)$$

Definition of gradient depends on the inner product

Entropy gradient in entropic inner product

$$g = (\text{grad}S)_f \Leftrightarrow (D_f S)(x) = \langle g, x \rangle_f$$

$$\text{or } S(f + \varepsilon x) = S(f) + \varepsilon \langle g, x \rangle_f + o(\varepsilon)$$

Vector $\text{grad}S$ in entropic inner product gives the ***Newtonian direction*** for S (an undergraduate exercise).

The gradient should belong to a subspace of zero balances change: for

$$S(f) = -\int f(z) \ln f(z) dz$$

$$(\text{grad}S)_f = -f \left(\ln f - \int f(z) \ln f(z) dz \right)$$

The thermodynamic projector

The thermodynamic projector $\mathbf{P}$ onto space T_f is

$$P(J) = P^\perp(J) + \frac{(\text{grad}S)_f^\parallel \langle (\text{grad}S)_f^\perp, J \rangle_f}{\langle (\text{grad}S)_f^\parallel, (\text{grad}S)_f^\parallel \rangle_f}$$

Where orthogonality and all gradients are defined in the entropic inner product;

$P^\perp(J)$ is the orthogonal projector onto space T_f

$$(\text{grad}S)_f^\parallel = P^\perp((\text{grad}S)_f)$$

$$(\text{grad}S)_f^\perp = (1 - P^\perp)((\text{grad}S)_f)$$

Uniqueness theorem

The thermodynamic projector is the unique operator which transforms the arbitrary vector field equipped with the given Lyapunov function S into a vector field with the same Lyapunov function (and also this happens on any manifold which is not tangent to the levels of S).

