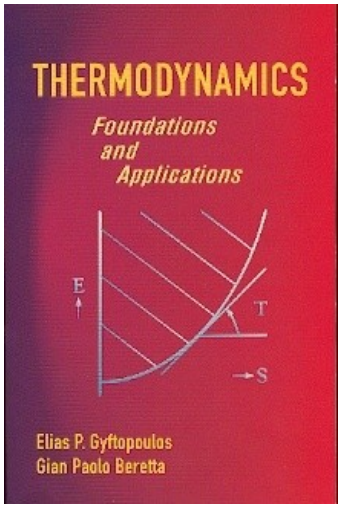
Mathematics helps engineers simplify chemical kinetics without understanding it



VirginiaTech, 310 Kelly Hall, Thursday, Jan 18, 3:30 PM

Gian Paolo Beretta

www.gianpaoloberetta.info

Department of Mechanical and Industrial Engineering

Università di Brescia

Via Branze 38, 25123 Brescia, Italy

LAB Fisica Tecnica Industriale

IMI

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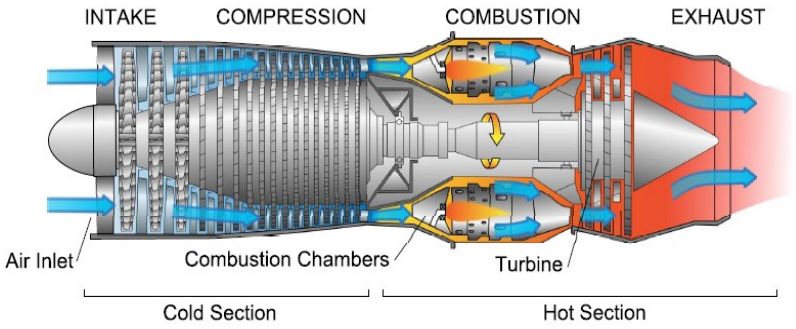
RCCE: Rate-Controlled Constrained-Equilibrium: A thermodynamically consistent approximation scheme to reduce the complexity of large detailed chemical kinetics models

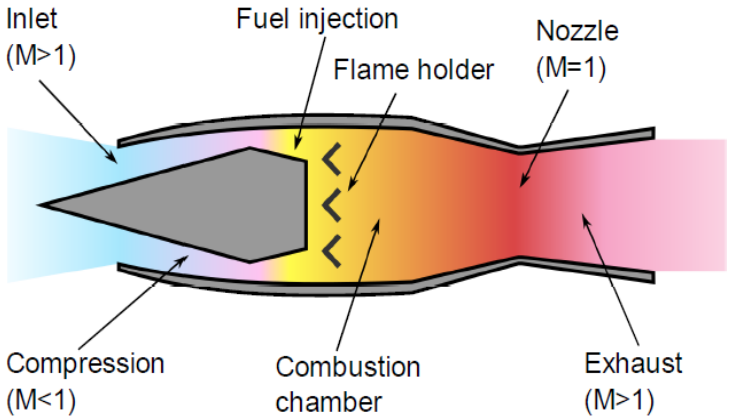
Modeling Hydrocarbon Combustion

Typical applications

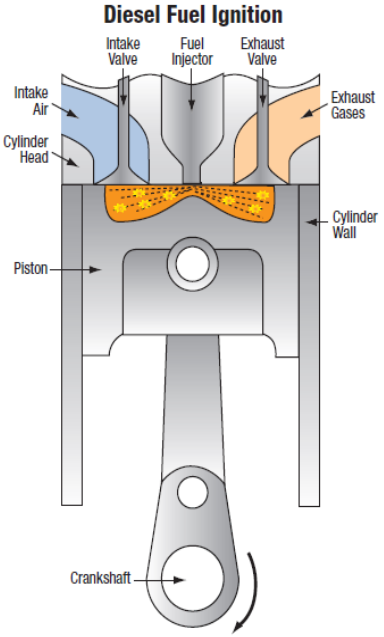
Jet Engine



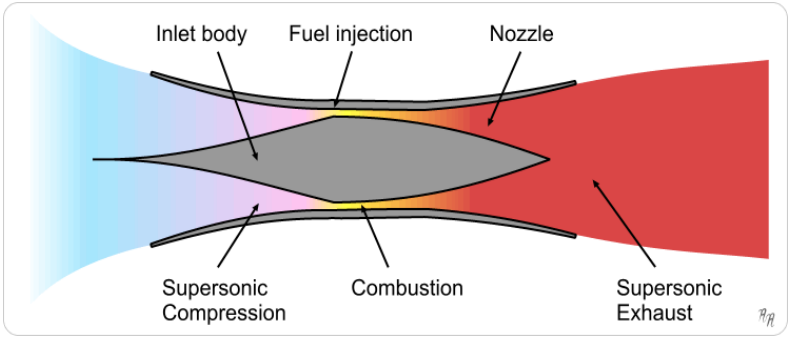
Ramjet



Diesel Engine



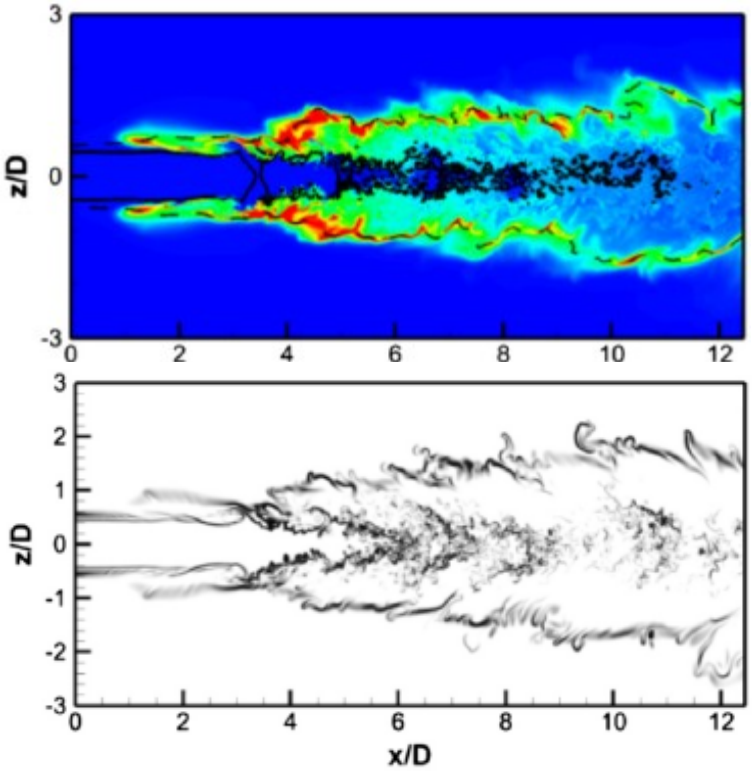
Scramjet

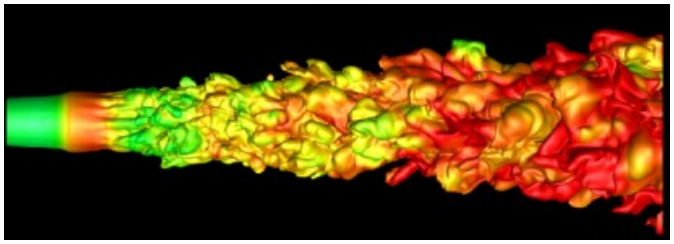


Modeling Hydrocarbon Combustion

Typical applications

Jet flames – DNS and CFD simulations



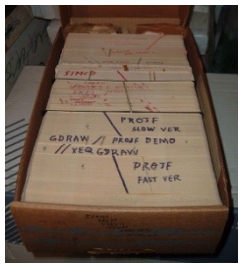


DEPARTMENT OF MECHANICAL ENGINEERING

CONSTRAINED EQUILIBRIUM VERSION OF THE N.A.S.A. TN D-7056 COMPUTER PROGRAM

BY

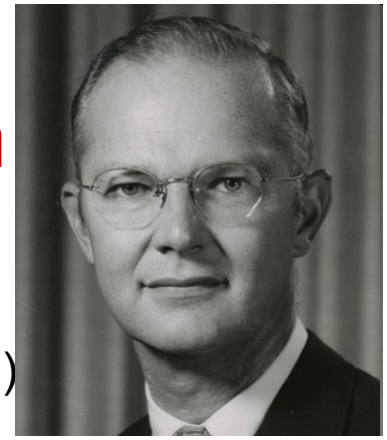
GIAN PAOLO BERETTA
RESEARCH ASSISTANT



SLOAN AUTOMOTIVE LABORATORY
INTERNAL REPORT
JANUARY 1979

www.jameskeckcollectedworks.org

RCCE – Rate Controlled Constrained Equilibrium



James C. Keck (1924-2010)
www.jameskeckcollectedworks.org

Formulation:

- **Keck, Gillespie,** *Combustion and Flame*, 17, 237 (**1971**)
- **Beretta, Keck,** *ASME Book H0341C*, 3, 135 (**1986**)
- **Keck,** *Progr. Energy Comb. Sci.*, 16, 125 (**1990**)
- **Tang, Pope,** *Comb. Theory Mod.*, 8, 255 (**2004**)
- **Beretta, Keck, Janbozorgi, Metghalchi,** *Entropy*, 14, 92 (**2012**)

Identification of the optimal set of Constraints:

- **Careful examination of the underlying chemistry** (Keck and coworkers)
- **Level of Importance** (Lol, Rigopolous – 2009)
- **Greedy Algorithm** (Hiremath et. al. – 2010, 2011)
- **Degree of Disequilibrium Algorithm** (DoD, Janbozorgi, Metghalchi – 2012)
- **ASVDADD (**Beretta, Janbozorgi, Metghalchi, *Comb. Flame*, 168, 342, 2016)

Rocket propulsion example

Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion

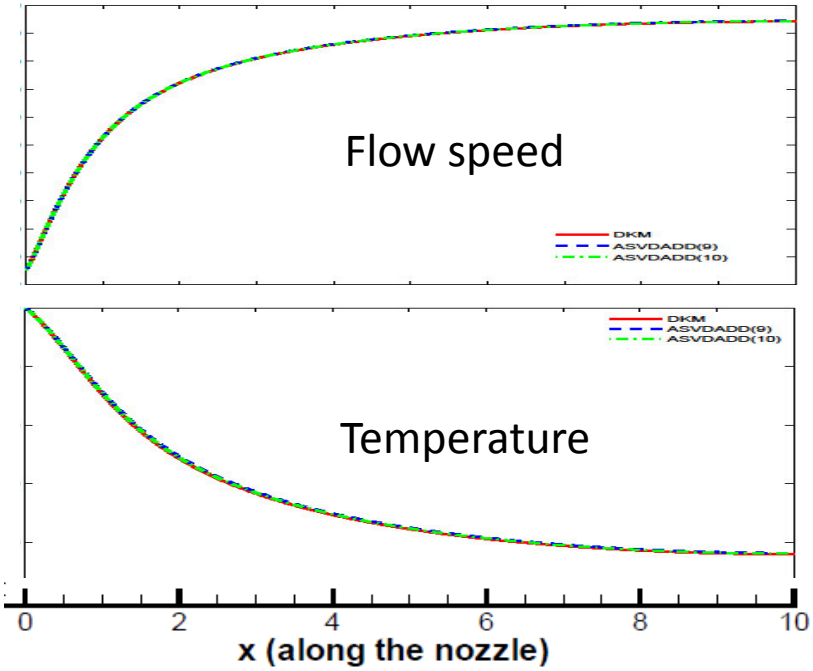
products of H_2-O_2 combustion enter nozzle at equilibrium

Ma =1
T = 3000 K
p = 2.5 MPa

Ma ~ 4
T ~ 1000 K
p ~ 10 kPa

The mixture remains close to equilibrium up to the throat where rapid expansion occurs.

Rapid expansion
Fast flow acceleration

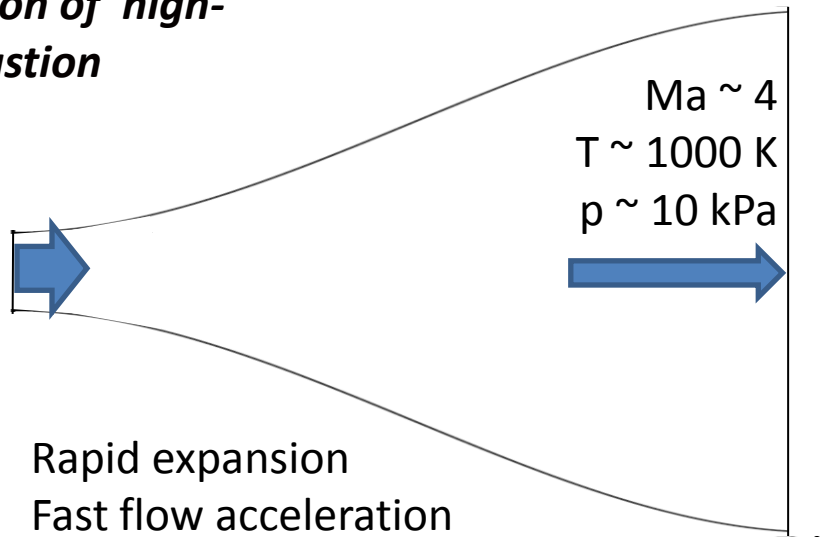


Detailed Kinetic Model (DKM)

Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion

products of H_2-O_2 combustion enter nozzle at equilibrium

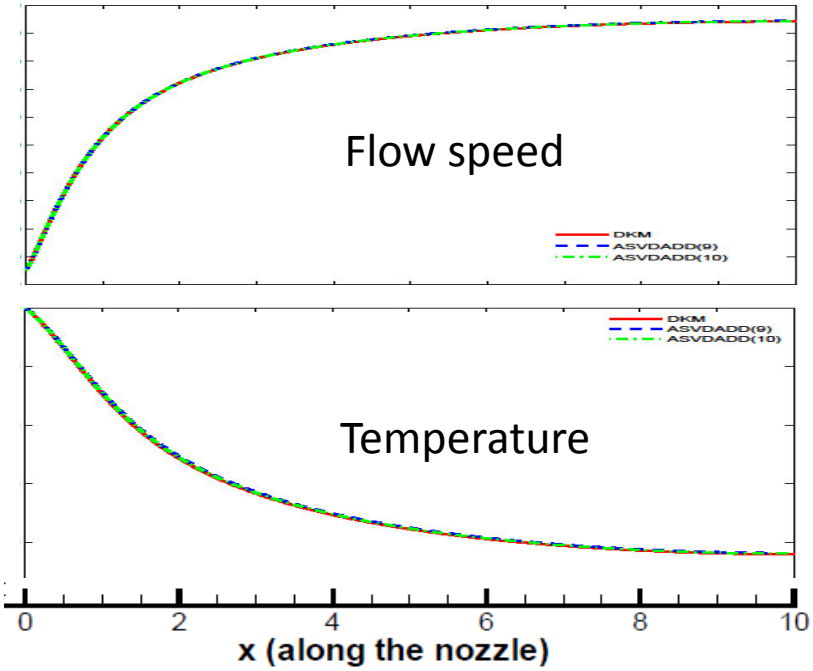
Ma =1
T = 3000 K
p = 2.5 MPa



Rapid expansion
Fast flow acceleration

	24 Reactions
1	O+O+M=O2+M
2	O+H+M=OH+M
3	H+H+M=H2+M
4	H+H+H2=H2+H2
5	H+H+H2O=H2+H2O
6	H+OH+M=H2O+M
7	H+O2+M=HO2+M
8	H+O2+O2=HO2+O2
9	H+O2+H2O=HO2+H2O
10	OH+OH+M=H2O2+M
11	O+H2=H+OH
12	O+HO2=OH+O2
13	O+H2O2=OH+HO2
14	H+O2=O+OH
15	H+HO2=O+H2O
16	H+HO2=O2+H2
17	H+HO2=OH+OH
18	H+H2O2=HO2+H2
19	H+H2O2=OH+H2O
20	OH+H2=H+H2O
21	OH+OH=O+H2O
22	OH+HO2=O2+H2O
23	OH+H2O2=HO2+H2O
24	HO2+HO2=O2+H2O2

8 Species
O
O2
H
H2
OH
H2O
HO2
H2O2



Element conservation constraints

Species
O
O2
H
H2
OH
H2O
HO2
H2O2

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2	Element conservation EO	Element conservation EH
11	O+H2=H+OH	-1	0	1	-1	1	0	0	0	0	0
13	O+H2O2=OH+HO2	-1	0	0	0	1	0	1	-1	0	0
14	H+O2=O+OH	1	-1	-1	0	1	0	0	0	0	0
18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1	0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0	0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0	0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1	0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0	0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0	0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0	0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1	0	0
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0	0	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0	0	0
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0	0	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0	0	0
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1	0	0
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0	0	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1	0	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0	0	0
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0	0	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0	0	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0	0	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0	0	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0	0	0

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}}$$

$$\dot{N}_j = \sum_{j=1}^{n_s} \nu_{j\ell}\ (r_\ell^+ - r_\ell^-)$$

Reaction ℓ:

$$\sum_{j=1}^{n_s} \nu_{j\ell}^+ \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}} \mathrm{H}_{a_{2j}^{\mathrm{EL}}} = \sum_{j=1}^{n_s} \nu_{j\ell}^- \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}} \mathrm{H}_{a_{2j}^{\mathrm{EL}}}$$

Stoichiometric coefficients:

$$\nu_{j\ell} = \nu_{j\ell}^- - \nu_{j\ell}^+$$

$$\sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$$

Vector representation

Species	Element conservation EO	EH
O	1	0
O2	2	0
H	0	1
H2	0	2
OH	1	1
H2O	1	2
HO2	2	1
H2O2	2	2

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2			
11	O+H2=H+OH	-1	0	1	-1	1	0	0	0		0	0
13	O+H2O2=OH+HO2	-1	0	0	0	1	0	1	-1		0	0
14	H+O2=O+OH	1	-1	-1	0	1	0	0	0		0	0
18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1		0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0		0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0		0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1		0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0		0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0		0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0		0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1		0	0
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0		0	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0		0	0
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0		0	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0		0	0
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1		0	0
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0		0	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1		0	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0		0	0
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0		0	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0		0	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0		0	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0		0	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0		0	0

$\boldsymbol{a}_i^{\mathrm{EL}}$

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}}$$

$$\dot{N}_j = \sum_{j=1}^{n_s} \nu_{j\ell}\ (r_\ell^+ - r_\ell^-)$$

Reaction ℓ:

$$\sum_{j=1}^{n_s} \nu_{j\ell}^+ \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}}\mathrm{H}_{a_{2j}^{\mathrm{EL}}} = \sum_{j=1}^{n_s} \nu_{j\ell}^- \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}}\mathrm{H}_{a_{2j}^{\mathrm{EL}}}$$

Stoichiometric coefficients:

$$\nu_{j\ell} = \nu_{j\ell}^- - \nu_{j\ell}^+$$

$$\sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$$

$\boldsymbol{\nu}_\ell$

$$\boldsymbol{a}_i^{\mathrm{EL}} \cdot \boldsymbol{\nu}_\ell = 0$$

Vector representation

Species	Element conservation EO	EH
O	1	0
O2	2	0
H	0	1
H2	0	2
OH	1	1
H2O	1	2
HO2	2	1
H2O2	2	2

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2			
11	O+H2=H+OH	-1	0	1	-1	1	0	0	0		0	0
13	O+H2O2=OH+HO2	-1	0	0	0	1	0	1	-1		0	0
14	H+O2=O+OH	1	-1	-1	0	1	0	0	0		0	0
18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1		0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0		0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0		0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1		0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0		0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0		0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0		0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1		0	0
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0		0	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0		0	0
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0		0	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0		0	0
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1		0	0
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0		0	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1		0	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0		0	0
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0		0	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0		0	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0		0	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0		0	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0		0	0

a_i^{EL}

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$$\dot{N}_j = \sum_{j=1}^{n_s} \nu_{j\ell} \ (r_\ell^+ - r_\ell^-)$$

Reaction ℓ:

$$\sum_{j=1}^{n_s} \nu_{j\ell}^+ \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}} \mathrm{H}_{a_{2j}^{\mathrm{EL}}} = \sum_{j=1}^{n_s} \nu_{j\ell}^- \ \mathrm{O}_{a_{1j}^{\mathrm{EL}}} \mathrm{H}_{a_{2j}^{\mathrm{EL}}}$$

Stoichiometric coefficients:

$$\nu_{j\ell} = \nu_{j\ell}^- - \nu_{j\ell}^+$$

$b_{i\ell}^{\mathrm{EL}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$

$\boldsymbol{\nu}_\ell$

$$\boldsymbol{a}_i^{\mathrm{EL}} \cdot \boldsymbol{\nu}_\ell = 0$$

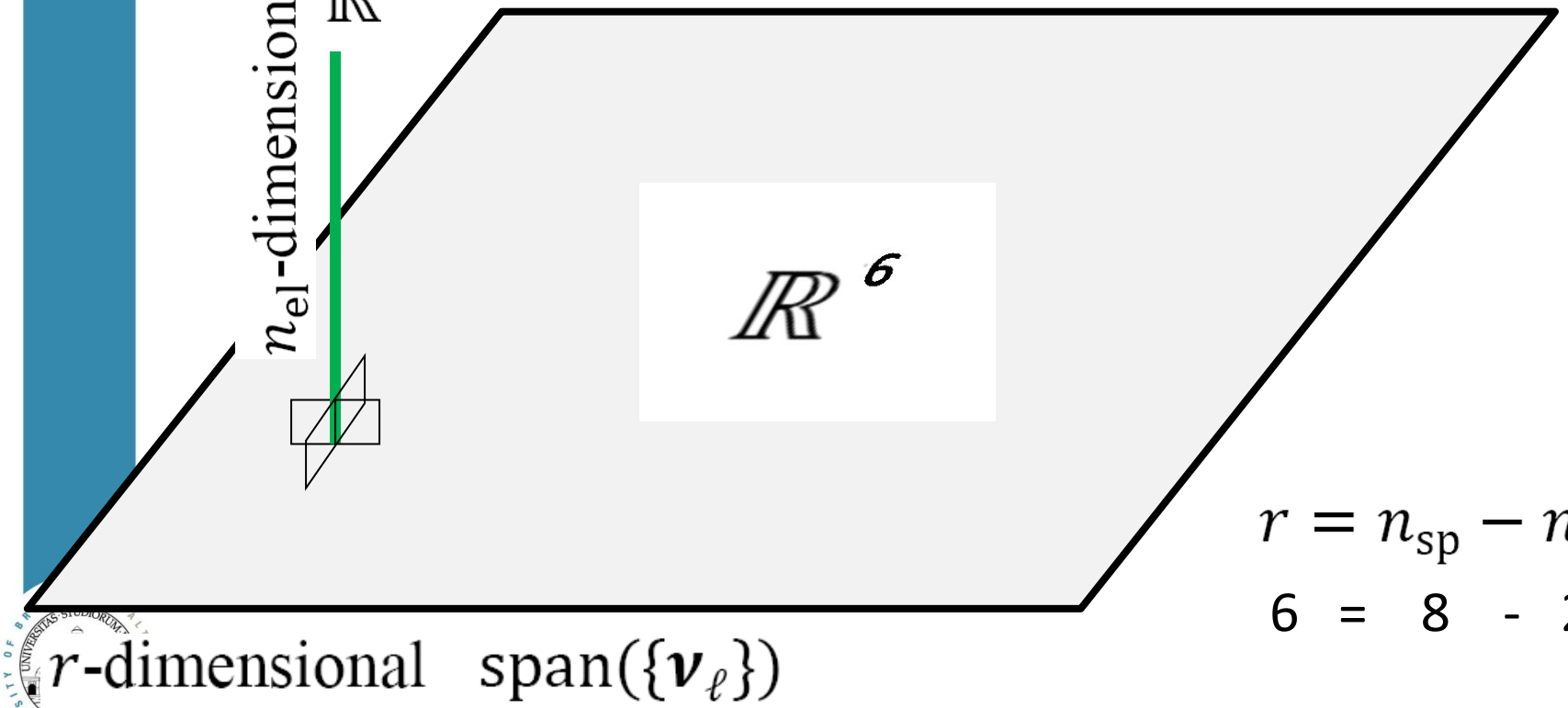
Vector representation

$$\mathbb{R}^{n_{\mathrm{sp}}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{\mathrm{EL}}\})$$

$\mathbb{R}^8$ $\mathbb{R}^6$ $\mathbb{R}^2$

reactive subspace

inhert subspace



$$r = n_{\mathrm{sp}} - n_{\mathrm{el}}$$

6 = 8 - 2

At thermodynamic equilibrium … (inlet)

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL}, a

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}}$$

At thermodynamic equilibrium … (inlet)

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL},

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}}$$

$$-\frac{1}{RT}\sum_{j=1}^{n_s} \mu_j(T, p, \boldsymbol{X})\, \nu_{j\ell} = 0$$

Necessary condition for chemical equilibrium

Chemical potentials

At thermodynamic equilibrium … (inlet)

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL}, a

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}}$$

$$-\frac{1}{RT}\sum_{j=1}^{n_s} \mu_j(T, p, \boldsymbol{X})\, \nu_{j\ell} = 0$$

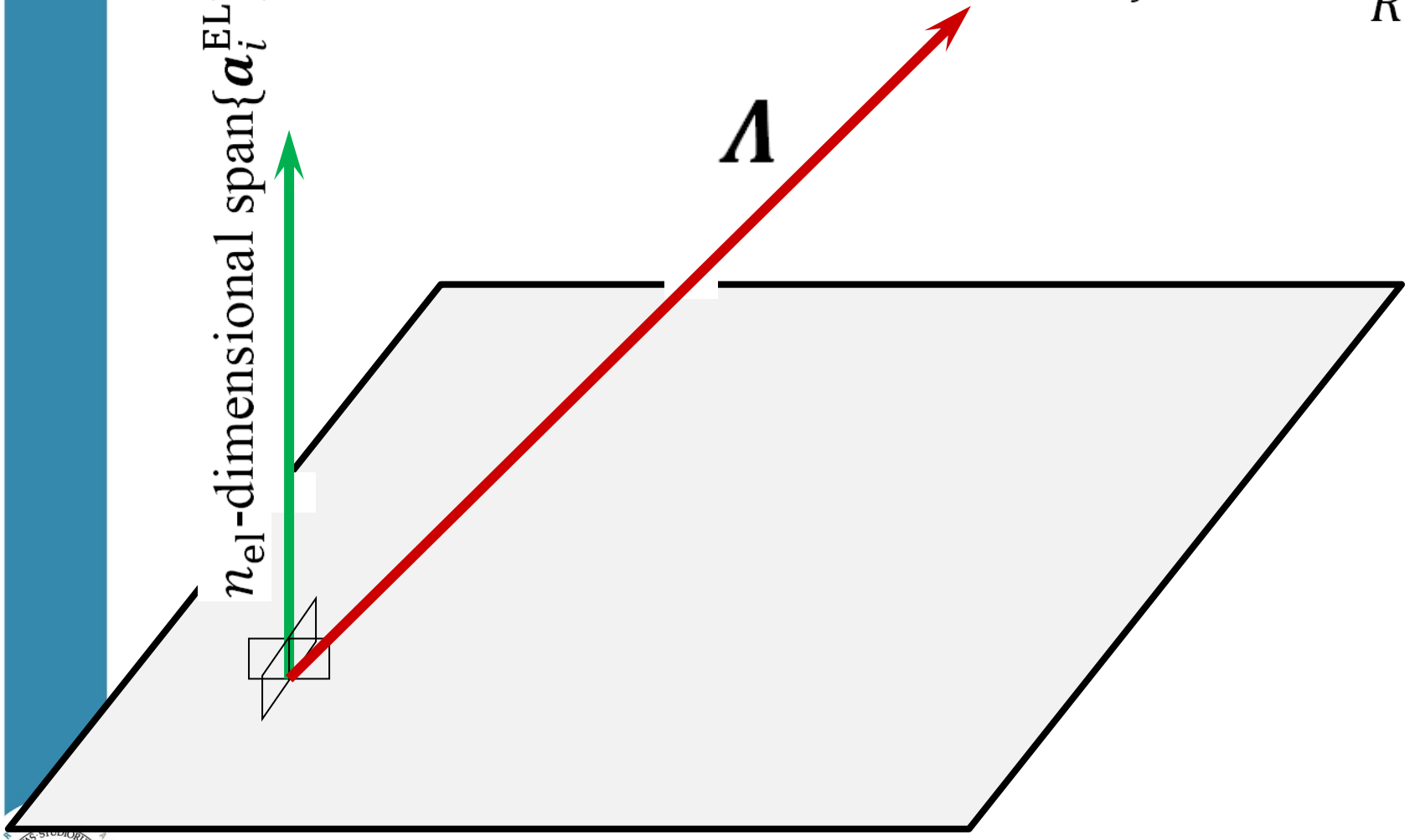
Necessary condition for chemical equilibrium

Chemical potentials

$$\Lambda_j = -\frac{\mu_j(T, p, \boldsymbol{X})}{RT}$$

$$\mathbb{R}^{n_{\mathrm{sp}}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{\mathrm{EL}}\})$$

$$\Lambda_j = -\frac{\mu_j(T, p, \boldsymbol{X})}{RT}$$



r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{\mathrm{sp}} - n_{\mathrm{el}}$

At thermodynamic equilibrium … (inlet)

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL},

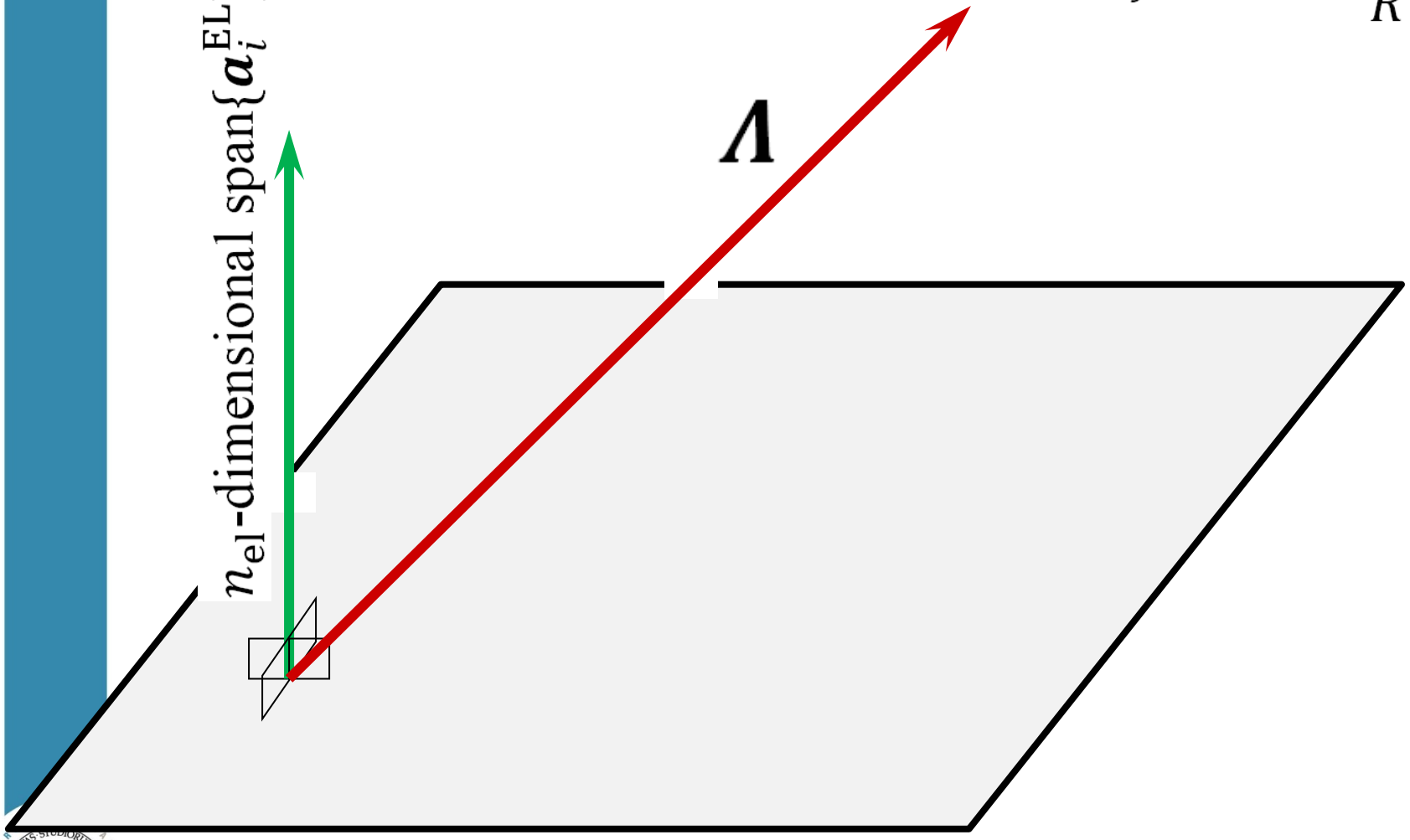
$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}}$$

$$-\frac{1}{RT}\sum_{j=1}^{n_s} \mu_j(T,p,\boldsymbol{X})\,\nu_{j\ell} = \sum_{j=1}^{n_s} \Lambda_j\,\nu_{j\ell} = \boldsymbol{\Lambda}\cdot\boldsymbol{\nu}_\ell = 0$$

$$\Lambda_j = -\frac{\mu_j(T,p,\boldsymbol{X})}{RT}$$

$$\mathbb{R}^{n_{\mathrm{sp}}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{\mathrm{EL}}\})$$

$$\Lambda_j = -\frac{\mu_j(T, p, \boldsymbol{X})}{RT}$$

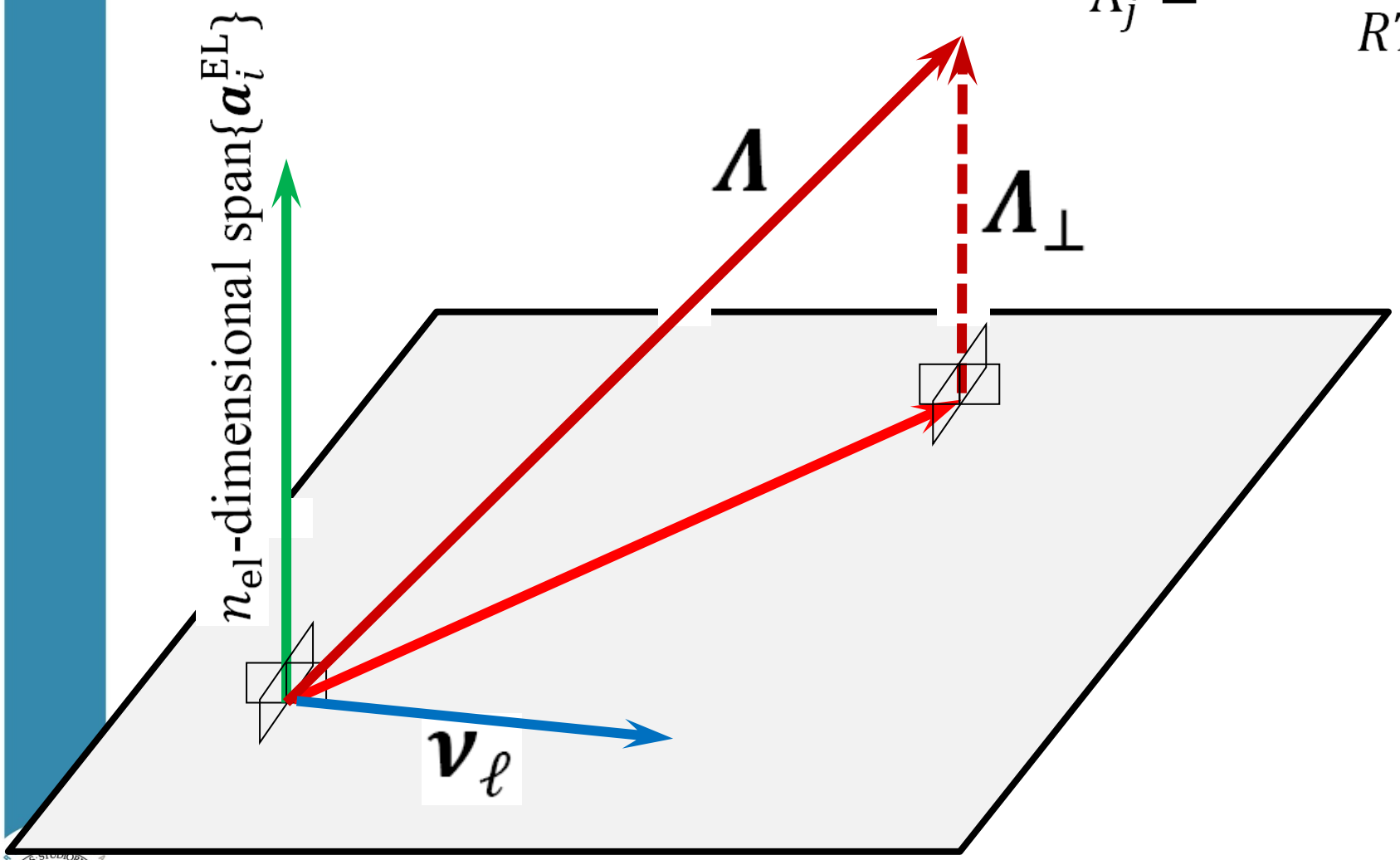


r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{\mathrm{sp}} - n_{\mathrm{el}}$

$$\mathbb{R}^{n_{\mathrm{sp}}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{\mathrm{EL}}\})$$

$$\Lambda_j = -\frac{\mu_j(T, p, \boldsymbol{X})}{RT}$$



r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{\mathrm{sp}} - n_{\mathrm{el}}$

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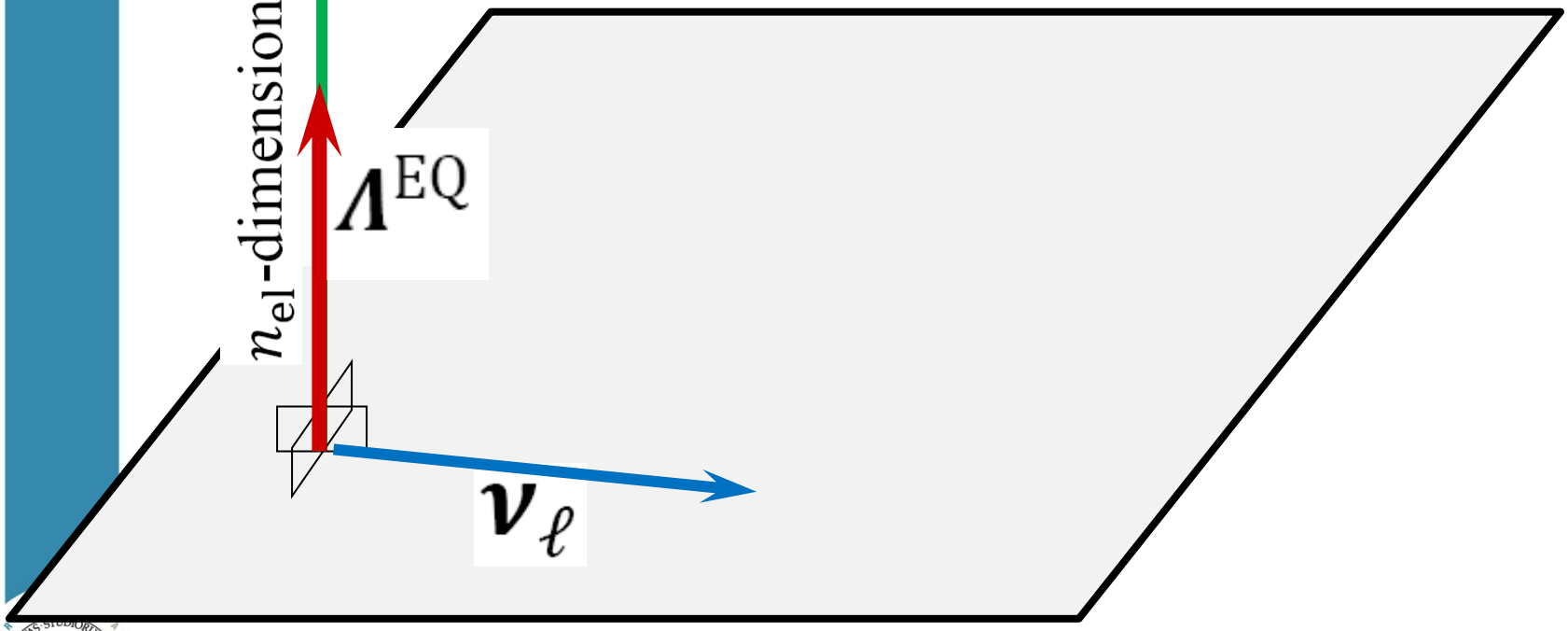
at chemical equilibrium:

$$\boldsymbol{\Lambda}^{\mathrm{EQ}} \cdot \boldsymbol{\nu}_\ell = 0 \qquad \textbf{implies:} \qquad \boldsymbol{\Lambda}^{\mathrm{EQ}} = \sum_{i=1}^{n_{\mathrm{el}}} \gamma_i^{\mathrm{EL}} \boldsymbol{a}_i^{\mathrm{EL}}$$



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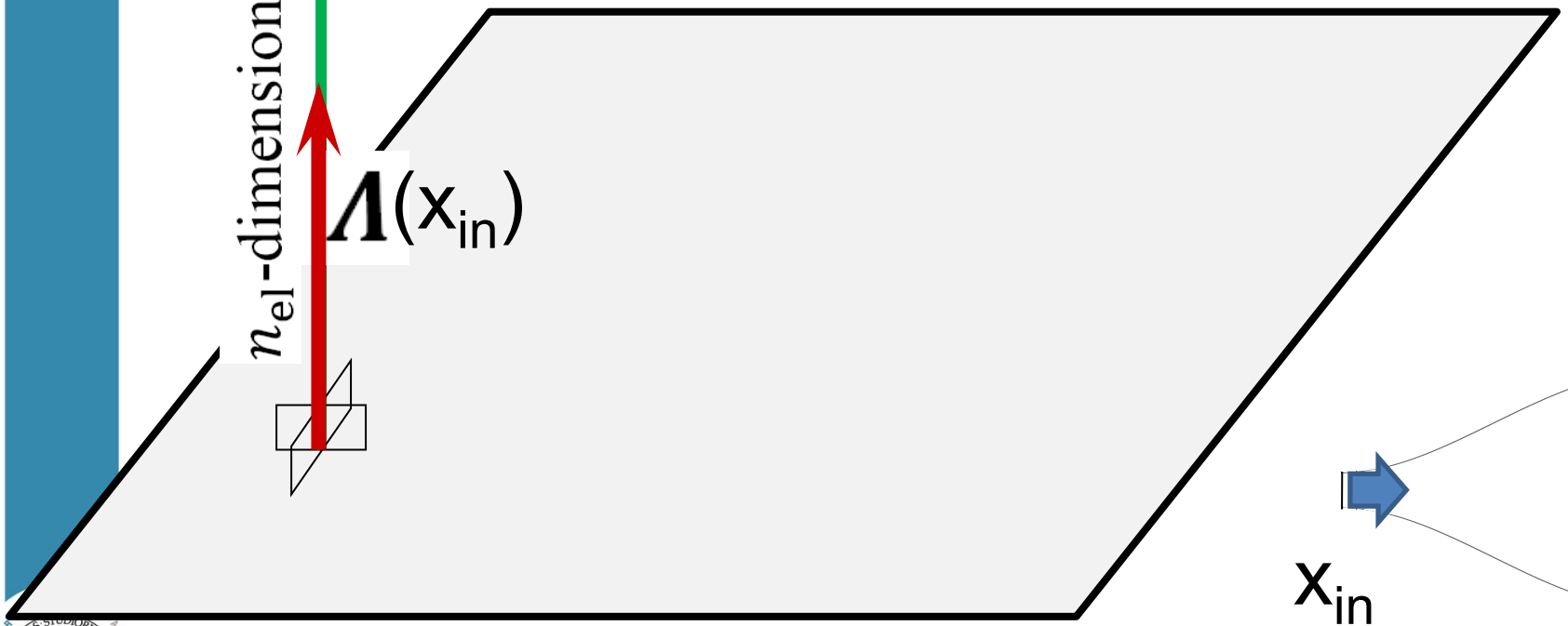