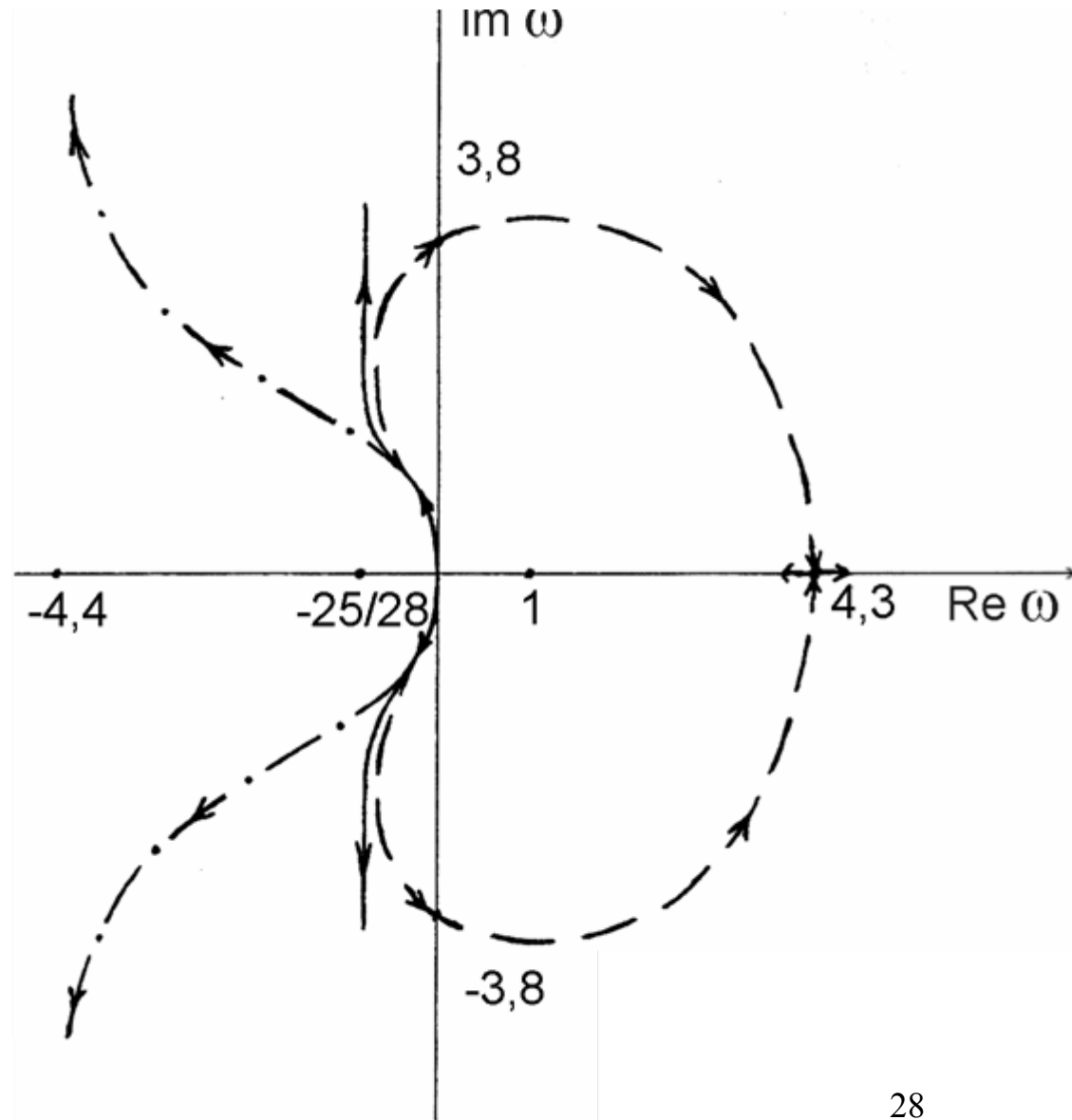
Free lunch

The requirement is: the thermodynamic projector preserves the *sign* of entropy production. As additional consequences from this requirement we have:

- The thermodynamic projector preserves the ***value*** of entropy production (not only the *sign* of it);
- The thermodynamic projector transforms a system with Onsager reciprocity relations into a system with the Onsager reciprocity relations (*it preserves the Onsager relations*).

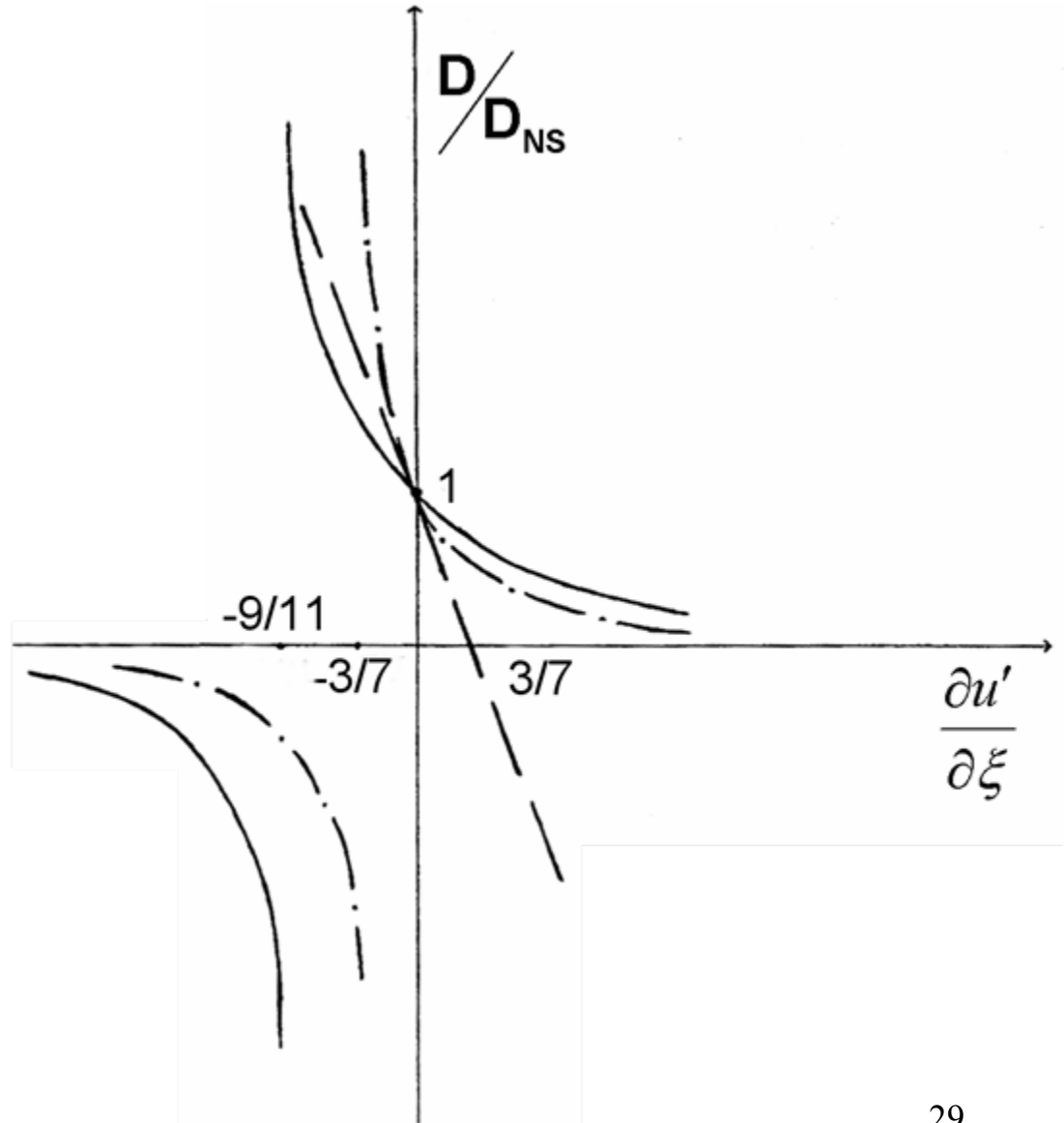
Bobylev instability of Burnett equations