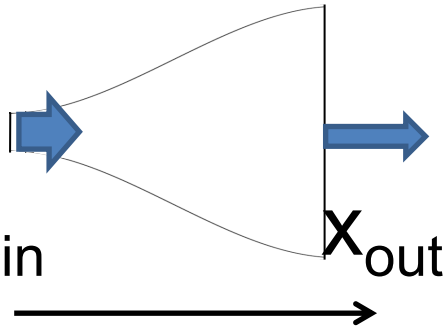

At thermodynamic equilibrium … (inlet)

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL},

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}}$$

$$-\frac{1}{T}\sum_{j=1}^{n_s} \mu_j(T, p, \boldsymbol{X})\, \nu_{j\ell} = \sum_{j=1}^{n_s} \Lambda_j\, \nu_{j\ell} = \boldsymbol{\Lambda} \cdot \boldsymbol{\nu}_\ell = 0$$

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For ideal gas behavior, $\mu_j(T,p,\boldsymbol{X}) = g_{j,\mathrm{pure}}(T,p) + RT\ln(X_j)$, the constrained minimization yields the composition $\boldsymbol{X}^{\mathrm{E}}$

$$\ln X_j^{\mathrm{CE}} = -\frac{1}{RT} g_{j,\mathrm{pure}}(T,p) - \sum_{i=1}^{n_{\mathrm{el}}} \gamma_i^{\mathrm{EL}} a_{ij}^{\mathrm{EL}}$$

and, therefore, recalling that $b_{i\ell}^{\mathrm{EL}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$,

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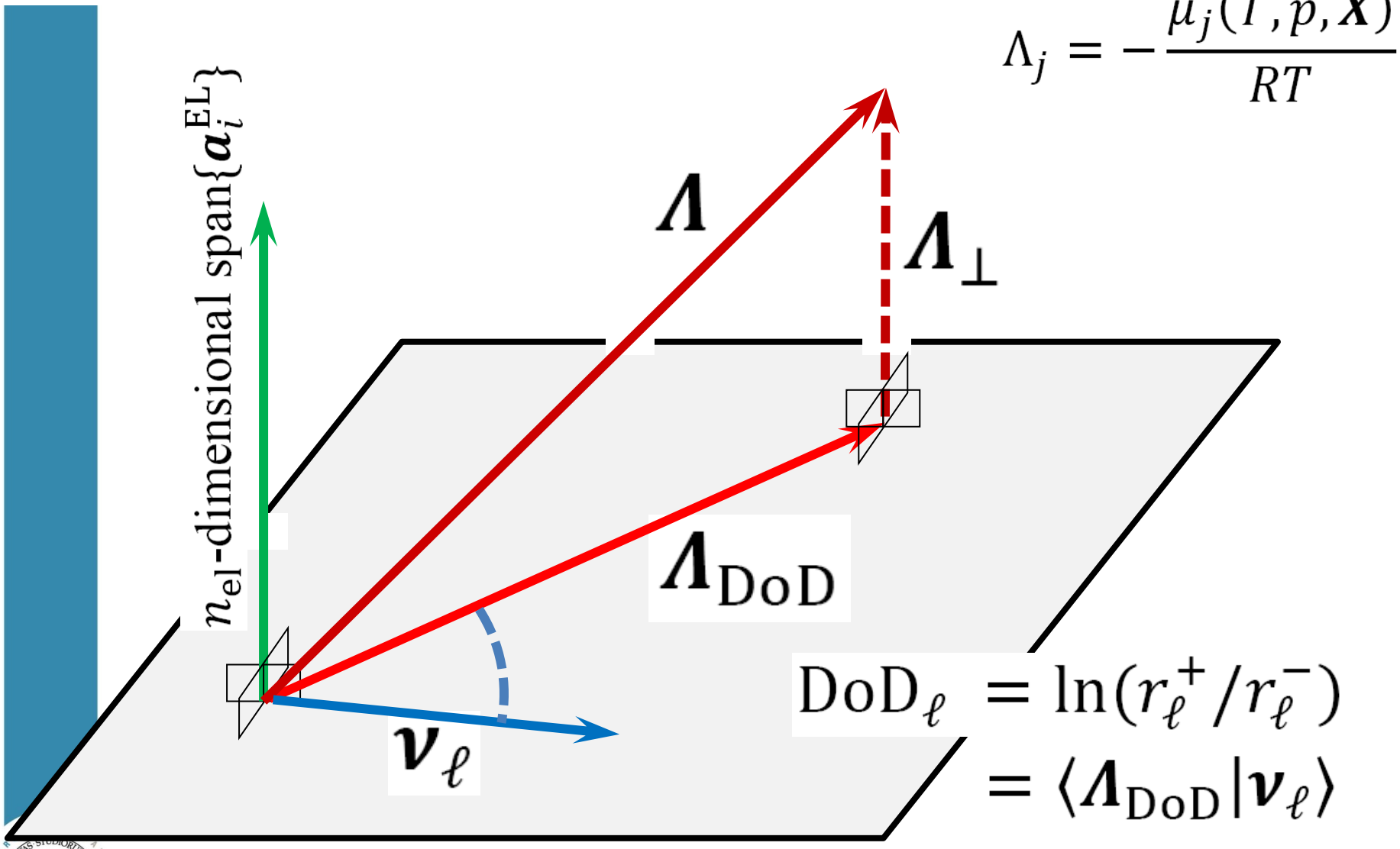
and, therefore, recalling that $b_{i\ell}^{\mathrm{EL}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$,

$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-) = -\frac{1}{RT} \sum_{j=1}^{n_s} \nu_{j\ell}\, \mu_j = 0$$

Degree of disequilibrium of reaction ℓ

$$\mathbb{R}^{n_{\mathrm{sp}}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{\mathrm{EL}}\})$$

$$\Lambda_j = -\frac{\mu_j(T, p, \boldsymbol{X})}{RT}$$



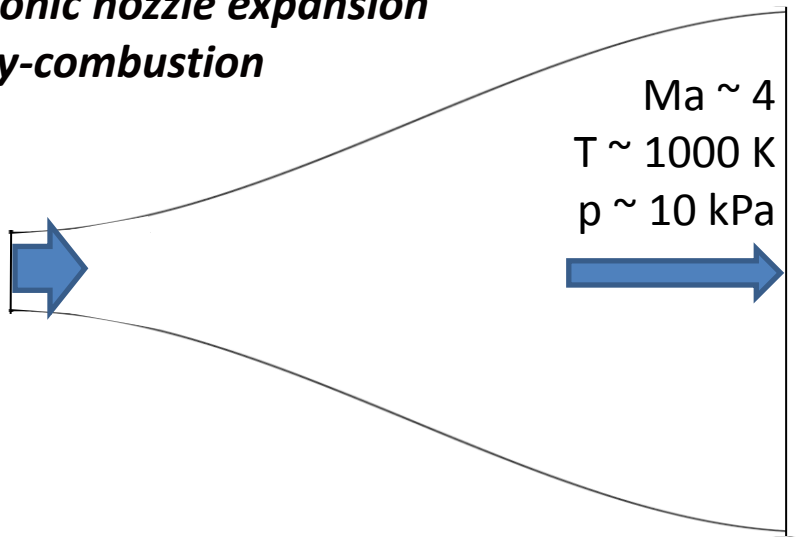
$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-)$$
$$= \langle \boldsymbol{\Lambda}_{\mathrm{DoD}} | \boldsymbol{\nu}_\ell \rangle$$

r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{\mathrm{sp}} - n_{\mathrm{el}}$

Detailed Kinetic Model (DKM)

ROCKET EXAMPLE: Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion



Governing equations

$$\frac{1}{\rho}\frac{d\rho}{dx}+\frac{1}{u}\frac{du}{dx}+\frac{1}{A}\frac{dA}{dx}=0$$ continuity

$$\rho u\frac{du}{dx}+\frac{dp}{dx}=0$$ momentum

$$[N_j]\frac{du}{dx}+u\frac{d[N_j]}{dx}+u[N_j]\left(\frac{1}{A}\frac{dA}{dx}\right)=\dot{\omega}_j$$ species concentrations

$$\rho u\left(\sum_{j=1}^{N_{sp}} C_{p_j}Y_j\right)\frac{dT}{dx}+\sum_{i=j}^{N_{sp}} h_j M_j\dot{\omega}_j+\rho u^2\frac{du}{dx}=0$$ energy

$$p=\mathrm{N}R_uT$$ ideal gas

8 species: H, H_2, O, O_2, H_2O, OH, HO_2, H_2O_2

Rate equations

$$\dot{\omega}_j=\sum_{\ell=1}^{n_r}\nu_{j\ell}\,(r_\ell^+-r_\ell^-)$$

$$r_\ell^\pm=k_\ell^\pm(T)\prod_{j=1}^{n_s}[N_j]^{\nu_{j\ell}^\pm}$$

$$k_\ell^+(T)=A_\ell^+T^{b_\ell^+}\exp\left(-E_\ell^+/RT\right)$$

$$k_\ell^-(T)=k_\ell^+(T)/K_\ell^{co}(T)$$

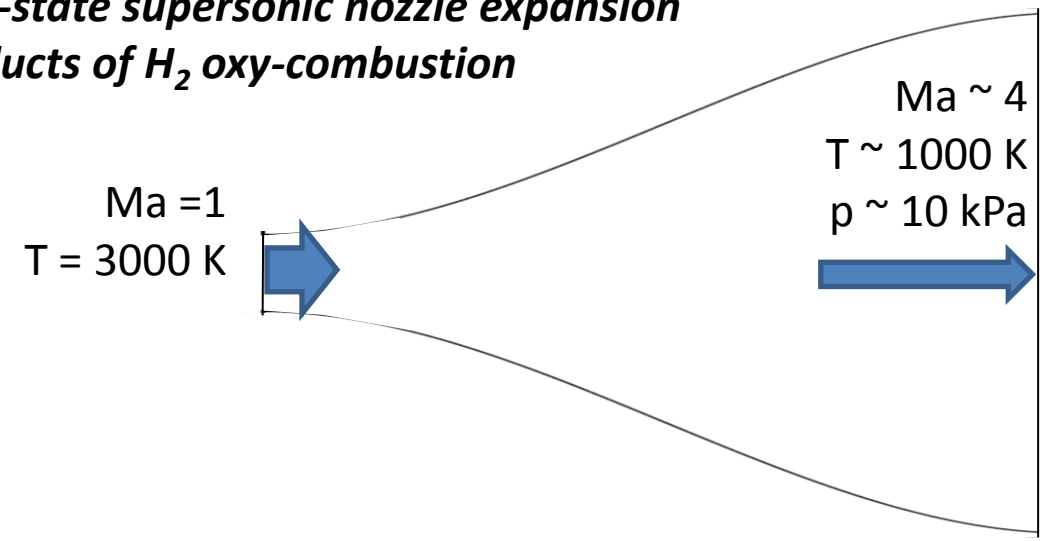
$$K_\ell^{co}(T)=(p_o/RT)^{\nu_\ell}\exp\left(-\Delta g_\ell^o(T)/RT\right)$$

$$\Delta g_\ell^o(T)=\sum_{j=1}^{n_s}\nu_{j\ell}\,g_{jj}(T,p_o)$$

24 reactions

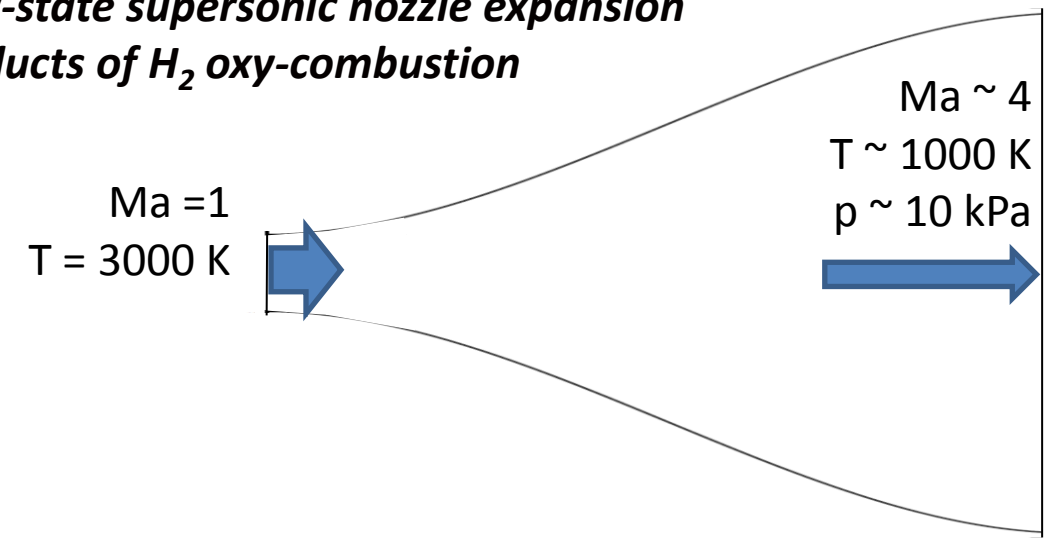
Frozen kinetics yields poor approximation

ROCKET EXAMPLE: Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion



Assuming shifting equilibrium also yields poor approximation…

ROCKET EXAMPLE: Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion



Rate constants for 24 reactions (DKM)

$$k_\ell^+(T) = A_\ell^+ T^{b_\ell^+} \exp(-E_\ell^+/RT)$$

	Reactions	A	b	E
1	O+O+M=O2+M	1.20E+17	-1	0
2	O+H+M=OH+M	5.00E+17	-1	0
3	H+H+M=H2+M	1.00E+18	-1	0
4	H+H+H2=H2+H2	9.00E+16	-0.6	0
5	H+H+H2O=H2+H2O	6.00E+19	-1.3	0
6	H+OH+M=H2O+M	2.20E+22	-2	0
7	H+O2+M=HO2+M	2.80E+18	-0.9	0
8	H+O2+O2=HO2+O2	2.08E+19	-1.2	0
9	H+O2+H2O=HO2+H2O	1.13E+19	-0.8	0
10	OH+OH+M=H2O2+M	7.40E+13	-0.4	0
11	O+H2=H+OH	3.87E+04	2.7	6260
12	O+HO2=OH+O2	2.00E+13	0	0
13	O+H2O2=OH+HO2	9.63E+06	2	4000
14	H+O2=O+OH	2.65E+16	-0.7	17041
15	H+HO2=O+H2O	3.97E+12	0	671
16	H+HO2=O2+H2	4.48E+13	0	1068
17	H+HO2=OH+OH	8.40E+13	0	635
18	H+H2O2=HO2+H2	1.21E+07	2	5200
19	H+H2O2=OH+H2O	1.00E+13	0	3600
20	OH+H2=H+H2O	2.16E+08	1.5	3430
21	OH+OH=O+H2O	3.57E+04	2.4	-2110
22	OH+HO2=O2+H2O	1.45E+13	0	-500
23	OH+H2O2=HO2+H2O	2.00E+12	0	427
24	HO2+HO2=O2+H2O2	1.30E+11	0	-1630

Governing equations

$$\frac{1}{\rho}\frac{d\rho}{dx} + \frac{1}{u}\frac{du}{dx} + \frac{1}{A}\frac{dA}{dx} = 0$$ continuity

$$\rho u\frac{du}{dx} + \frac{dp}{dx} = 0$$ momentum

$$[N_j]\frac{du}{dx} + u\frac{d[N_j]}{dx} + u[N_j]\left(\frac{1}{A}\frac{dA}{dx}\right) = \dot{\omega}_j$$ speci / conce

$$\rho u\left(\sum_{j=1}^{N_{sp}} C_{p_j} Y_j\right)\frac{dT}{dx} + \sum_{i=j}^{N_{sp}} h_j M_j \dot{\omega}_j + \rho u^2 \frac{du}{dx} = 0$$

$$p = \mathrm{N} R_u T$$ ideal gas

Rate equations

$$\dot{\omega}_j = \sum_{\ell=1}^{n_r} \nu_{j\ell}\,(r_\ell^+ - r_\ell^-)$$

$$r_\ell^\pm = k_\ell^\pm(T)\prod_{j=1}^{n_s}[N_j]^{\nu_{j\ell}^\pm}$$

$$k_\ell^+(T) = A_\ell^+ T^{b_\ell^+} \exp(-E_\ell^+/RT)$$

$$k_\ell^-(T) = k_\ell^+(T)/K_\ell^{co}(T)$$

$$K_\ell^{co}(T) = (p_o/RT)^{\nu_\ell} \exp(-\Delta g_\ell^o(T)/RT)$$

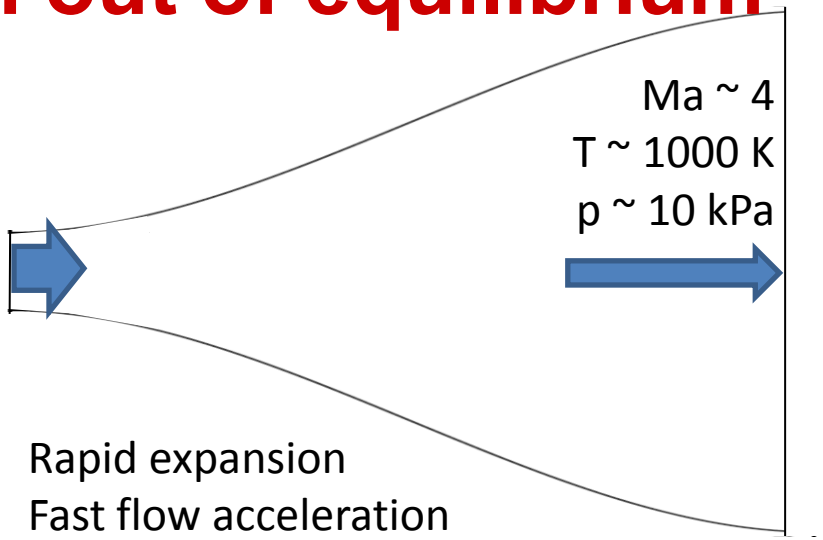
$$\Delta g_\ell^o(T) = \sum_{j=1}^{n_s} \nu_{j\ell}\, g_{jj}(T, p_o)$$

24 reactions

…because the rapid expansion throws the composition out of equilibrium

products of H_2-O_2 combustion enter nozzle at equilibrium

Ma =1
T = 3000 K
p = 2.5 MPa

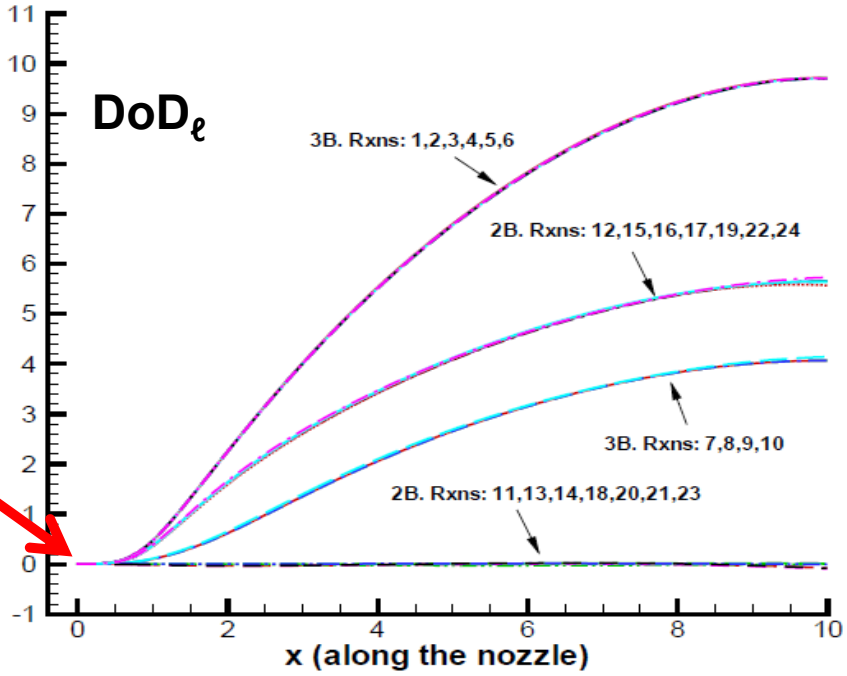


Short residence time (few ms)
Chemistry does not keep up
Composition goes off equilibrium
Degrees of disequilibrium build up

Rapid expansion
Fast flow acceleration

$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-) = -\frac{1}{RT}\sum_{j=1}^{n_s} \nu_{j\ell}\,\mu_j$$

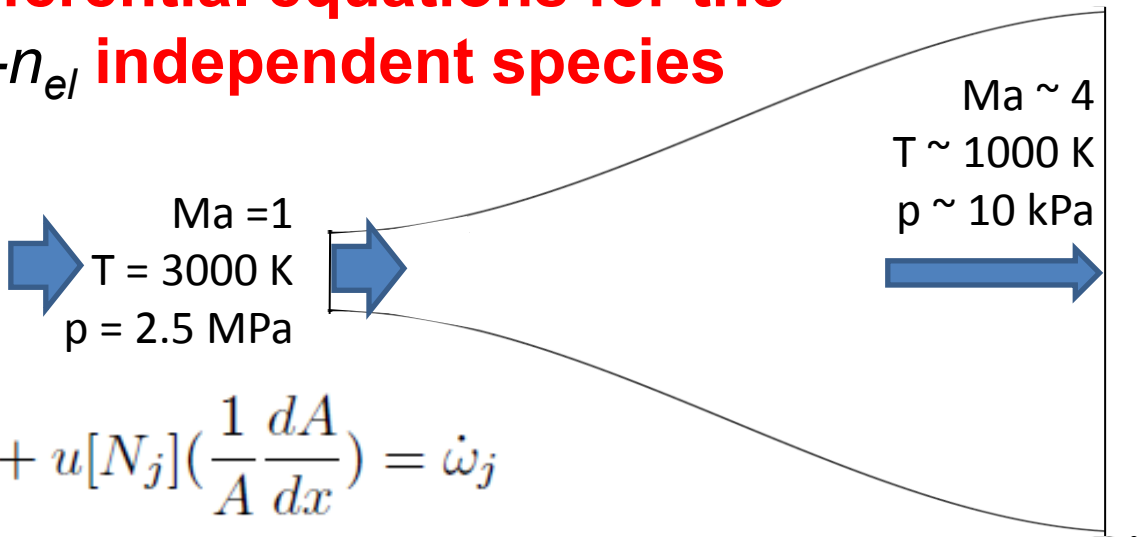
all DoD's = 0



The composition is thrown out of equilibrium due to rapid expansion

So, we need to consider the full DKM

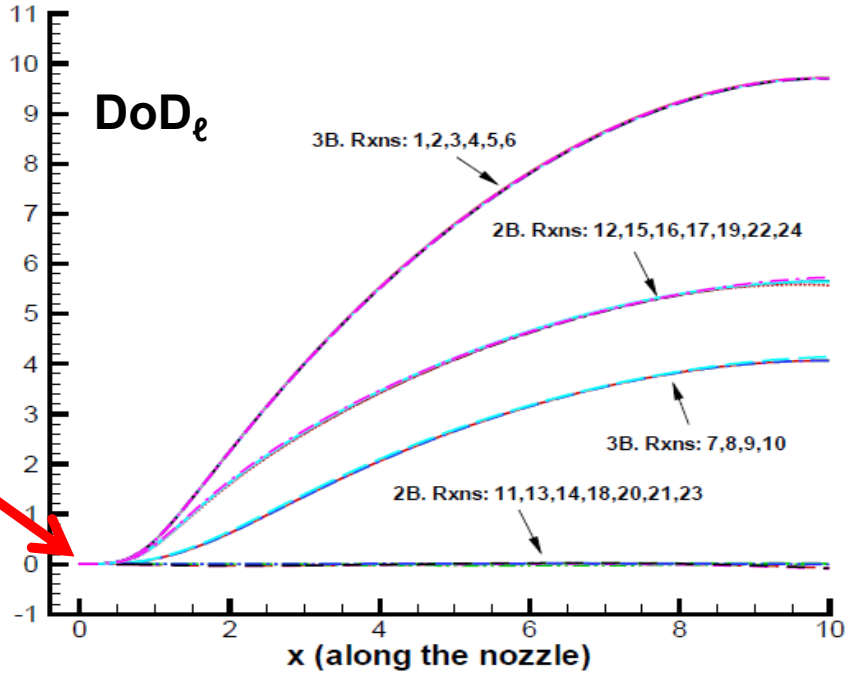
Including the differential equations for the rates of all n_{sp}-n_{el} independent species



$$[N_j]\frac{du}{dx} + u\frac{d[N_j]}{dx} + u[N_j]\left(\frac{1}{A}\frac{dA}{dx}\right) = \dot{\omega}_j$$

$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-)$$
$$= -\frac{1}{RT}\sum_{j=1}^{n_s} \nu_{j\ell}\,\mu_j$$

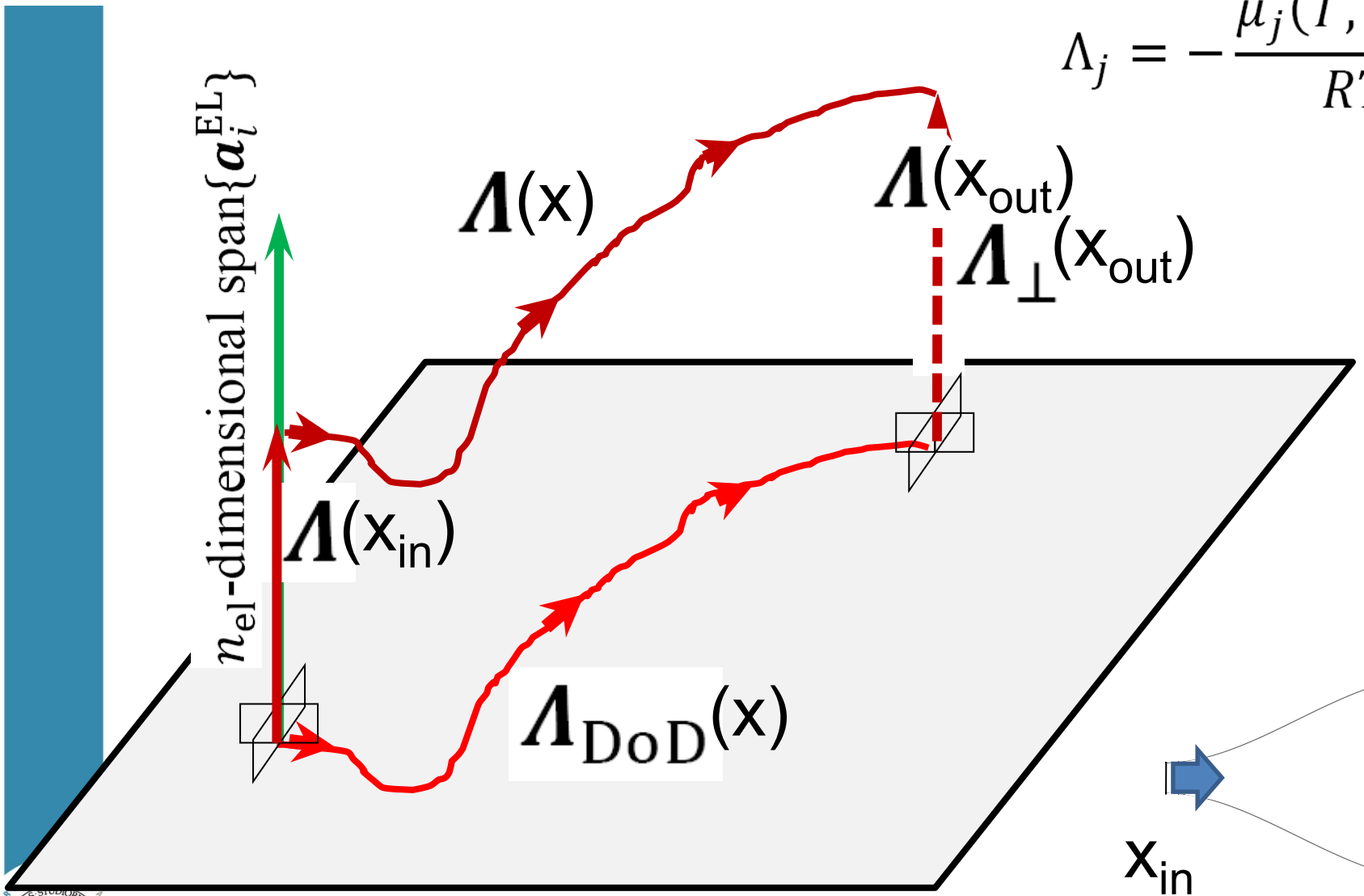
all DoD's = 0



The composition is thrown out of equilibrium due to rapid expansion

$$\mathbb{R}^{n_{sp}} = \mathrm{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \mathrm{span}(\{\boldsymbol{a}_i^{EL}\})$$

$$\Lambda_j = -\frac{\mu_j(T,p,\boldsymbol{X})}{RT}$$



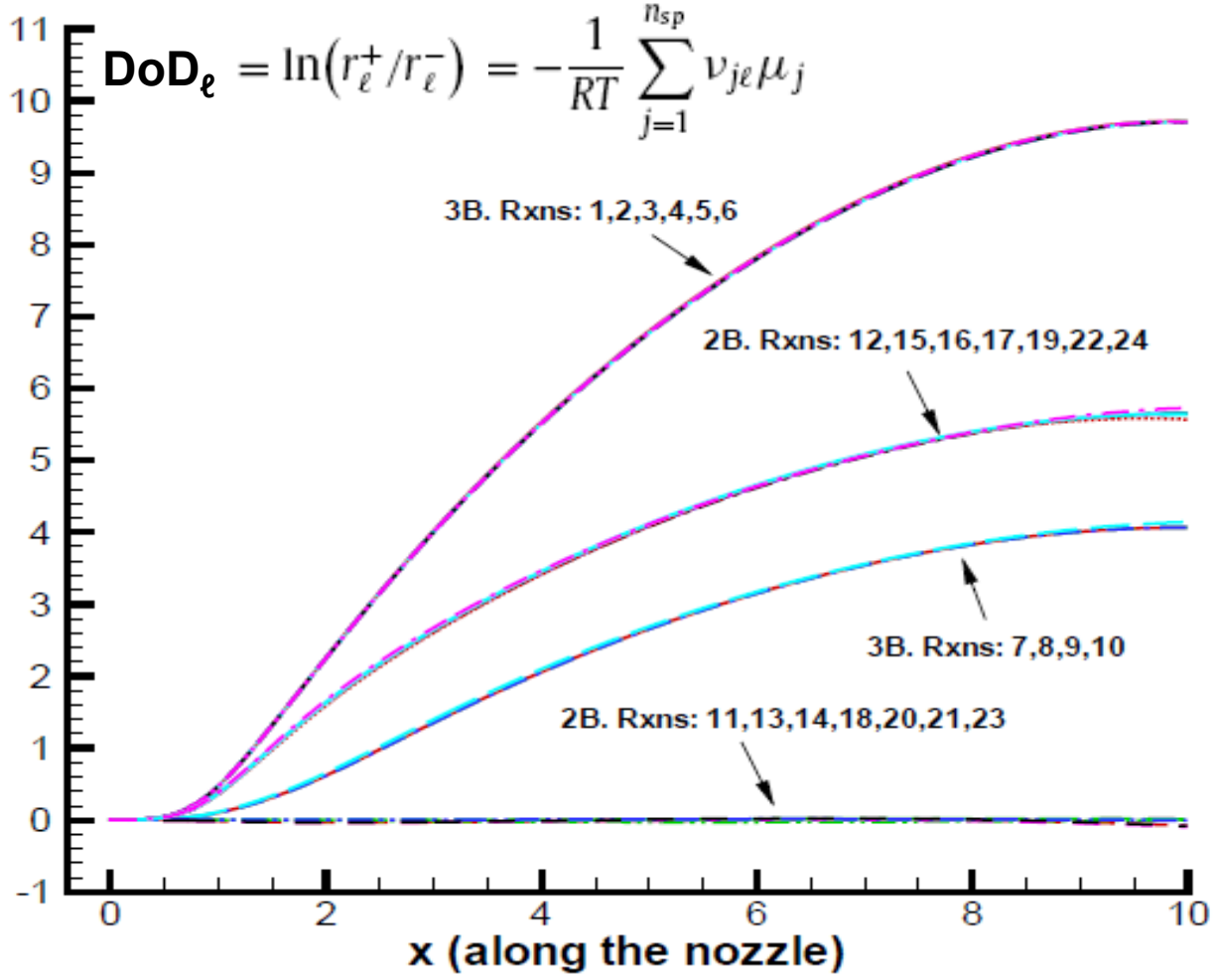
r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{sp} - n_{el}$

x = downstream nozzle coordinate

Most reactions get off equilibrium…

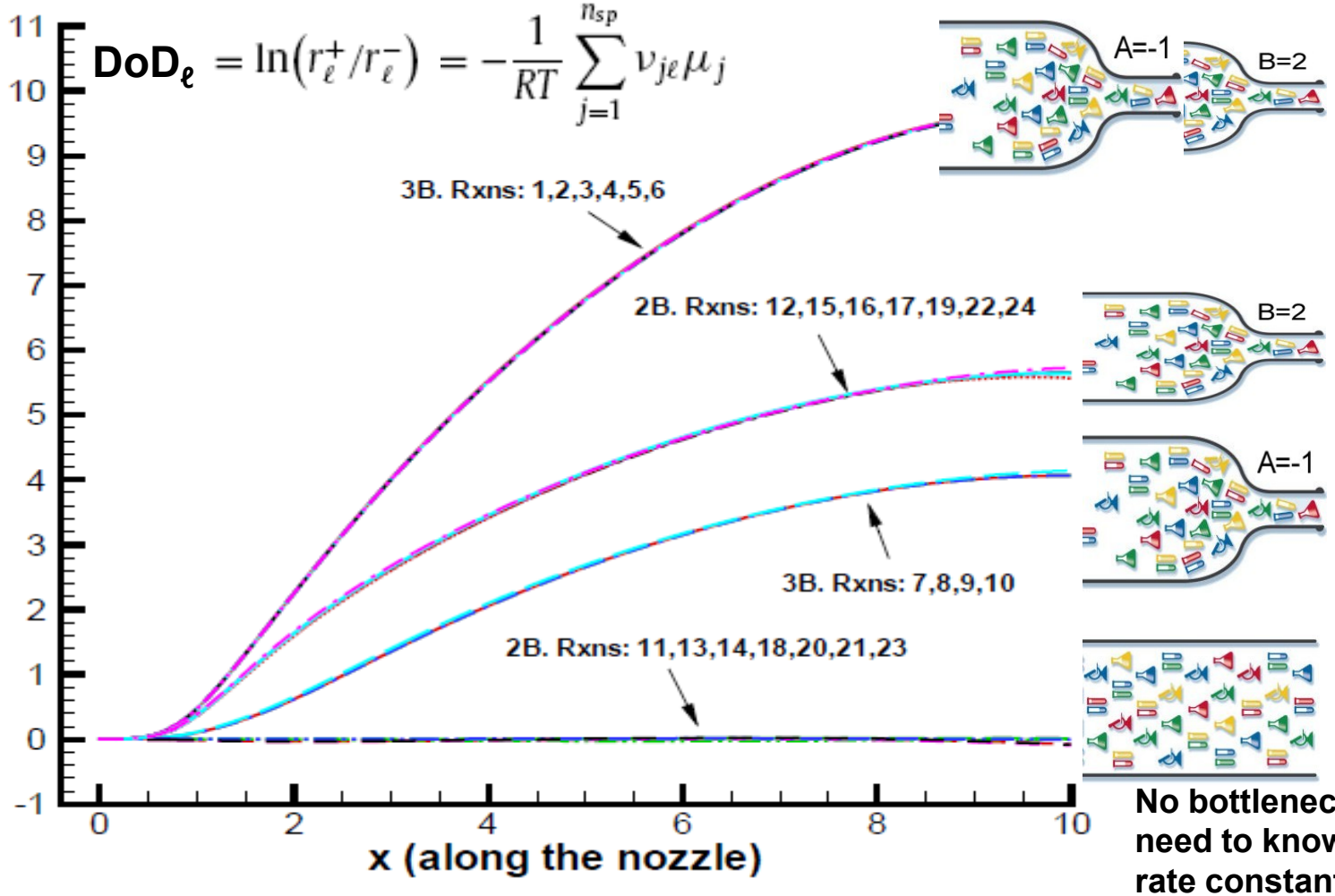
… but only few slow mechanisms are responsible for it



Janbozorgi, Metghalchi, AIAA Journal ofPropulsion and Power, Vol. 28, 677 (2012)

Most reactions get off equilibrium…

… but only few ~~slow mechanisms~~ are responsible for it bottleneck mechanisms



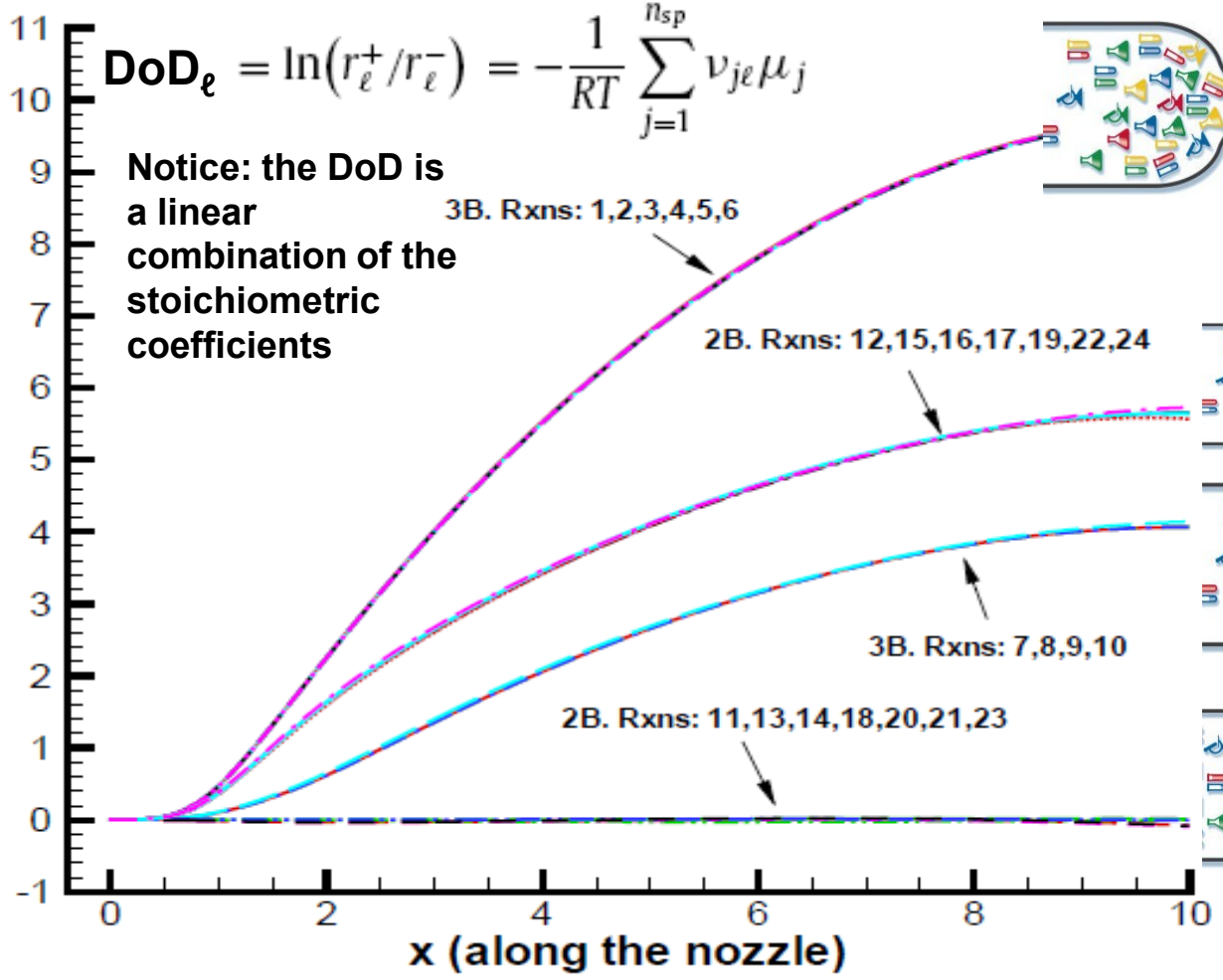
No bottleneck = no need to know the rate constants of these reactions

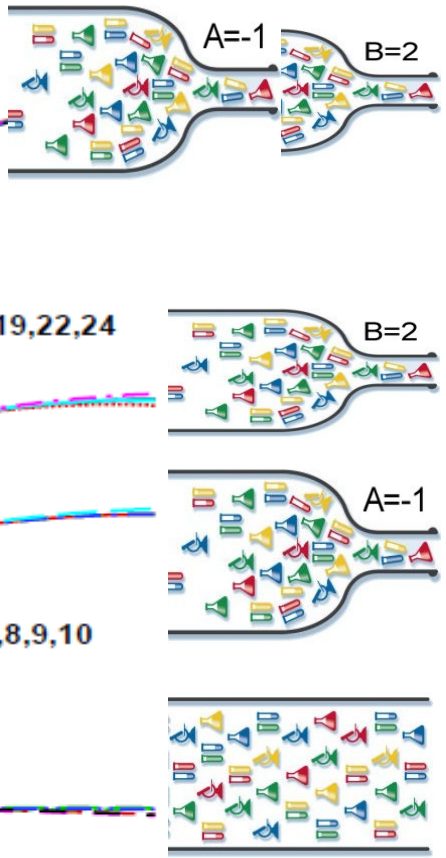
RCCE model reduction strategy

1) Identify the main bottleneck mechanisms
2) Identify the associated constraints

$$\mathrm{DoD}_\ell = \ln\left(r_\ell^+ / r_\ell^-\right) = -\frac{1}{RT}\sum_{j=1}^{n_{sp}} \nu_{j\ell}\mu_j$$