Acoustic dispersion curves for Burnett approximation (dashed line), for first iteration of MIM (solid line), and for regularization of the Burnett approximation via partial summing of the Chapman-Enskog expansion (punctuated dashed line). Arrows indicate an increase of k^2 .



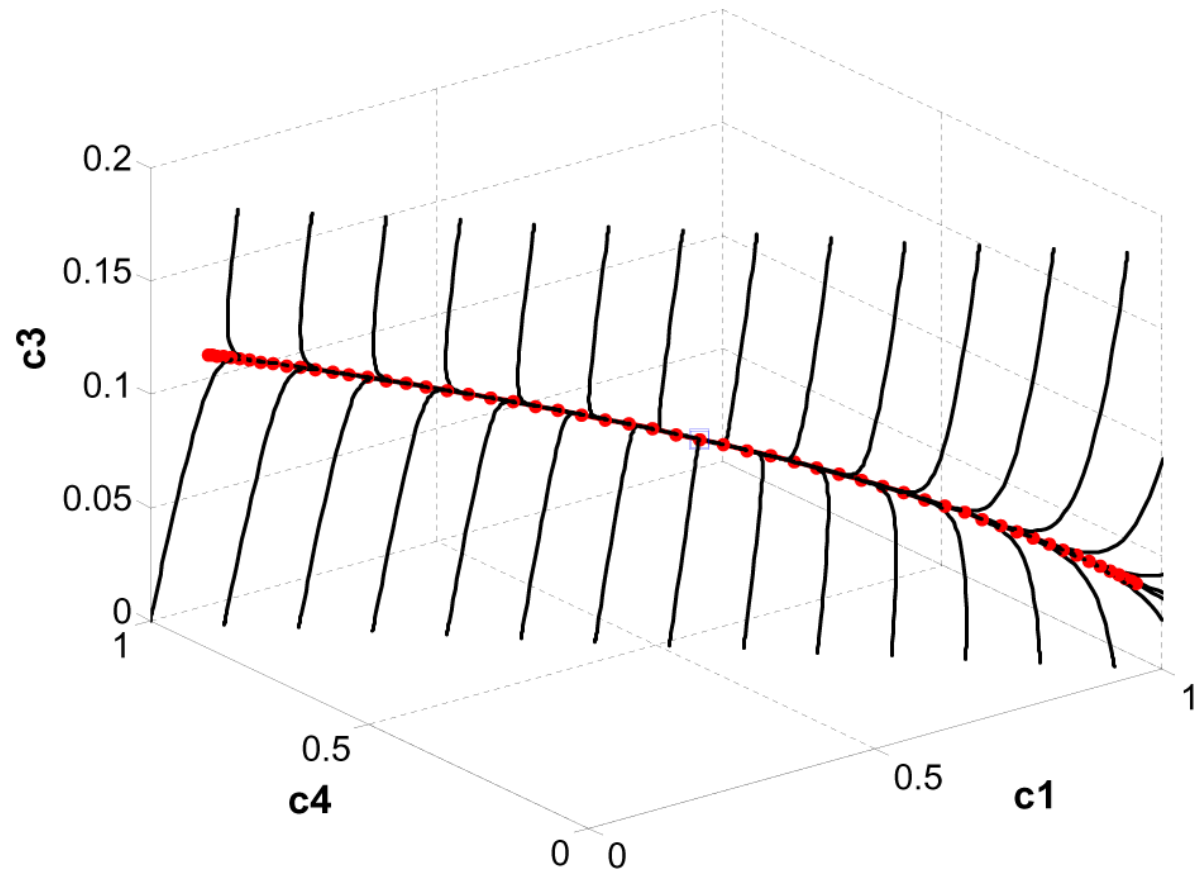
Negative viscosity for Burnett equations

Dependency of viscosity on compression for Burnett approximation (dashed line), for first iteration of MIM (solid line), and for partial summing (punctuated dashed line).