Notice: the DoD is a linear combination of the stoichiometric coefficients

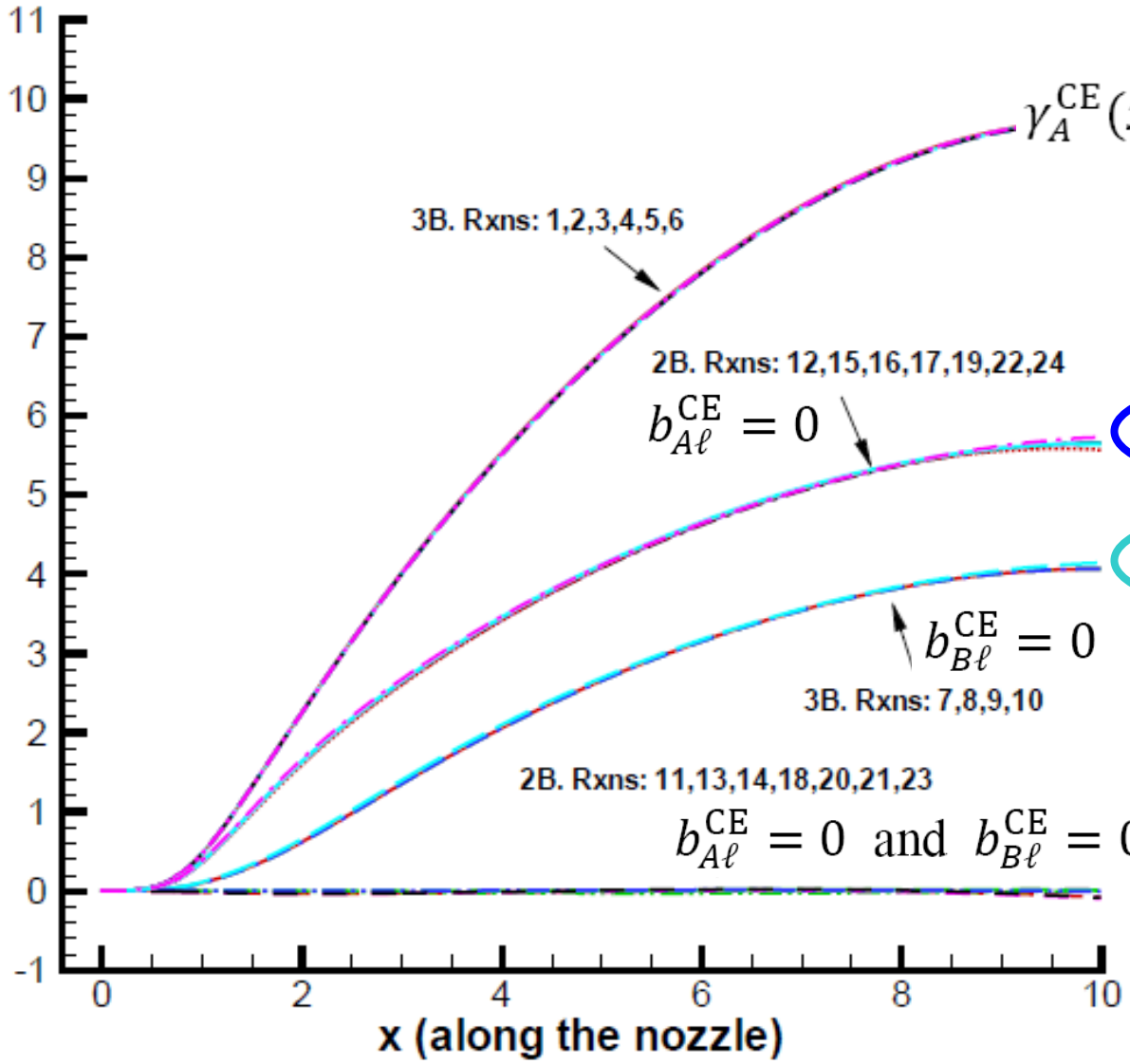




No bottleneck = no need to know the rate constants of these reactions

RCCE = Rate Controlled Constrained Equilibrium

DoD analysis allows constraint identification



$$\mathrm{DoD}_\ell = \gamma_A^{CE} b_{A\ell}^{CE} + \gamma_B^{CE} b_{B\ell}^{CE}$$

$$\mathrm{DoD}_\ell(x) = \gamma_A^{CE}(x)\, b_{A\ell}^{CE} + \gamma_B^{CE}(x)\, b_{B\ell}^{CE}$$

local equilibrium

The ***equilibrium composition*** $\boldsymbol{X}^{\mathrm{E}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL}, and a se

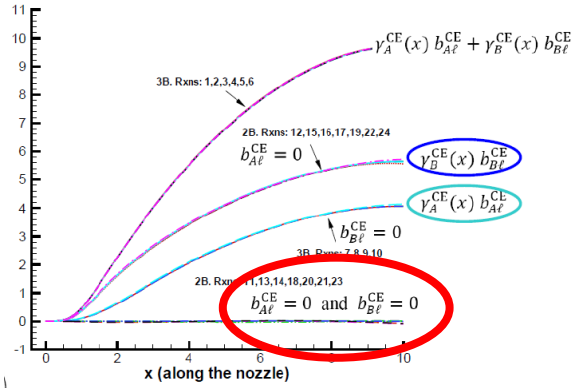
$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}} \qquad X_j^{\mathrm{E}} = \frac{[N_j]}{\sum_{j=1}^{n_{sp}} [N_j]}$$

For ideal gas behavior, $\mu_j(T, p, \boldsymbol{X}) = g_{j,\mathrm{pure}}(T, p) + RT\ln(X_j)$, the constrained minimization yields the composition $\boldsymbol{X}^{\mathrm{E}}$

$$\ln X_j^{\mathrm{E}} = -\frac{1}{RT} g_{j,\mathrm{pure}}(T, p) - \sum_{i=1}^{n_{\mathrm{el}}} \gamma_i^{\mathrm{EL}} a_{ij}^{\mathrm{EL}}$$

and, therefore, recalling that $b_{i\ell}^{\mathrm{EL}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$,

$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-) = -\frac{1}{RT} \sum_{j=1}^{n_s} \nu_{j\ell}\, \mu_j = 0$$



RCCE concept: local constrained equilibrium

The ***constrained equilibrium composition*** $\boldsymbol{X}^{\mathrm{CE}}$ minimizes the Gibbs free energy for the instantaneous local values of temperature T, pressure p, element amounts N_i^{EL}, and a set of $n_{\mathrm{c}}(<r)$ rate-controlling constraint densities $c_i(\mathbf{N})$,

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{EL}} N_j = N_i^{\mathrm{EL}} \qquad \text{for } i = 1,\ldots,n_{\mathrm{el}}$$

$$\sum_{j=1}^{n_{sp}} a_{ij}^{\mathrm{CE}} N_j = c_i(\mathbf{N}) \qquad \text{for } i = 1,\ldots,n_{\mathrm{c}}$$

$$X_j^{\mathrm{CE}} = \frac{[N_j]}{\sum_{j=1}^{n_{sp}} [N_j]}$$

For ideal gas behavior, $\mu_j(T,p,\boldsymbol{X}) = g_{j,\mathrm{pure}}(T,p) + RT\ln(X_j)$, the constrained minimization yields the composition $\boldsymbol{X}^{\mathrm{CE}}$

$$\ln X_j^{\mathrm{CE}} = -\frac{1}{RT} g_{j,\mathrm{pure}}(T,p) - \sum_{i=1}^{n_{\mathrm{el}}} \gamma_i^{\mathrm{EL}} a_{ij}^{\mathrm{EL}} - \sum_{i=1}^{n_{\mathrm{c}}} \gamma_i^{\mathrm{CE}} a_{ij}^{\mathrm{CE}}$$

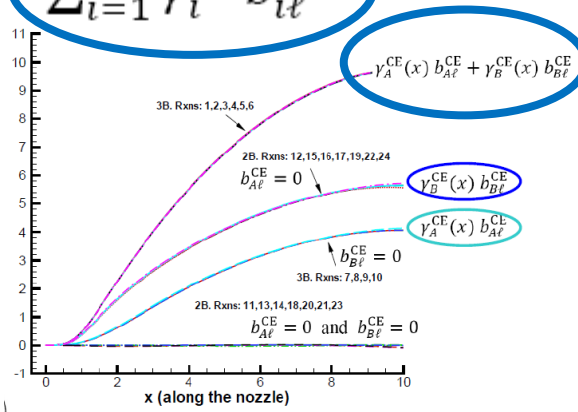
and, therefore, recalling that $b_{i\ell}^{\mathrm{EL}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$,

$$\mathrm{DoD}_\ell = \ln(r_\ell^+ / r_\ell^-) = -\frac{1}{RT} \sum_{j=1}^{n_s} \nu_{j\ell}\, \mu_j = \sum_{i=1}^{n_{\mathrm{c}}} \gamma_i^{\mathrm{CE}} b_{i\ell}^{\mathrm{CE}}$$

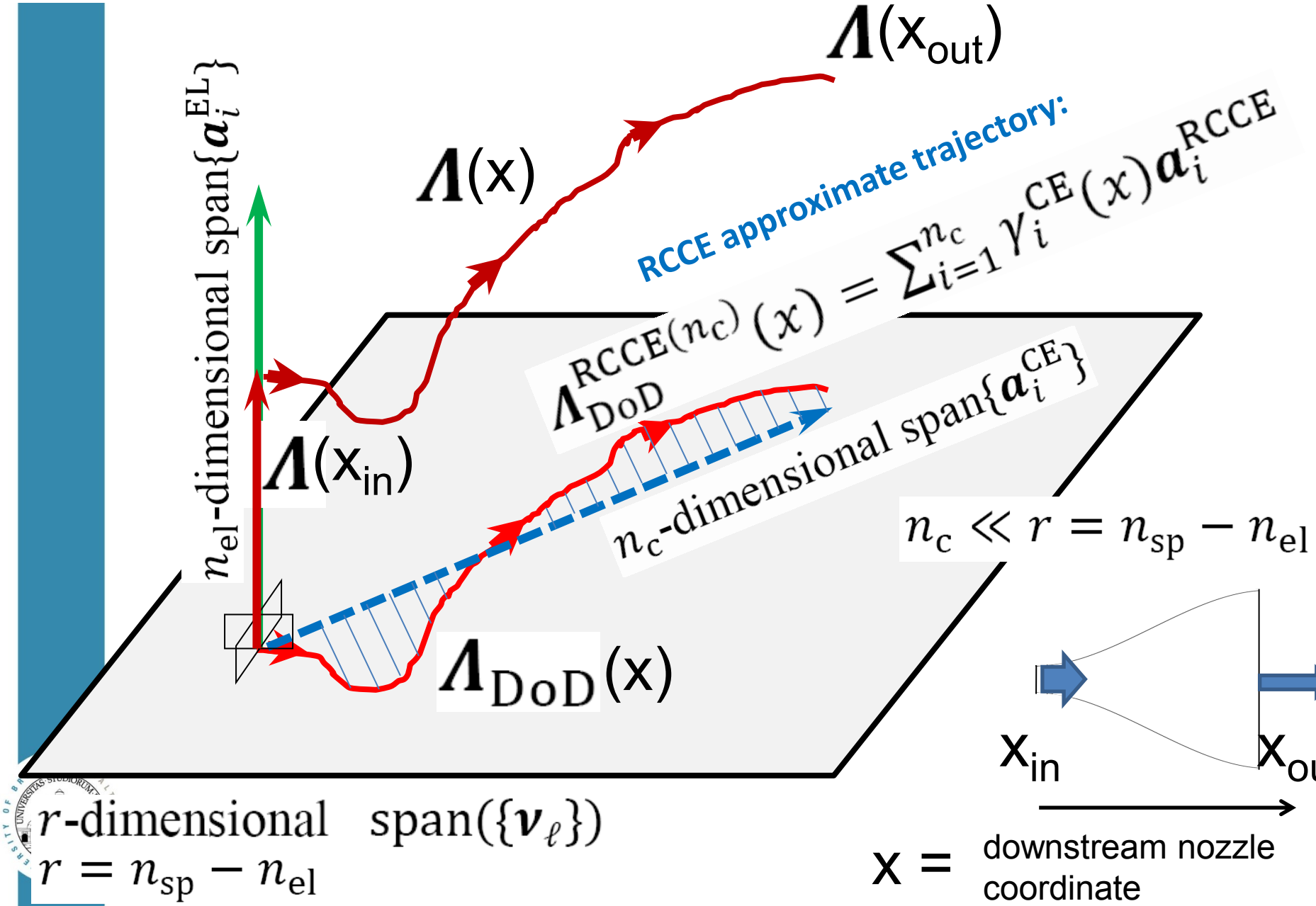
where $b_{i\ell}^{\mathrm{CE}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{CE}} \nu_{j\ell}$.

$$\mathrm{DoD}_\ell(x) = \boldsymbol{\Lambda}_{\mathrm{DoD}}^{\mathrm{CE}(n_{\mathrm{c}})}(t_p) \cdot \boldsymbol{\nu}_\ell$$

$$\boldsymbol{\Lambda}_{\mathrm{DoD}}^{\mathrm{CE}(n_{\mathrm{c}})}(x) = \sum_{i=1}^{n_{\mathrm{c}}} \gamma_i^{\mathrm{CE}}(x) \boldsymbol{a}_i^{\mathrm{CE}}$$



$$\mathbb{R}^{n_{sp}} = \text{span}(\{\boldsymbol{\nu}_\ell\}) \oplus \text{span}(\{\boldsymbol{a}_i^{EL}\})$$



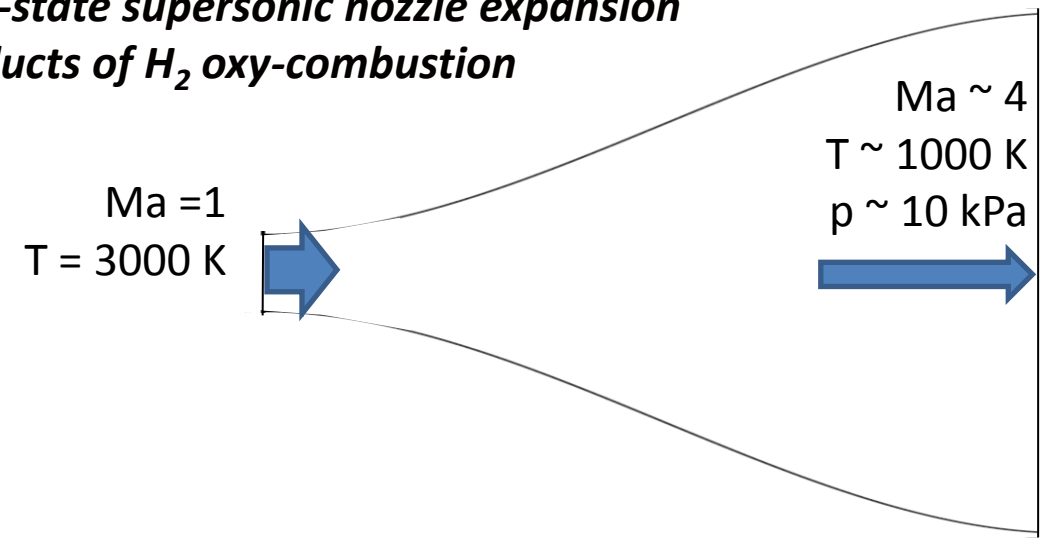
r-dimensional span$(\{\boldsymbol{\nu}_\ell\})$

$r = n_{sp} - n_{el}$

x = downstream nozzle coordinate

RCCE yields excellent predictions, IF we select the 'right' constraints

ROCKET EXAMPLE: Steady-state supersonic nozzle expansion of high-temperature products of H_2 oxy-combustion



Rate equations for the constraint potentials

$\dot{\gamma}_k^{\mathrm{EL}}$ $\dot{\gamma}_k^{\mathrm{RC}}$

conven use $\beta = 1/R$ of the temperature and the notation $N_j = [N_j]V$ for the number of moles of species j, u_{jj} and c_{vjj} for the molar s nternal energy capacity at constant volume of species j, Φ for the viscous dissipation function (usually negligible),

$$\sum_{k=1}^{n_{\mathrm{el}}} \dot{\gamma}_k^{\mathrm{EL}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{EL}} N_j a_{ij}^{\mathrm{EL}} + \sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{RC}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{RC}} N_j a_{ij}^{\mathrm{EL}} = -\frac{\dot{\beta}}{\beta} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \beta u_{jj} a_{ij}^{\mathrm{EL}} + \frac{\dot{V}}{V} \sum_{j=1}^{n_{\mathrm{sp}}} N_j a_{ij}^{\mathrm{EL}} + \sum_{j=1}^{n_{\mathrm{sp}}} a_{ij}^{\mathrm{EL}} \dot{N}_j^{\rightarrow} \qquad \text{for } i = 1, \ldots, n_{\mathrm{el}} \tag{7}$$

$$\sum_{k=1}^{n_{\mathrm{el}}} \dot{\gamma}_k^{\mathrm{EL}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{EL}} N_j a_{ij}^{\mathrm{RC}} + \sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{RC}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{RC}} N_j a_{ij}^{\mathrm{RC}} = -\frac{\dot{\beta}}{\beta} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \beta u_{jj} a_{ij}^{\mathrm{RC}} + \frac{\dot{V}}{V} \sum_{j=1}^{n_{\mathrm{sp}}} N_j a_{ij}^{\mathrm{RC}} + \sum_{j=1}^{n_{\mathrm{sp}}} a_{ij}^{\mathrm{RC}} \dot{N}_j^{\rightarrow} - \dot{c}_{i,\mathrm{chem}}(\beta, p, \boldsymbol{N}) \qquad \text{for } i = 1, \ldots, n_{\mathrm{c}} \tag{8}$$

$$\sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{EL}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{EL}} N_j \beta u_{jj} + \sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{RC}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{RC}} N_j \beta u_{jj} = -\frac{\dot{\beta}}{\beta} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \left(\beta^2 u_{jj}^2 + \frac{c_{vjj}}{R} \right) + \frac{\dot{V}}{V} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \beta u_{jj} + \beta \dot{E}^{\rightarrow} + \beta p \dot{V} - \beta V \Phi \tag{9}$$

$$\sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{EL}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{EL}} N_j + \sum_{k=1}^{n_{\mathrm{c}}} \dot{\gamma}_k^{\mathrm{RC}} \sum_{j=1}^{n_{\mathrm{sp}}} a_{kj}^{\mathrm{RC}} N_j = -\frac{\dot{\beta}}{\beta} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \left(\beta u_{jj} + 1 \right) - \frac{\dot{p}}{p} \sum_{j=1}^{n_{\mathrm{sp}}} N_j \tag{10}$$

where $\dot{N}_j^{\rightarrow}$ and $\dot{E}^{\rightarrow}$ denote the species and energy transport rates (positive if outgoing) and the bottleneck source terms are

$$\dot{c}_{i,\mathrm{chem}}(\beta, p, \boldsymbol{N}) = V \sum_{\ell=1}^{n_{\mathrm{r}}} \left(\sum_{m=1}^{n_{\mathrm{sp}}} a_{im}^{\mathrm{RC}} \nu_{m\ell} \right) \left[\frac{k_\ell^+(\beta, p)}{V^{\nu_\ell^+}} \prod_{j=1}^{n_{\mathrm{sp}}} (N_j)^{\nu_{j\ell}^+} - \frac{k_\ell^-(\beta, p)}{V^{\nu_\ell^-}} \prod_{j=1}^{n_{\mathrm{sp}}} (N_j)^{\nu_{j\ell}^-} \right] \tag{11}$$

and of course the composition is that given by Eq. (1), i.e.,

$$N_j = \beta p V X_j = \exp\left(-g_{j,\mathrm{pure}}(\beta, p)\beta - \sum_{i=1}^{n_{\mathrm{el}}} \gamma_i^{\mathrm{EL}} a_{ij}^{\mathrm{EL}} - \sum_{i=1}^{n_{\mathrm{c}}} \gamma_i^{\mathrm{RC}} a_{ij}^{\mathrm{RC}} \right) \qquad \text{for } j = 1, \ldots, n_{\mathrm{sp}} \tag{12}$$

The above $n_{\mathrm{el}} + n_{\mathrm{nc}} + 2$ implicit differential equations together with the n_{sp} Eqs. (12) can be solved for given values of $\dot{E}^{\rightarrow}$, $V(t)$, and the $\dot{N}_j^{\rightarrow}$, to yield the $n_{\mathrm{sp}} + 2$ state variables $\beta(t)$, $p(t)$, and $N_j(t)$, and the $n_{\mathrm{el}} + n_{\mathrm{c}}$ constraint-potentials $\gamma_i^{\mathrm{EL}}(t)$ and $\gamma_i^{\mathrm{RC}}(t)$.

It is important to notice that in Eqs. (11) only the chemical reactions that are not equilibrated contribute to $\dot{c}_{i,\mathrm{chem}}$, i.e., only those for which $b_{i\ell}^{\mathrm{RC}} = \sum_{m=1}^{n_{\mathrm{sp}}} a_{im}^{\mathrm{RC}} \nu_{m\ell} \neq 0$. In fact, from Eqs. (2), (14) and (6) we can write

$$\phi_\ell^{\mathrm{DKM}} = \sum_{j=1}^{n_{\mathrm{sp}}} \Lambda_{\mathrm{DoD},jz}^{\mathrm{DKM}} \nu_{j\ell} = \sum_{j=1}^{n_{\mathrm{sp}}} \nu_{j\ell} \sum_{k=1}^{r} U_{jk} \sigma_k V_{kz} = \sum_{k=1}^{r} \left(\sum_{j=1}^{n_{\mathrm{sp}}} \nu_{j\ell} U_{jk} \right) \sigma_k V_{kz} = \sum_{i=1}^{r} b_{i\ell} \sigma_i V_{iz} = \sum_{i=1}^{r} b_{i\ell} \sigma_i \gamma_{iz}^{\mathrm{DKM}} \qquad \text{where we defined} \qquad b_{i\ell} = \sum_{j=1}^{n_{\mathrm{sp}}} \nu_{j\ell} U_{ji} \tag{13}$$

which shows that within the RCCE approximation, whereby we set to zero the singular values $\sigma_{n_{\mathrm{c}}+1} = \sigma_{n_{\mathrm{c}}+2} = \cdots = \sigma_r = 0$ and we set $a_{ij}^{\mathrm{RC}} = U_{ji}$ for $i = 1, \ldots, n_{\mathrm{c}}$, the DoD's are given by

$$\phi_\ell^{\mathrm{RCCE}} = \sum_{i=1}^{n_{\mathrm{c}}} b_{i\ell}^{\mathrm{RC}} \sigma_i V_{iz} = \sum_{i=1}^{n_{\mathrm{c}}} b_{i\ell}^{\mathrm{RC}} \gamma_{iz}^{\mathrm{RC}} \tag{14}$$

and therefore the reactions that contribute to $\dot{c}_{i,\mathrm{chem}}$, those with $b_{i\ell}^{\mathrm{RC}} \neq 0$, are those with a nonzero DoD.

Rate equations for the constraint potentials

$\dot{\gamma}_k^{\mathrm{EL}}$ $\dot{\gamma}_k^{\mathrm{RC}}$

conven use $\beta = 1/R$ of the temperature and the notation $N_j = [N_j]V$ for the number of moles of species j, u_{jj} and c_{vjj} for the molar s nternal energy capacity at constant volume of species j, Φ for the viscous dissipation function (usually negligible),

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$$\phi_\ell^{\mathrm{RCCI}}$$

and therefore the reactions that contribute to $\dot{c}_{i,\mathrm{chem}}$, those wi

EQUATIONS

differential equations	$n_{\mathrm{el}} + n_{\mathrm{nc}} + 2$
algebraic equations	n_{sp}

UNKNOWNS

state variables (T,p,$\boldsymbol{N}$)	$n_{\mathrm{sp}} + 2$
constraint potentials	$n_{\mathrm{el}} + n_{\mathrm{c}}$

RCCE advantage

$$X_j^{\mathrm{CE}} = \frac{[N_j]}{\sum_{j=1}^{n_{sp}} [N_j]}$$

$$\ln X_j^{\mathrm{CE}} = -\frac{1}{RT} g_{j,\mathrm{pure}}(T,p) - \sum_{i=1}^{n_{el}} \gamma_i^{\mathrm{EL}} a_{ij}^{\mathrm{EL}} - \sum_{i=1}^{n_c} \gamma_i^{\mathrm{CE}} a_{ij}^{\mathrm{CE}}$$

RCCE composition depends on only $2+n_{el}+n_c$ parameters

So, instead of the n_s species balance equations

$$[N_j]\frac{du}{dx} + u\frac{d[N_j]}{dx} + u[N_j]\left(\frac{1}{A}\frac{dA}{dx}\right) = \dot{\omega}_j$$

we need only $2+n_{el}+n_c$ differential equations

$n_{el}+n_c \ll n_s$

Hydrogen/Oxygen: 2 + 2	8
Methane/Air simplified: 3 + 10	29
Methane/Air full: 5 + 11	53

Complexity of comprehensive DKM's for hydrocarbon fuels

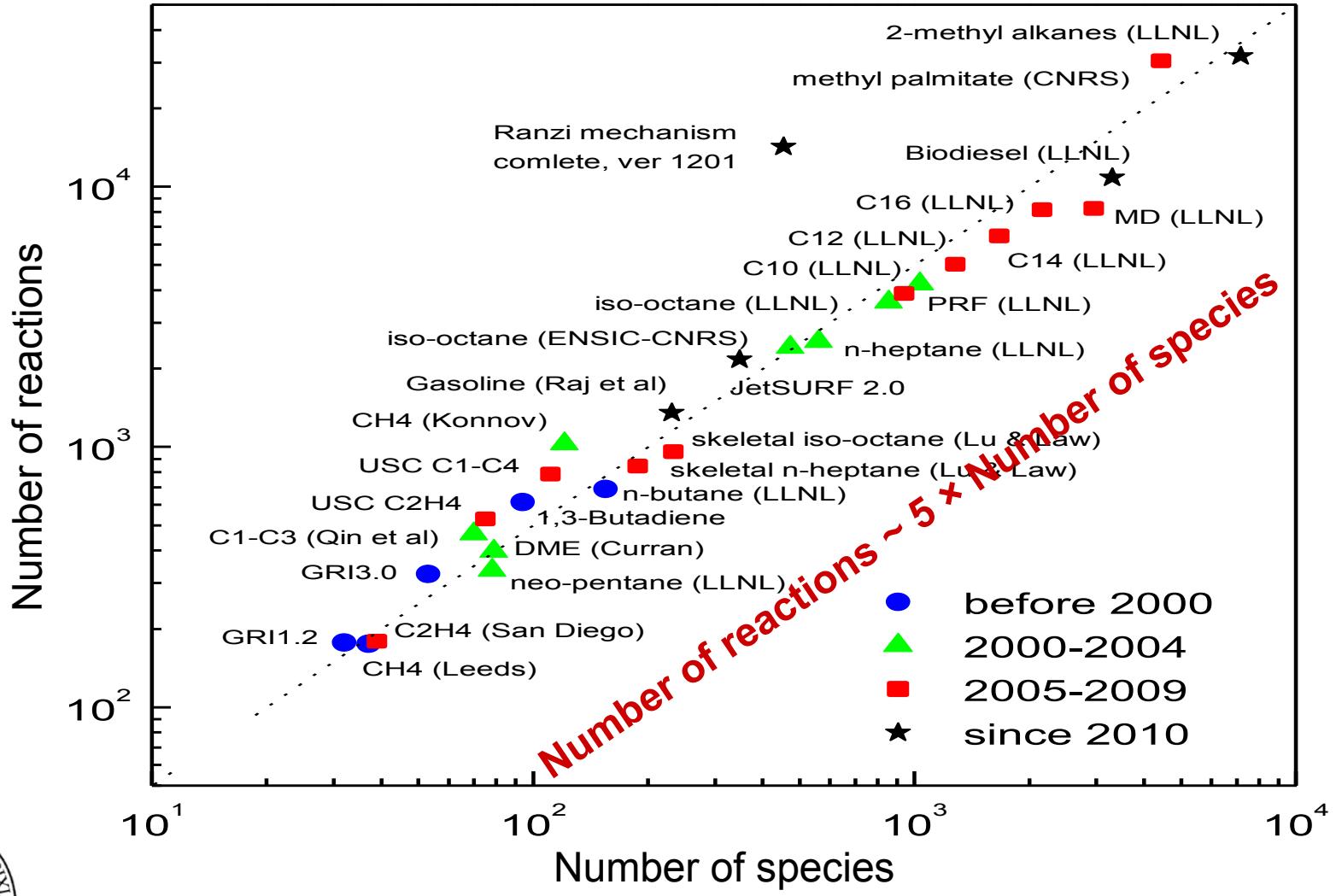

Figure modified form of Lu & Law (2009)

RCCE advantage

$$X_j^{CE} = \frac{[N_j]}{\sum_{j=1}^{n_{sp}} [N_j]}$$

$$\ln X_j^{CE} = -\frac{1}{RT} g_{j,\text{pure}}(T,p) - \sum_{i=1}^{n_{el}} \gamma_i^{EL} a_{ij}^{EL} - \sum_{i=1}^{n_c} \gamma_i^{CE} a_{ij}^{CE}$$

RCCE composition depends on only $2+n_{el}+n_c$ parameters

- **No need to cut the list of species**
  (yields excellent results also for the minor species)
- **No need to cut the list of reactions**
  (but only those 'less orthogonal' to the constraints contribute)
  (so the method is 'forgiving' with respect to poor rate constants)
- **No need to check thermodynamic consistency**
  (second law compatibility automatically satisfied)

$$n_{el}+n_c << n_s$$

Hydrogen/Oxygen: 2 + 2	8
Methane/Air simplified: 3 + 10	29
Methane/Air full: 5 + 11	53

But how do we find the ‘right’ constraints

Reaction	A	n	E_a
H_2/O_2 Chain Reactions			
$\dot{H} + O_2 = \dot{O} + \dot{O}H$	1.91×10^{14}	0.00	16.44
$\dot{O} + H_2 = \dot{H} + \dot{O}H$	5.08×10^{4}	2.67	6.292
$\dot{O}H + H_2 = \dot{H} + H_2O$	2.16×10^{8}	1.51	3.43
$\dot{O} + H_2O = \dot{O}H + \dot{O}H$	2.97×10^{6}	2.02	13.4
H_2/O_2 Dissociation/Recombination Reactions			
$H_2 + M = \dot{H} + \dot{H} + M$	4.57×10^{19}	−1.40	105.1
$\dot{O} + \dot{O} + M = O_2 + M$	6.17×10^{15}	−0.50	0.00
$\dot{O} + \dot{H} + M = O\dot{H} + M$	4.72×10^{18}	−1.00	0.00
$\dot{H} + \dot{O}H + M = H_2O + M$	4.50×10^{22}	−2.00	0.00
Formation and consumption of $H\dot{O}_2$			
$\dot{H} + O_2 + M = H\dot{O}_2 + M$	3.48×10^{16}	−0.41	−1.12
$\dot{H} + O_2 = H\dot{O}_2$	1.48×10^{12}	0.60	0.00
$H\dot{O}_2 + \dot{H} = H_2 + O_2$	1.66×10^{13}	0.00	0.82
$H\dot{O}_2 + \dot{H} = \dot{O}H + \dot{O}H$	7.08×10^{13}	0.00	0.30
$H\dot{O}_2 + \dot{O} = \dot{O}H + O_2$	3.25×10^{13}	0.00	0.00
$H\dot{O}_2 + \dot{O}H = H_2O + O_2$	2.89×10^{13}	0.00	−0.50
Formation and Consumption of H_2O_2			
$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	4.2×10^{14}	0.00	11.98
$H\dot{O}_2 + H\dot{O}_2 = H_2O_2 + O_2$	1.3×10^{11}	0.00	−1.629
$H_2O_2 + M = \dot{O}H + O\dot{H} + M$	1.27×10^{17}	0.00	45.5
$H_2O_2 = \dot{O}H + O\dot{H}$	2.95×10^{14}	0.00	48.4
$H_2O_2 + \dot{H} = H_2O + \dot{O}H$	2.41×10^{13}	0.00	3.97
$H_2O_2 + \dot{H} = H_2 + H\dot{O}_2$	6.03×10^{13}	0.00	7.95
$H_2O_2 + \dot{O} = \dot{O}H + H\dot{O}_2$	9.55×10^{06}	2.00	3.97
$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	1.0×10^{12}	0.00	0.00
$H_2O_2 + \dot{O}H = H_2O + H\dot{O}_2$	5.8×10^{14}	0.00	9.56

Slow dissociation/recombination
three body reactions
(M - Total Moles)

Chain branching/propagating
reactions
(FV - Free Valence)

-O-O- bond breaking reactions
(FO - Free Oxygen)

and many others based on deep studies of the detailed mechanisms

James C. Keck (1924-2010)
www.jameskeckcollectedworks.org

M – Total Moles

Slow dissociation/recombination
(three body collisions)

Species
O
O2
H
H2
OH
H2O
HO2
H2O2

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2	Typical constraints M	FV	FO
										1	2	1
										1	0	0
										1	1	0
										1	0	0
										1	1	1
										1	0	1
										1	1	0
										1	0	0
11	O+H2=H+OH	-1	0	1	-1	1	0	0	0	0	0	0
13	O+H2O2=OH+HO2	-1	0	0	0	1	0	1	-1	0	0	0
14	H+O2=O+OH	1	-1	-1	0	1	0	0	0	0	2	2
18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1	0	0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0	0	0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0	0	0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1	0	0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0	-1	0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0	-1	0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0	-1	0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1	-1	-2	-2
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0	0	-2	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0	0	0	2
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0	0	-2	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0	0	0	2
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1	0	0	2
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0	0	-2	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1	0	-2	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0	-1	-4	-2
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0	-1	-2	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0	-1	-2	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0	-1	-2	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0	-1	-2	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0	-1	-2	0

$$a_i^{\mathrm{M}}$$

$$b_{i\ell}^{\mathrm{M}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{M}} \nu_{j\ell}$$

$$O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$$

Species
O
O2
H
H2
OH
H2O
HO2
H2O2

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2	Typical constraints M	FV	FO
										1	2	1
										1	0	0
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11	O+H2=H+OH	-1	0	1	-1	1	0	0	0	0	0	0
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18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1	0	0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0	0	0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0	0	0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1	0	0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0	-1	0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0	-1	0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0	-1	0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1	-1	-2	-2
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0	0	-2	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0	0	0	2
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0	0	-2	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0	0	0	2
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1	0	0	2
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0	0	-2	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1	0	-2	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0	-1	-4	-2
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0	-1	-2	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0	-1	-2	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0	-1	-2	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0	-1	-2	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0	-1	-2	0

M – Total Moles

Slow dissociation/recombination
(three body collisions)

$$b_{i\ell}^{\mathrm{M}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{M}} \nu_{j\ell}$$

FV – Free Valence

Chain branching/propagating reactions

$$\boldsymbol{a}_i^{\mathrm{FV}}$$

$$b_{i\ell}^{\mathrm{FV}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{FV}} \nu_{j\ell}$$

$$\mathrm{H\dot{O}_2} + \dot{\mathrm{H}} = \mathrm{H_2} + \mathrm{O_2}$$

Species	
O	
O2	
H	
H2	
OH	
H2O	
HO2	
H2O2	

	Reaction	O	O2	H	H2	OH	H2O	HO2	H2O2	Typical constraints M	FV	FO
11	O+H2=H+OH	-1	0	1	-1	1	0	0	0	0	0	0
13	O+H2O2=OH+HO2	-1	0	0	0	1	0	1	-1	0	0	0
14	H+O2=O+OH	1	-1	-1	0	1	0	0	0	0	2	2
18	H+H2O2=HO2+H2	0	0	-1	1	0	0	1	-1	0	0	0
20	OH+H2=H+H2O	0	0	1	-1	-1	1	0	0	0	0	0
21	OH+OH=O+H2O	1	0	0	0	-2	1	0	0	0	0	0
23	OH+H2O2=HO2+H2O	0	0	0	0	-1	1	1	-1	0	0	0
7	H+O2+M=HO2+M	0	-1	-1	0	0	0	1	0	-1	0	0
8	H+O2+O2=HO2+O2	0	-1	-1	0	0	0	1	0	-1	0	0
9	H+O2+H2O=HO2+H2O	0	-1	-1	0	0	0	1	0	-1	0	0
10	OH+OH+M=H2O2+M	0	0	0	0	-2	0	0	1	-1	-2	-2
12	O+HO2=OH+O2	-1	1	0	0	1	0	-1	0	0	-2	0
15	H+HO2=O+H2O	1	0	-1	0	0	1	-1	0	0	0	2
16	H+HO2=O2+H2	0	1	-1	1	0	0	-1	0	0	-2	0
17	H+HO2=OH+OH	0	0	-1	0	2	0	-1	0	0	0	2
19	H+H2O2=OH+H2O	0	0	-1	0	1	1	0	-1	0	0	2
22	OH+HO2=O2+H2O	0	1	0	0	-1	1	-1	0	0	-2	0
24	HO2+HO2=O2+H2O2	0	1	0	0	0	0	-2	1	0	-2	0
1	O+O+M=O2+M	-2	1	0	0	0	0	0	0	-1	-4	-2
2	O+H+M=OH+M	-1	0	-1	0	1	0	0	0	-1	-2	0
3	H+H+M=H2+M	0	0	-2	1	0	0	0	0	-1	-2	0
4	H+H+H2=H2+H2	0	0	-2	1	0	0	0	0	-1	-2	0
5	H+H+H2O=H2+H2O	0	0	-2	1	0	0	0	0	-1	-2	0
6	H+OH+M=H2O+M	0	0	-1	0	-1	1	0	0	-1	-2	0

M – Total Moles

Slow dissociation/recombination
(three body collisions)

$$b_{i\ell}^{\mathrm{M}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{M}} \nu_{j\ell}$$

FV – Free Valence

Chain branching/propagating reactions

$$b_{i\ell}^{\mathrm{FV}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{FV}} \nu_{j\ell}$$

FO – Free Oxygen

-O-O- bond breaking reactions

a_i^{FO}

$$b_{i\ell}^{\mathrm{FO}} = \sum_{j=1}^{n_s} a_{ij}^{\mathrm{FO}} \nu_{j\ell}$$

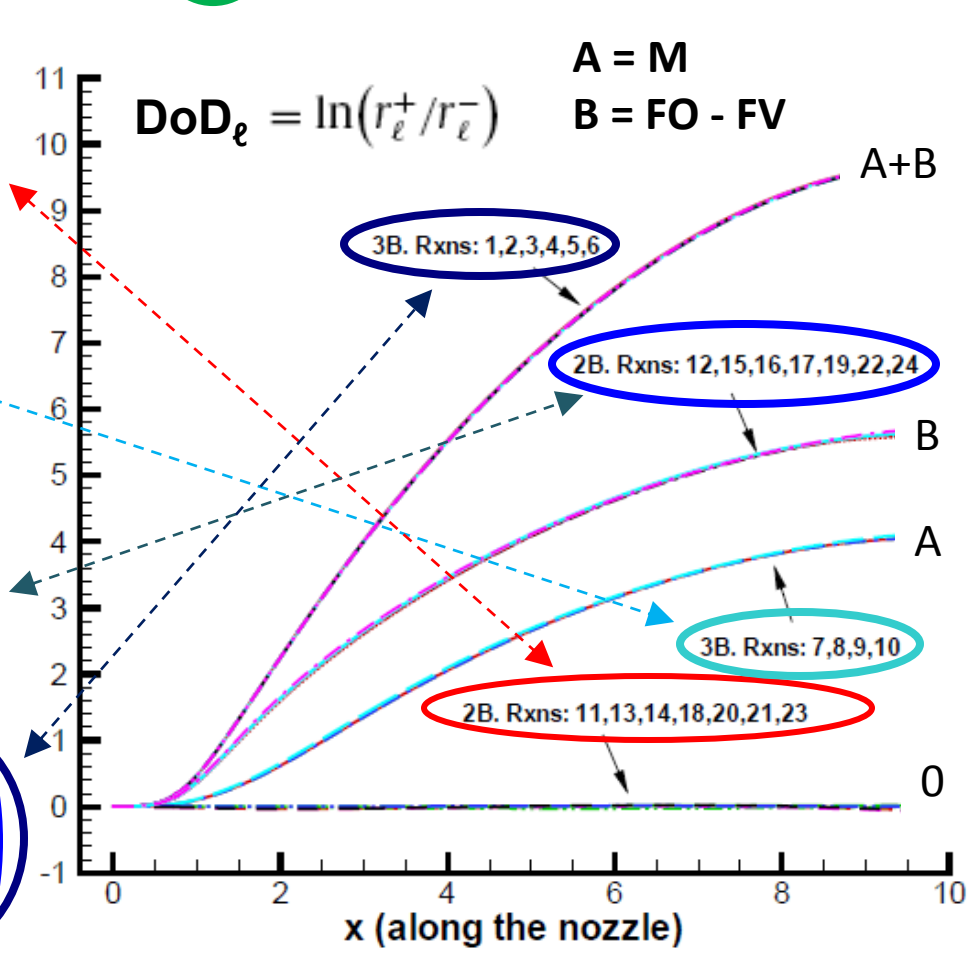
		Element conservation			Bottleneck constraints		
	Species	EO	EH			A	B
	O	1	0			1	-1
	O2	2	0			1	0
	H	0	1			1	-1
	H2	0	2			1	0
	OH	1	1			1	0
	H2O	1	2			1	1
	HO2	2	1			1	-1
	H2O2	2	2			1	0
	Reaction				Bottle-neck		
11	O+H2=H+OH	0	0		0	0	0
13	O+H2O2=OH+HO2	0	0		0	0	0
14	H+O2=O+OH	0	0		0	0	0
18	H+H2O2=HO2+H2	0	0		0	0	0
20	OH+H2=H+H2O	0	0		0	0	0
21	OH+OH=O+H2O	0	0		0	0	0
23	OH+H2O2=HO2+H2O	0	0		0	0	0
7	H+O2+M=HO2+M	0	0		A	-1	0
8	H+O2+O2=HO2+O2	0	0		A	-1	0
9	H+O2+H2O=HO2+H2O	0	0		A	-1	0
10	OH+OH+M=H2O2+M	0	0		A	-1	0
12	O+HO2=OH+O2	0	0		B	0	2
15	H+HO2=O+H2O	0	0		B	0	2
16	H+HO2=O2+H2	0	0		B	0	2
17	H+HO2=OH+OH	0	0		B	0	2
19	H+H2O2=OH+H2O	0	0		B	0	2
22	OH+HO2=O2+H2O	0	0		B	0	2
24	HO2+HO2=O2+H2O2	0	0		B	0	2
1	O+O+M=O2+M	0	0		A+B	-1	2
2	O+H+M=OH+M	0	0		A+B	-1	2
3	H+H+M=H2+M	0	0		A+B	-1	2
4	H+H+H2=H2+H2	0	0		A+B	-1	2
5	H+H+H2O=H2+H2O	0	0		A+B	-1	2
6	H+OH+M=H2O+M	0	0		A+B	-1	2

$$\sum_{j=1}^{n_s} a_{\mathrm{A}j}^{\mathrm{CE}} \nu_{j\ell} = b_{\mathrm{A}\ell}$$