Invariant grid for two-dimensional chemical system: $A1 + A2 \leftrightarrow A3 \leftrightarrow A2 + A4$

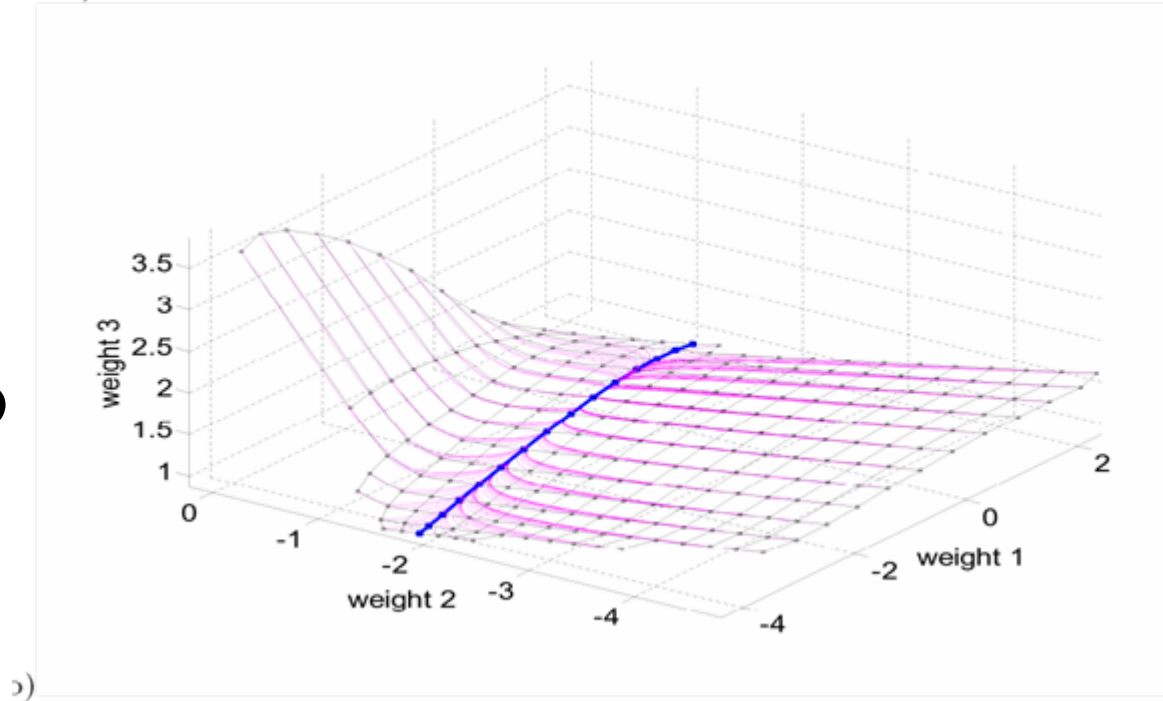
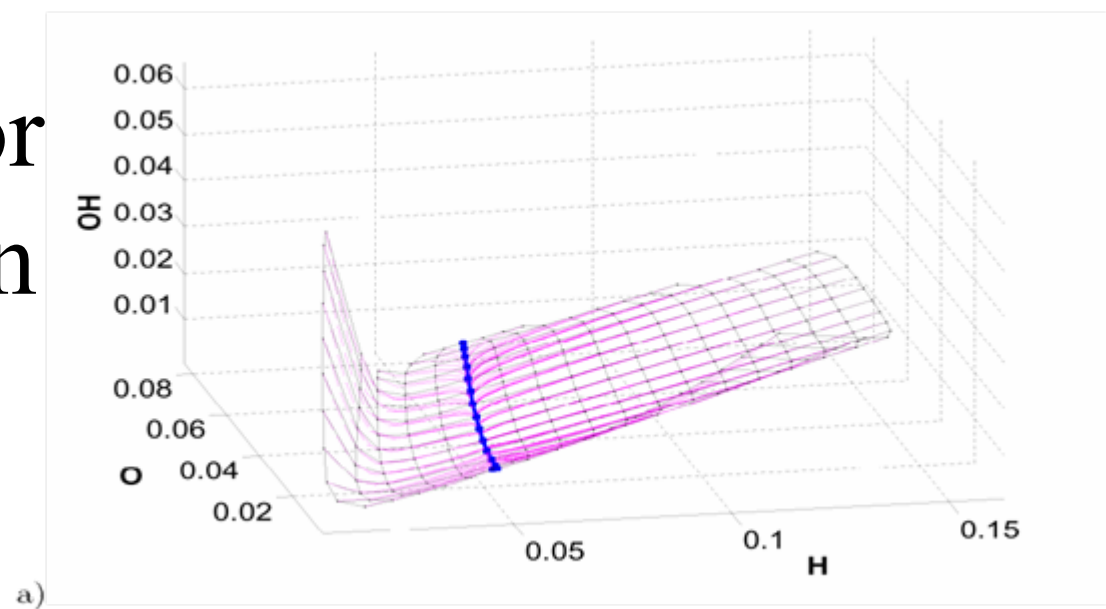
One-dimensional invariant grid (circles)
Projection onto the 3d-space of concentrations $c1$, $c4$, $c3$. The trajectories of the system in the phase space are shown by lines. The equilibrium point is marked by square. The system quickly reaches the grid and further moves along it.