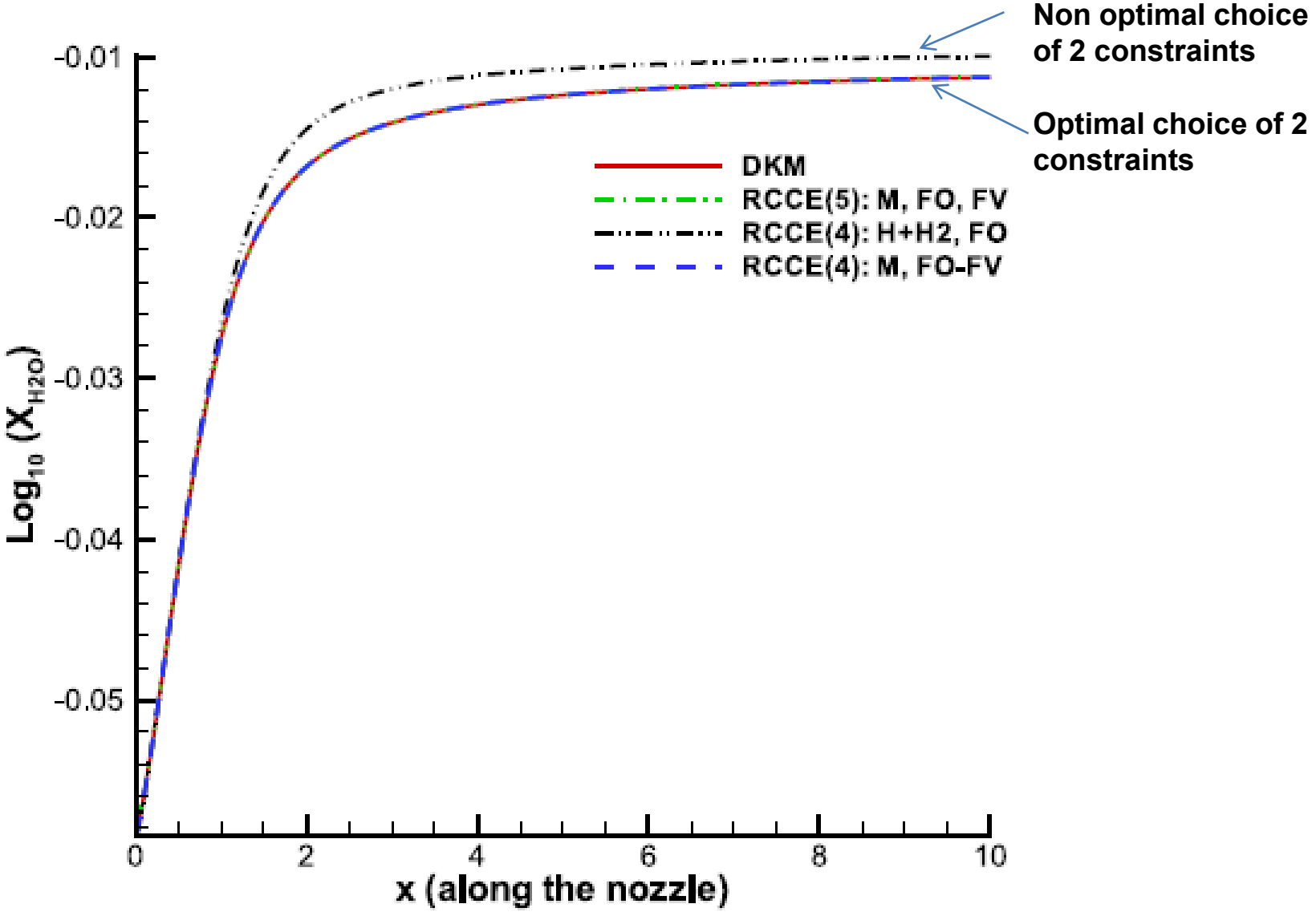
$$\sum_{j=1}^{n_s} a_{\mathrm{B}j}^{\mathrm{CE}} \nu_{j\ell} = b_{\mathrm{B}\ell}$$

$$\sum_{j=1}^{n_s} a_{ij}^{\mathrm{EL}} \nu_{j\ell} = 0$$

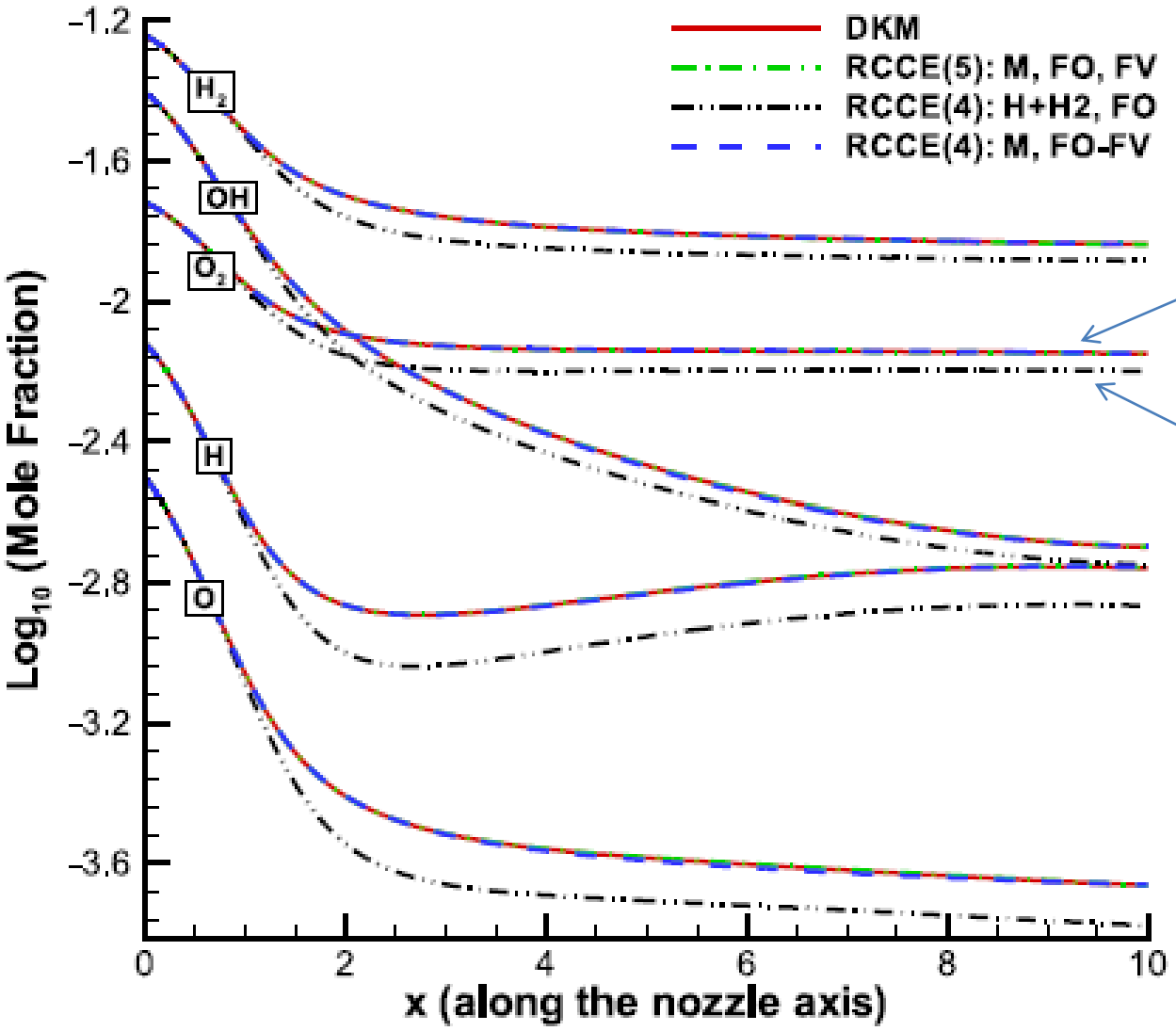
Group of reactions			
0	A	B	A+B
	✓		✓
		✓	✓
✓	✓	✓	✓



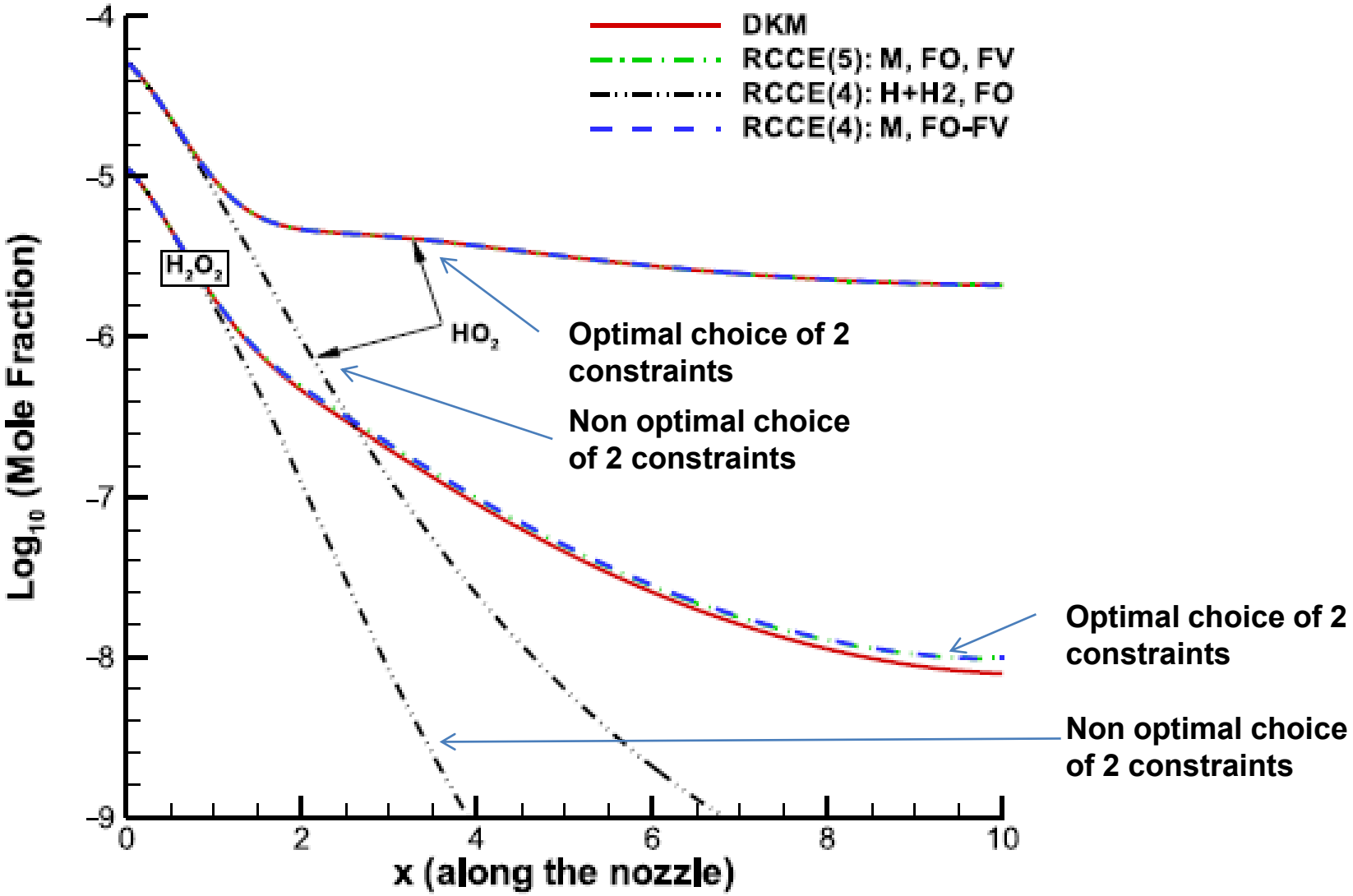
RCCE yields excellent predictions, IF we select the 'right' constraints



RCCE yields excellent predictions, IF we select the 'right' constraints



RCCE yields excellent predictions, IF we select the 'right' constraints

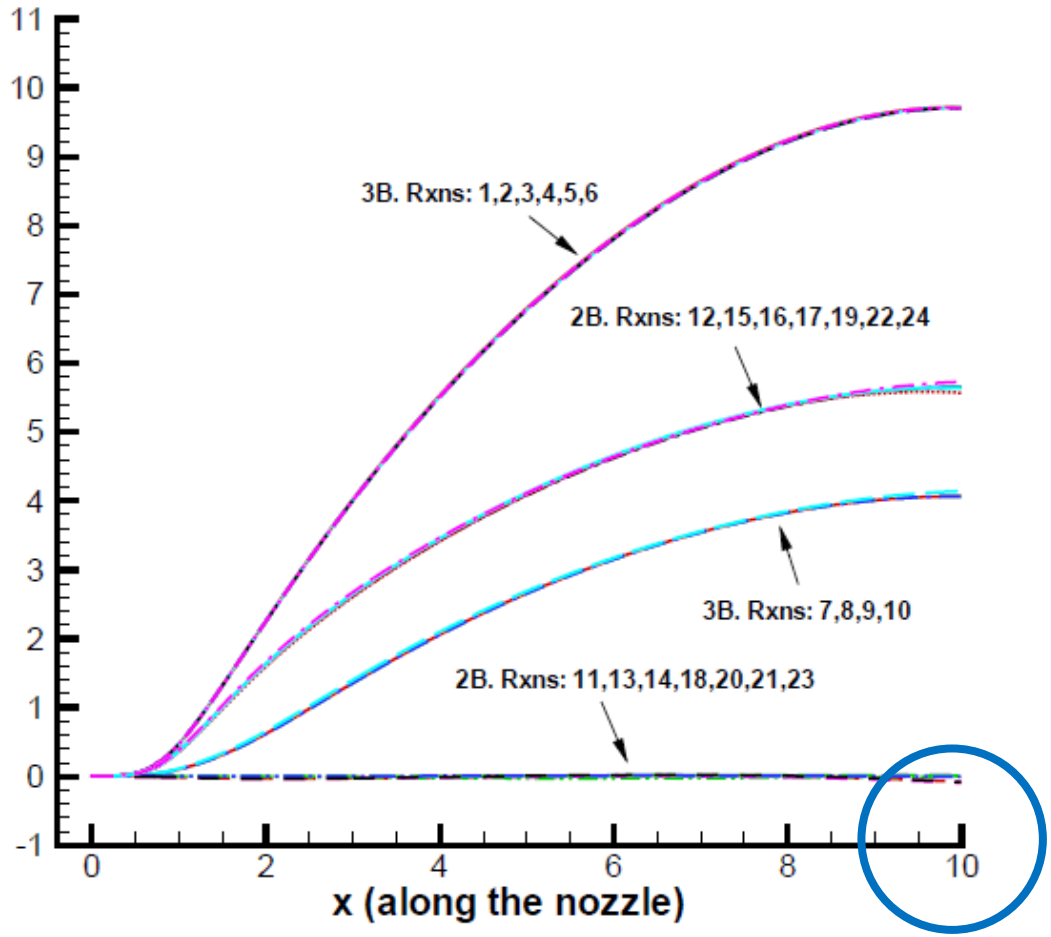


How to identify the ‘right’ constraints?

Our method: run a probe DKM and analyse the DoD traces

In simple cases relatively simple inspection is enough

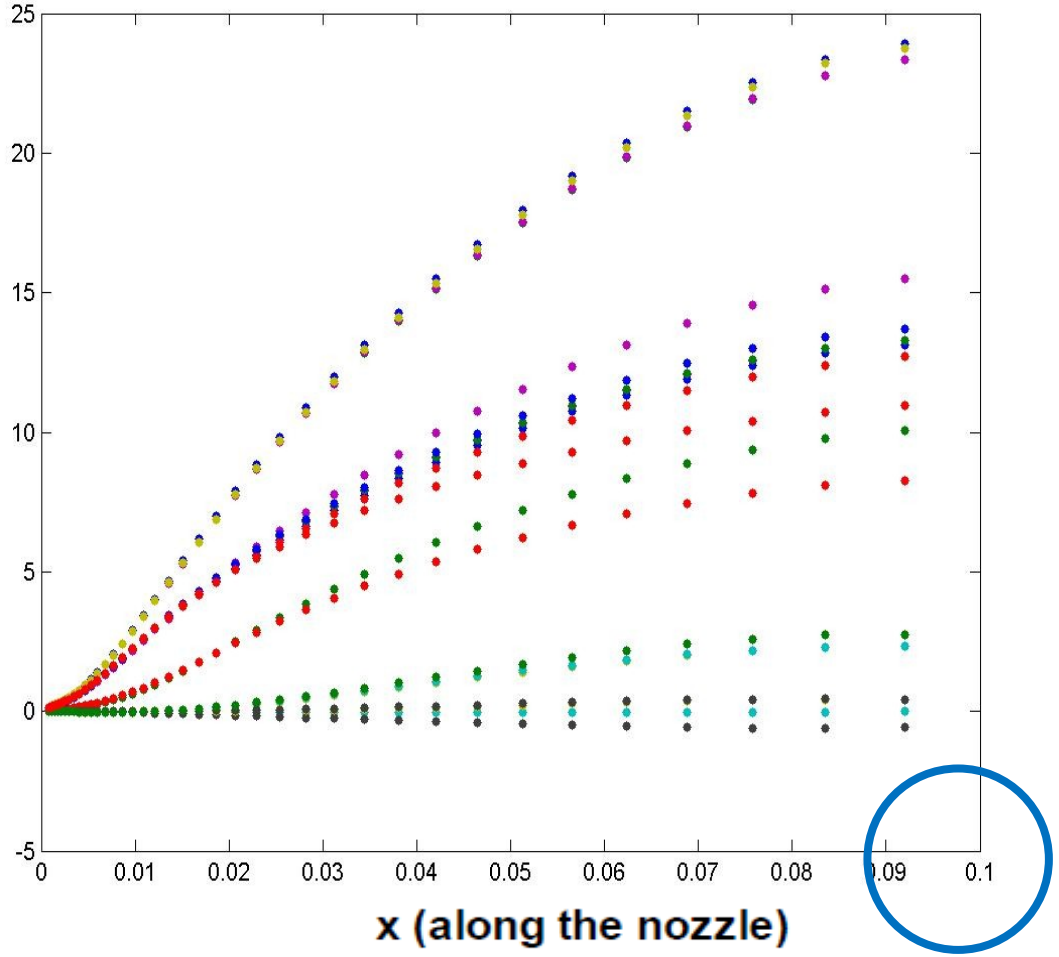
But how do we analyse more complex DoD traces?



How to identify the ‘right’ constraints?

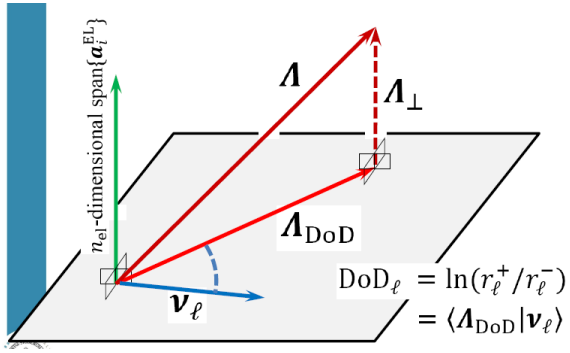
DoD(ℓ;x_p)
here with
ℓ = 1÷24
x_p = 1÷1700

only $r = n_{sp} - n_{el} = 8 - 2 = 6$
of these traces are independent

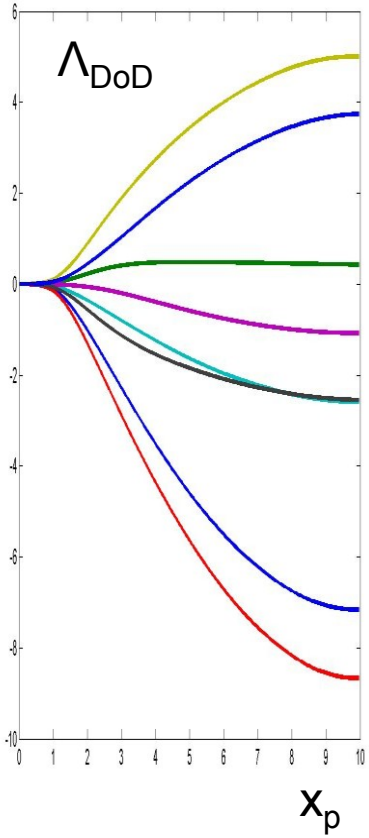


But how do we analyse more complex DoD traces?