Invariant grid for model Hydrogen burning

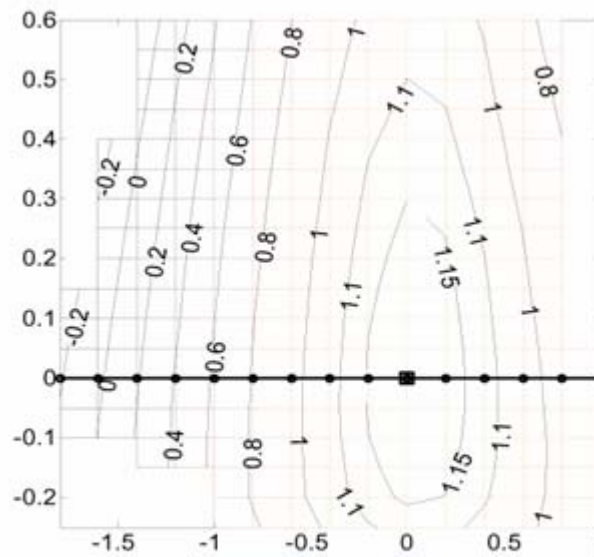
a) Projection onto the 3d-space of C_H , C_O , C_{OH} concentrations.

b) Projection onto the principal 3D-subspace.