ASVDADD method: Step 1: Run a probe DKM, get the DoD's and from them the Λ_{DoD} traces



$$\mathbf{DoD_\ell} = \phi_\ell = \ln(r_\ell^+/r_\ell^-) = \langle \Lambda_{DoD} | \nu_\ell \rangle$$



$\Lambda_{DoD}(x_p)$

x_p ⟶ 1700 columns (grid points)

8 rows ↓

0.000	…	0.001	…	0.001	…	0.002	…	0.004	…	0.005	…	0.008	…	0.010	…	0.014	…	0.018	…	0.024	…	0.032	…	0.042	…	0.055	…	0.071	…	0.092
-0.004	…	-0.054	…	-0.106	…	-0.179	…	-0.302	…	-0.517	…	-0.875	…	-1.422	…	-2.191	…	-3.198	…	-4.428	…	-5.846	…	-7.405	…	-9.029	…	-10.560	…	-11.592
0.001	…	0.015	…	0.030	…	0.049	…	0.082	…	0.137	…	0.222	…	0.330	…	0.435	…	0.508	…	0.549	…	0.579	…	0.618	…	0.671	…	0.725	…	0.734
-0.004	…	-0.071	…	-0.140	…	-0.235	…	-0.395	…	-0.671	…	-1.124	…	-1.804	…	-2.738	…	-3.927	…	-5.357	…	-6.993	…	-8.783	…	-10.640	…	-12.388	…	-13.592
-0.001	…	-0.019	…	-0.037	…	-0.063	…	-0.105	…	-0.178	…	-0.297	…	-0.479	…	-0.735	…	-1.069	…	-1.476	…	-1.942	…	-2.449	…	-2.977	…	-3.477	…	-3.832
0.000	…	-0.002	…	-0.003	…	-0.005	…	-0.011	…	-0.022	…	-0.046	…	-0.096	…	-0.192	…	-0.350	…	-0.569	…	-0.830	…	-1.115	…	-1.409	…	-1.681	…	-1.833
0.003	…	0.051	…	0.101	…	0.168	…	0.281	…	0.474	…	0.785	…	1.235	…	1.820	…	2.524	…	3.346	…	4.293	…	5.363	…	6.512	…	7.612	…	8.334
-0.002	…	-0.034	…	-0.067	…	-0.112	…	-0.185	…	-0.309	…	-0.503	…	-0.766	…	-1.065	…	-1.359	…	-1.633	…	-1.895	…	-2.149	…	-2.393	…	-2.618	…	-2.799
0.001	…	0.021	…	0.041	…	0.070	…	0.119	…	0.205	…	0.349	…	0.577	…	0.911	…	1.363	…	1.911	…	2.508	…	3.109	…	3.685	…	4.208	…	4.610

the rank of this matrix is only

$r = n_{sp} - n_{el} = 8 - 2 = 6$

ASVDADD method: Step 2: compute the Singular Value Decomposition of the $\Lambda_{DoD}(x_p)$ matrix

Given the 8 x 1700 matrix

$D = \Lambda_{DoD}(x_p)$

$$D = U \Sigma V^T$$

Beretta, Janbozorgi, Metghalchi, *Comb. Flame*, Vol.168, 342 (2016)

ASVDADD method: Step 2: compute the Singular Value Decomposition of the $\Lambda_{DoD}(x_p)$ matrix

Given matrix

$D = \Lambda_{DoD}(x_p)$

$$D = U \Sigma V^T$$

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

Beretta, Janbozorgi, Metghalchi, *Comb. Flame*, Vol.168, 342 (2016)

ASVDADD method: Step 3: choose a low-rank approximation of the $\Lambda_{DoD}(x_p)$ matrix

Given matrix
$D = \Lambda_{DoD}(x_p)$

Eckart-Young theorem

Given the $n_r \times P$ rectangular matrix $\boldsymbol{D}$ of rank $r = n_s - n_{el}$, the matrix $\widehat{\boldsymbol{D}}$ of $\text{rank}(\widehat{\boldsymbol{D}}) \leq n_c < r$ that minimizes $\left\|\boldsymbol{D} - \widehat{\boldsymbol{D}}\right\|_{\text{Frobenius}}$ is

$$\widehat{\boldsymbol{D}} = \boldsymbol{U}\,\widehat{\boldsymbol{\Sigma}}\,\boldsymbol{V}^T$$

where

$$\boldsymbol{D} = \boldsymbol{U}\,\boldsymbol{\Sigma}\,\boldsymbol{V}^T$$

is the canonical SVD of t
setting to zero its diagona

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

ASVDADD method: Step 3: choose a low-rank approximation of the $\Lambda_{DoD}(x_p)$ matrix

Given matrix
$D = \Lambda_{DoD}(x_p)$

Eckart-Young theorem

Given the $n_r \times P$ rectang

matrix $\widehat{\boldsymbol{D}}$ of rank$\left(\widehat{\boldsymbol{D}}\right) \leq r$

$$\widehat{\boldsymbol{D}} = \boldsymbol{U}\,\widehat{\boldsymbol{\Sigma}}\,\boldsymbol{V}^{\boldsymbol{T}}$$

where

$$\boldsymbol{D} = \boldsymbol{U}\,\boldsymbol{\Sigma}\,\boldsymbol{V}^{\boldsymbol{T}}$$

is the canonical SVD of t

setting to zero its diagona

Two constraints approximation

269.32	0	0	0	0	0	0	…
0	8.8739	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
…	…	…	…	…	…	…	…

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

ASVDADD choice of RCCE constraints: $a_{ij}^{\mathrm{RC}} = U_{ji}$

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ASVDADD method: Step 3: choose a low-rank approximation of the $\Lambda_{DoD}(x_p)$ matrix

Given matrix
$D = \Lambda_{DoD}(x_p)$

Eckart-Young theorem

Given the $n_r \times P$ rectang

matrix $\widehat{\boldsymbol{D}}$ of rank$\left(\widehat{\boldsymbol{D}}\right) \leq r$

$$\widehat{\boldsymbol{D}} = \boldsymbol{U}\,\widehat{\boldsymbol{\Sigma}}\,\boldsymbol{V}^{\boldsymbol{T}}$$

where

$$\boldsymbol{D} = \boldsymbol{U}\,\boldsymbol{\Sigma}\,\boldsymbol{V}^{\boldsymbol{T}}$$

is the canonical SVD of t

setting to zero its diagona

One constraint approximation

269.32	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
…	…	…	…	…	…	…	…

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

ASVDADD choice of RCCE constraints: $a_{ij}^{\mathrm{RC}} = U_{ji}$

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ASVDADD method: Step 4: pick the 'surviving' columns of the *U* matrix as RCCE constraints

Given matrix
$D = \Lambda_{DoD}(x_p)$

Eckart-Young theorem

Given the $n_r \times P$ rectang

matrix $\widehat{\boldsymbol{D}}$ of rank$(\widehat{\boldsymbol{D}}) \leq r$

$$\widehat{\boldsymbol{D}} = \boldsymbol{U}\widehat{\boldsymbol{\Sigma}}\boldsymbol{V}^T$$

where

$$\boldsymbol{D} = \boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{V}^T$$

is the canonical SVD of t

setting to zero its diagona

One constraint approximation

269.32	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
…	…	…	…	…	…	…	…

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

ASVDADD choice of RCCE constraints: $a_{ij}^{RC} = U_{ji}$

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ASVDADD meth… ‘surviving’ columns of the … constraints

269.32	0	0	0	0	0	0	0
0	8.8739	0	0	0	0	0	0
0	0	1.7137	0	0	0	0	0
0	0	0	0.2505	0	0	0	0
0	0	0	0	0.0458	0	0	0
0	0	0	0	0	0.0324	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

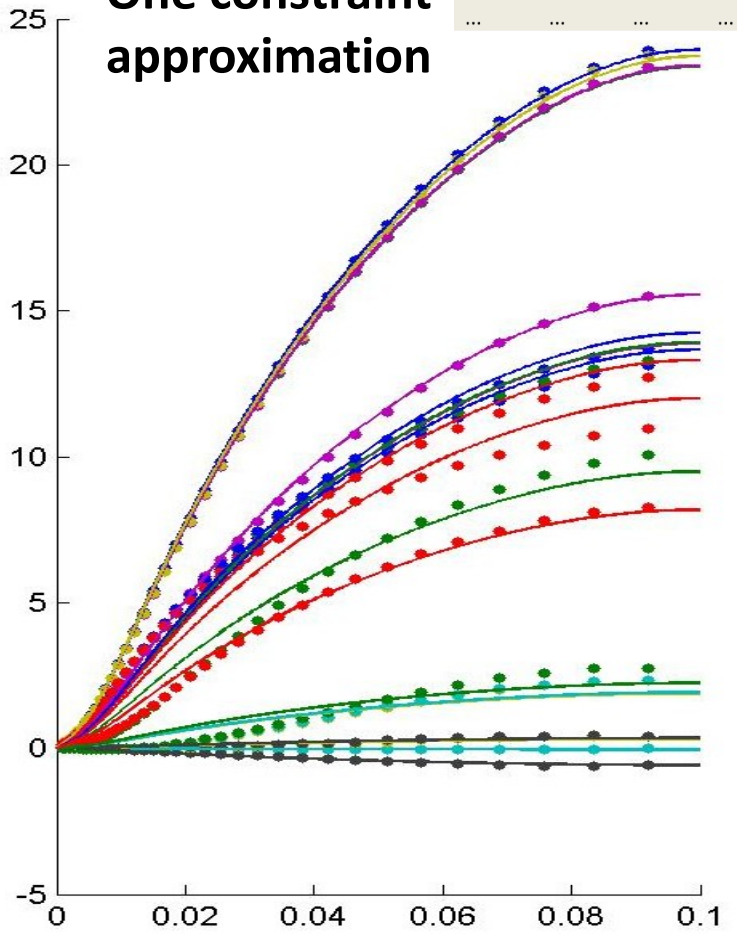
269.32	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
					0	0	…
					0	0	…
…	…	…	…	…	…	…	…

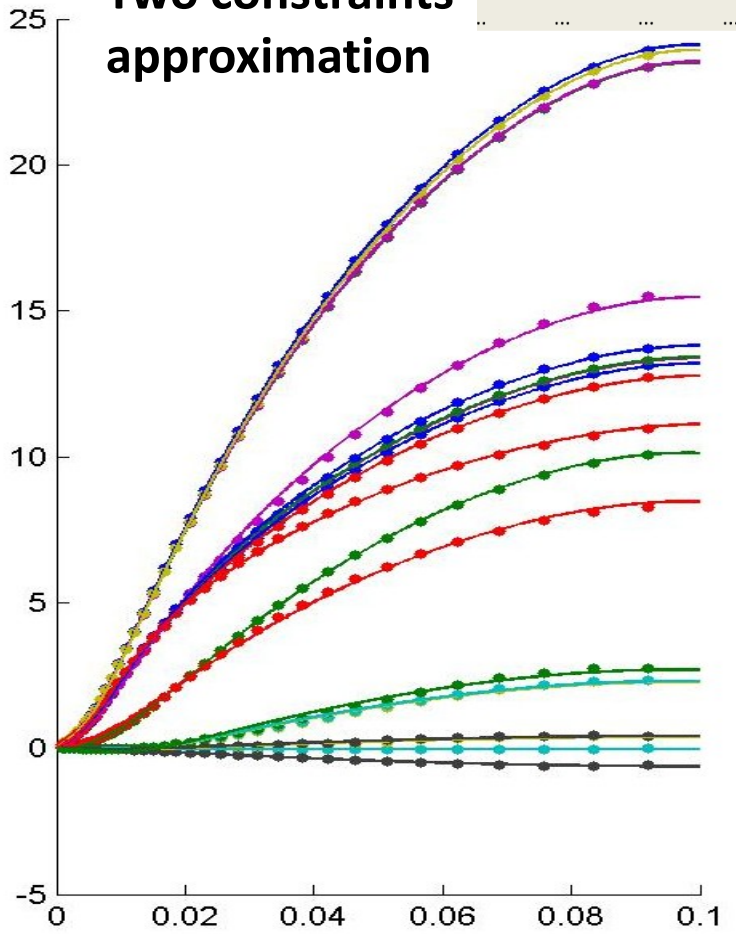
269.32	0	0	0	0	0	0	…
0	8.8739	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
0	0	0	0	0	0	0	…
					0	0	…
					0	0	…
…	…	…	…	…	…	…	…

One constraint approximation

Two constraints approximation

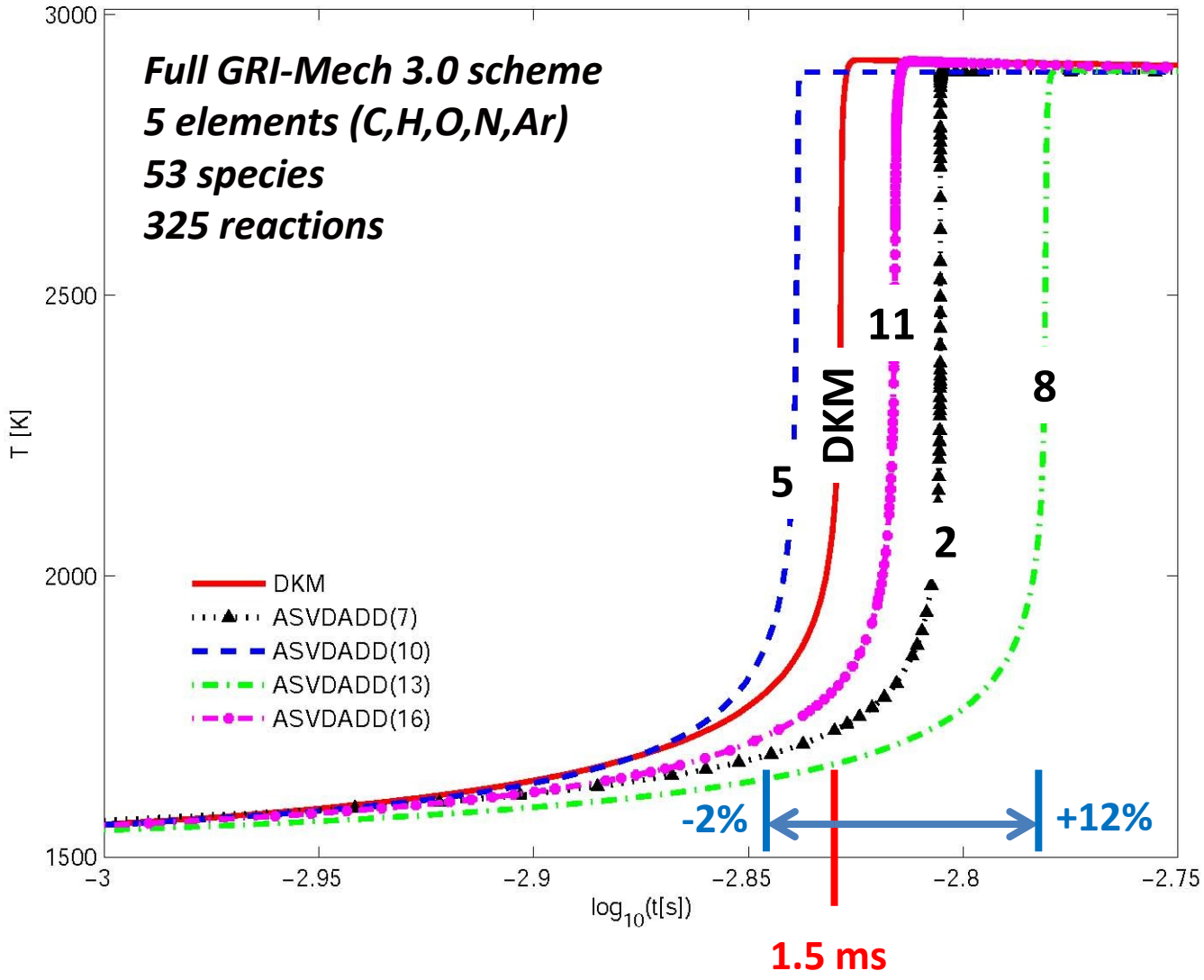
DoD_ℓ





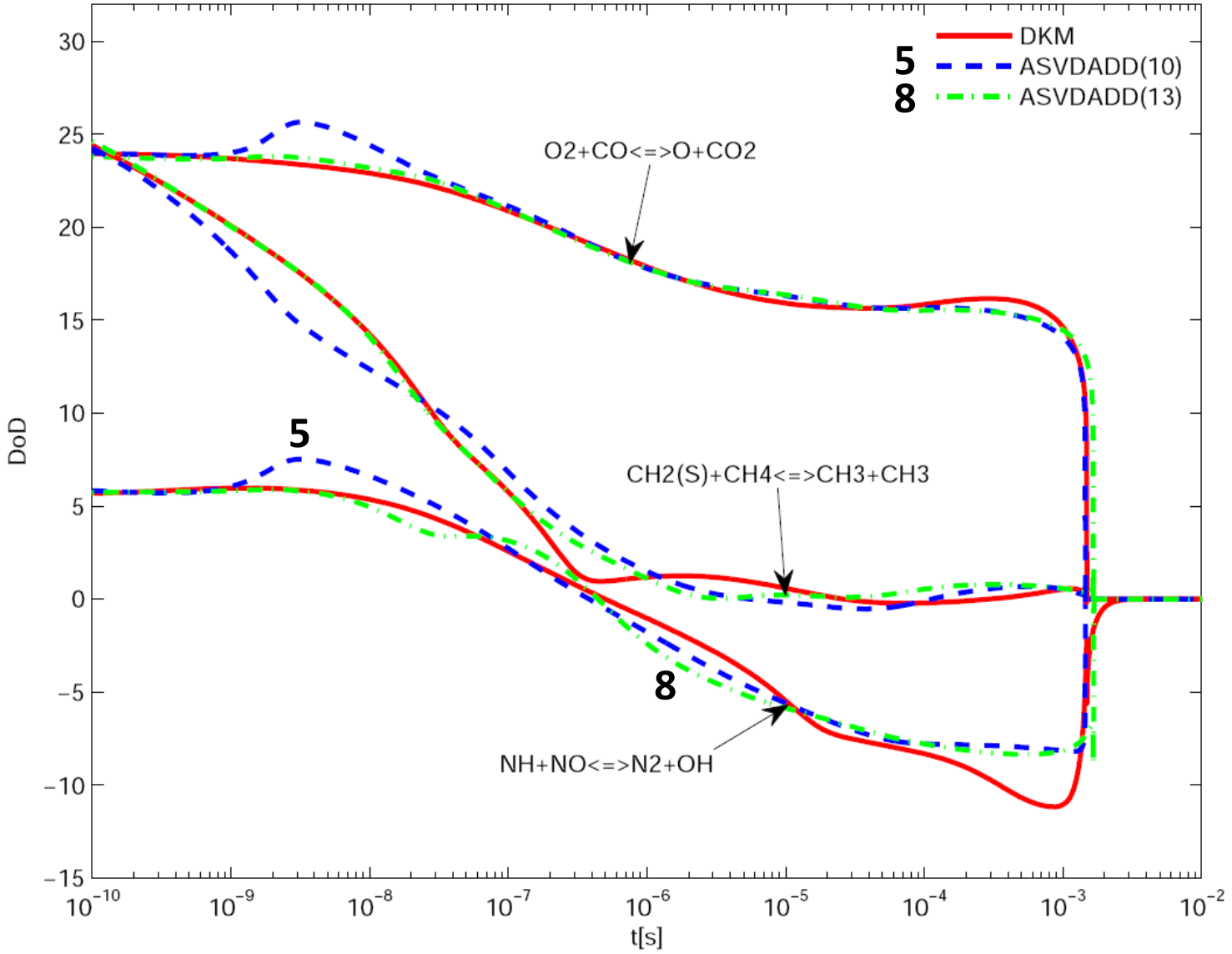
ASVDADD constraints are ‘optimal’ and yield excellent RCCE predictions

IGNITION DELAY : methane-air stoichiometric mixture at 1500 K and 1 atm.



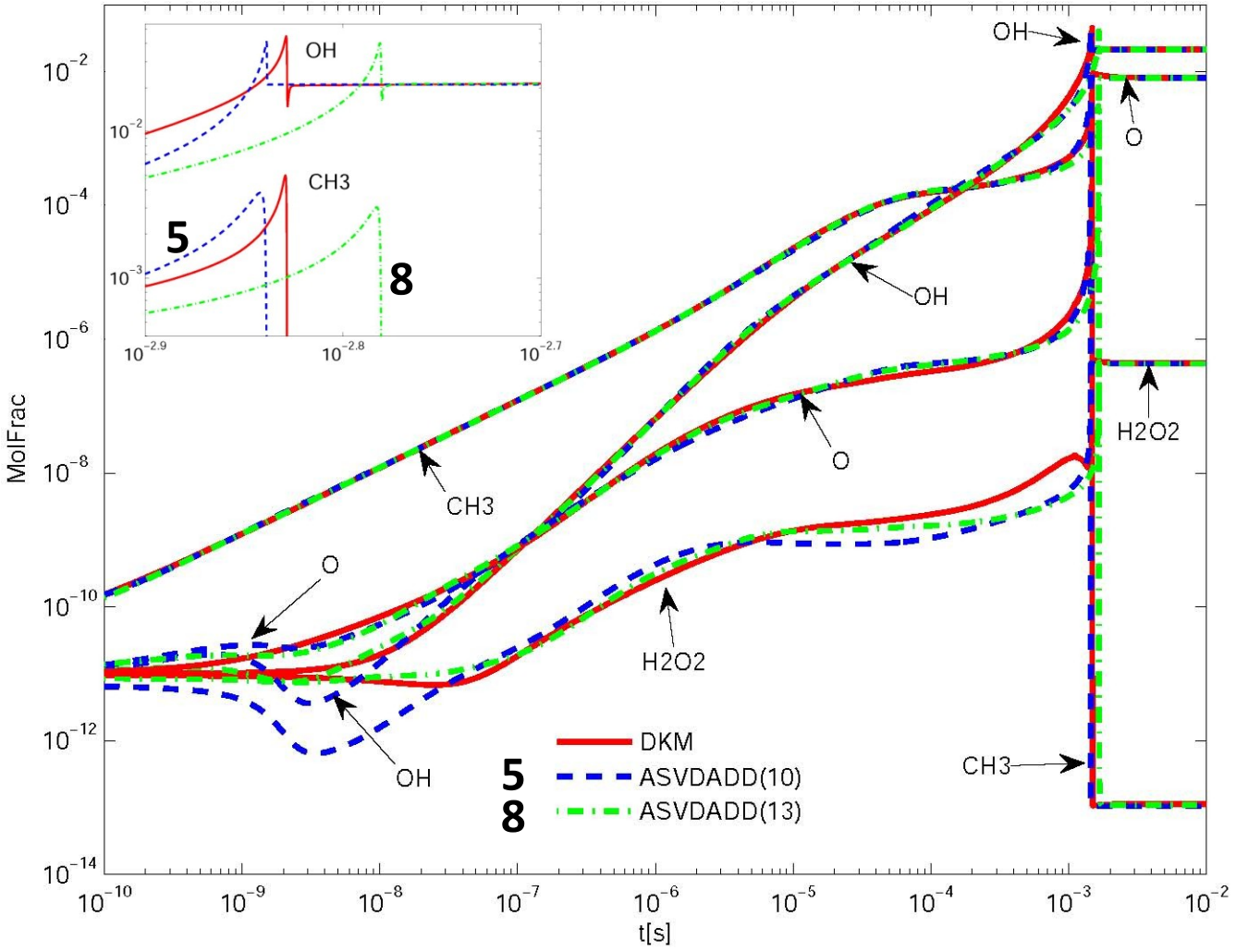
ASVDADD constraints are ‘optimal’ and yield excellent RCCE predictions

IGNITION EXAMPLE: methane-air stoichiometric mixture at 1500 K and 1 atm.



ASVDADD constraints are ‘optimal’ and yield excellent RCCE predictions

IGNITION EXAMPLE: methane-air stoichiometric mixture at 1500 K and 1 atm.



Conclusions and future work

With no need of any deep understanding of the kinetic mechanism, the ASVDADD algorithm finds optimal RCCE constraints from the analysis of a probe DKM solution.

Therefore, it should:

- be useful to develop tabular/in situ/adaptive strategies (such as alternating DKM / RCCE) for turbulent combustion simulations
- open up applicability of RCCE to other fields where complex kinetic models are needed (biochemistry, mechanobiology, economy)

FUTURE CHALLENGES:

- can the method suggest also a systematic scheme for skeletal mechanism reduction?
- translate/import the same model reduction strategy and variable selection strategy into the GENERIC / Steepert Entropy Ascent / Gradient Flow frameworks for non equilibrium thermodynamics