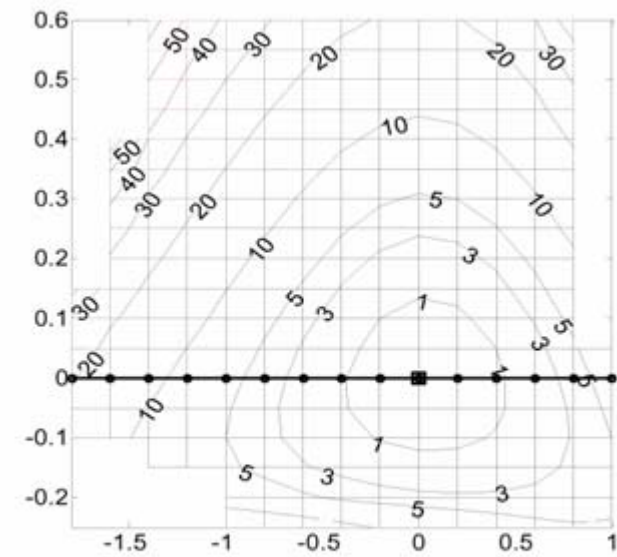


Invariant grid as a screen for visualizing different functions

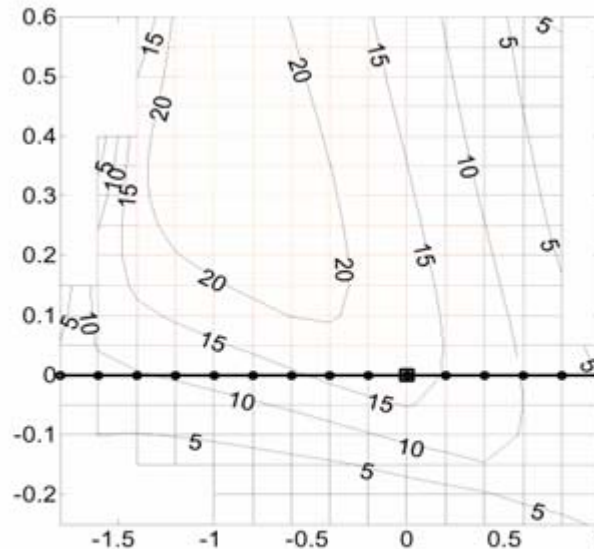
Model
Hydrogen
burning



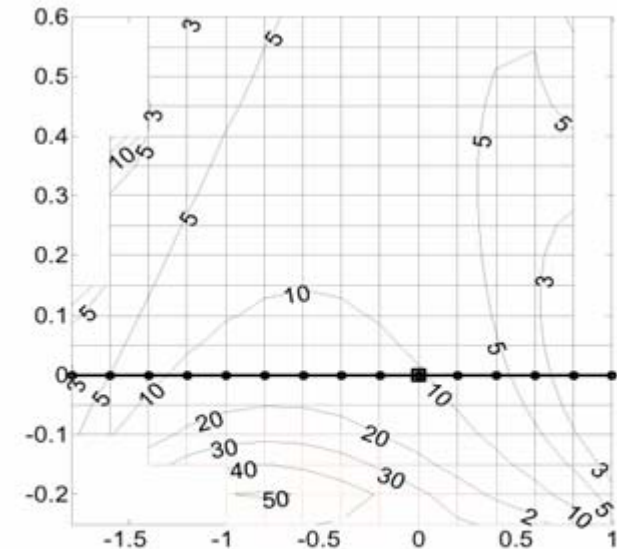
a) Entropy



b) Entropy Production



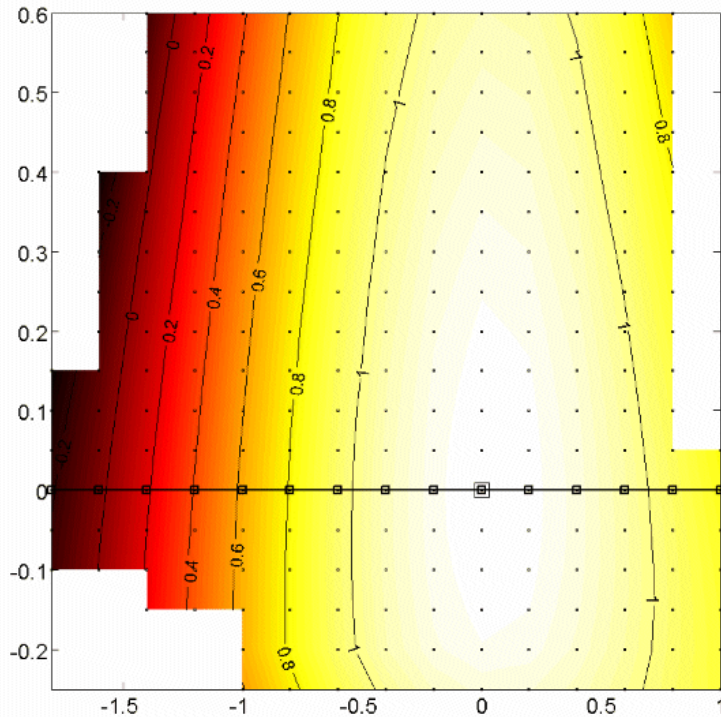
c) λ_3/λ_2 relation



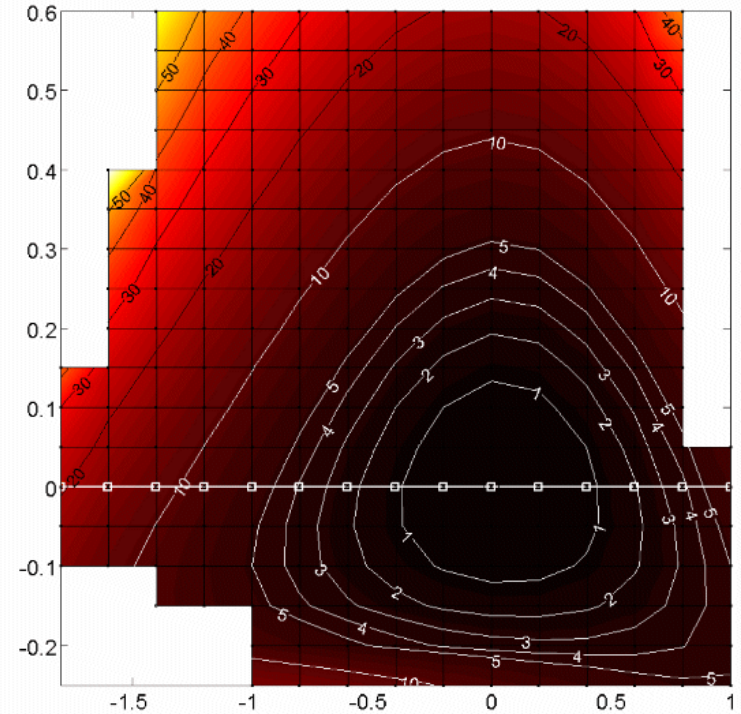
d) λ_2/λ_1 relation

Visualizing functions:

Entropy and entropy production



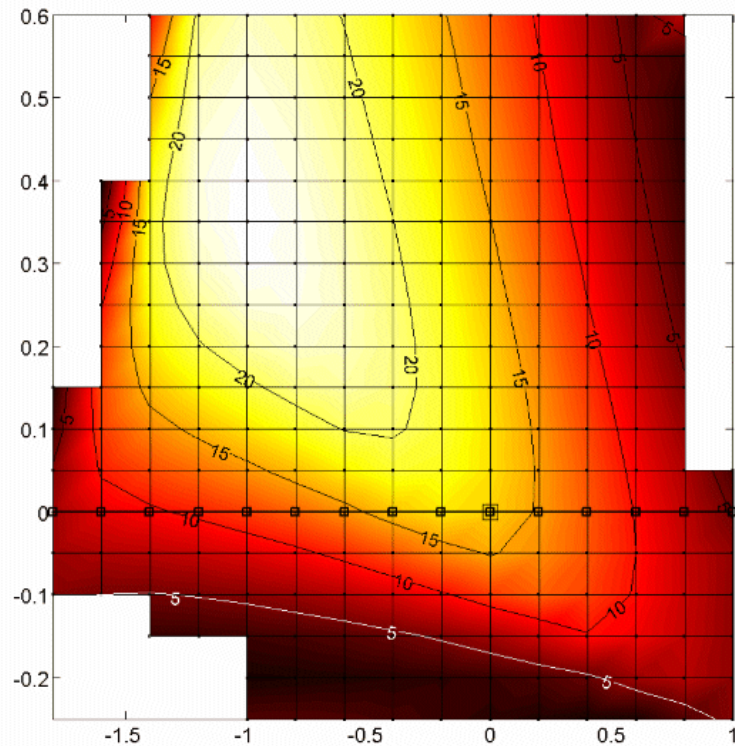
Entropy



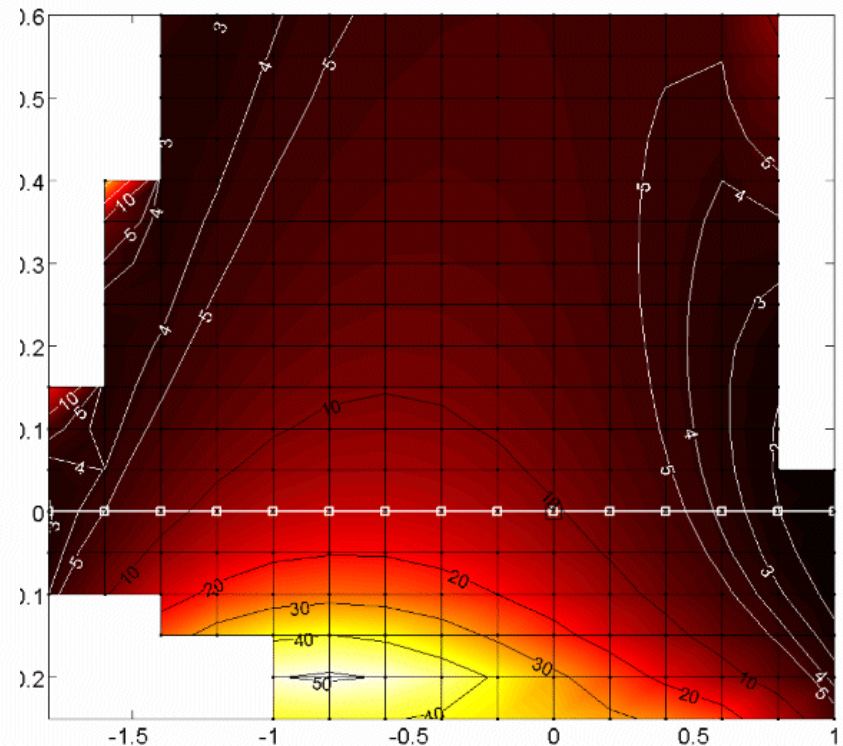
Entropy production

Visualizing functions:

Separation of relaxation times



$$\lambda_2/\lambda_1$$



$$\lambda_3/\lambda_2$$

Conclusion : Three reasons to use the thermodynamic projector

- **It guarantees the persistence of dissipation:** All the thermodynamic processes which should produce the entropy conserve this property after projecting, moreover, not only the sign of dissipation conserves, but the value of entropy production and the reciprocity relations too;

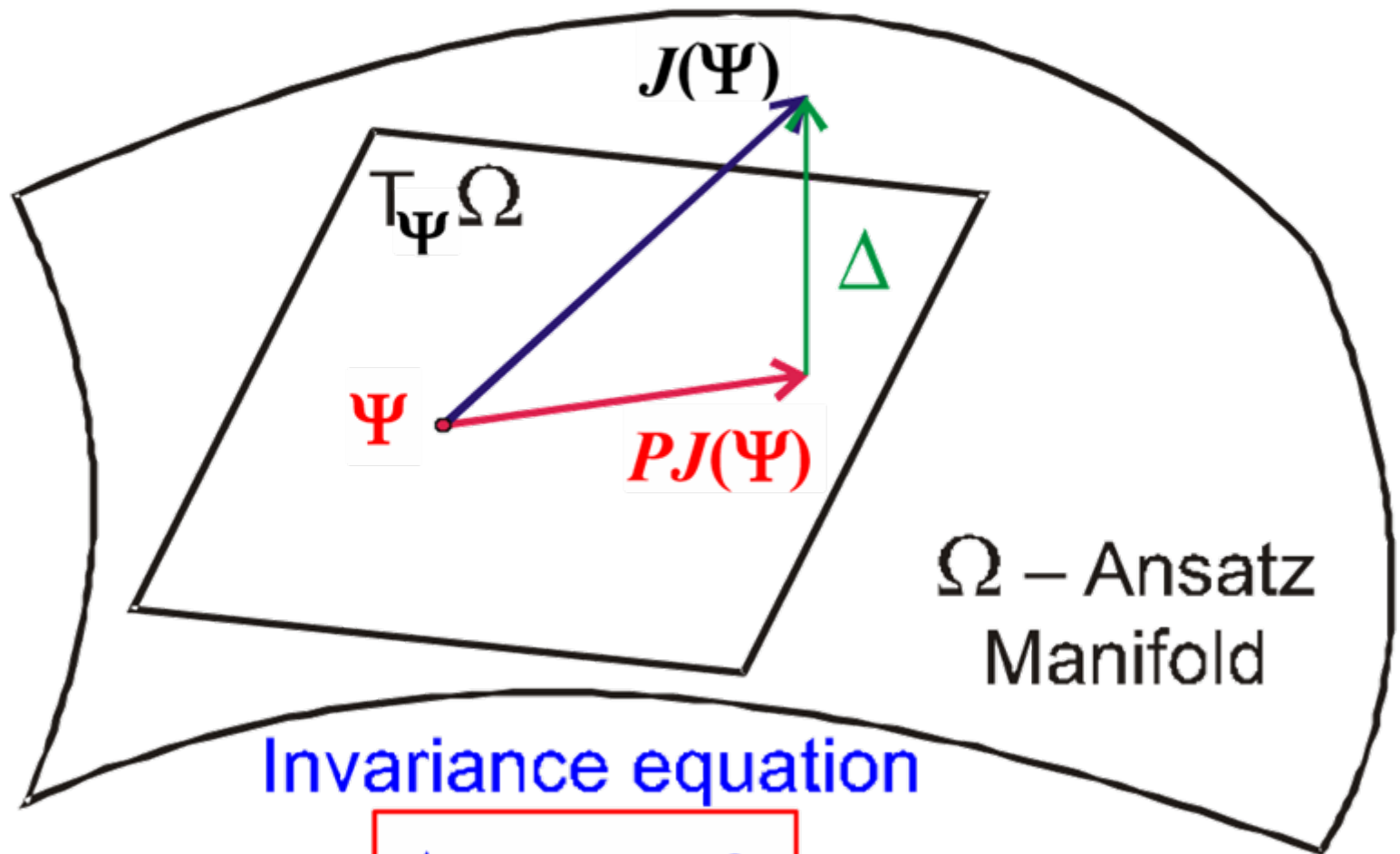
- **Universality:** The coefficients (and, more generally speaking, the right hand part) of kinetic equations are known significantly worse than the thermodynamic functionals, so, the universality of the thermodynamic projector (it depends only on thermodynamic data) makes the thermodynamic properties of projected system as reliable, as for the initial system;
- **It is easy** (much more easy than spectral projector, for example).

Most important items

- QE vs QSS;
- Defect of invariance and the invariance equation;
- The system of methods for solution;
- Thermodynamics projector

Invariance equation

$$d\Psi/dt = J(\Psi)$$



Invariance equation

$$\Delta = J - PJ = 0$$

Methods for Solution

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$$(\text{grad}S)_f^\parallel = P^\perp((\text{grad}S)_f)$$

$$(\text{grad}S)_f^\perp = (1 - P^\perp)((\text{grad}S)_f)$$

Thank you for your attention

Reprints on-line:

<http://www.math.le.ac.uk/people/ag153/>

Just GOOGLe Gorban