Reactive flash: Unified formulation and efficient resolution

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Mixtures: Modeling, analysis and computing

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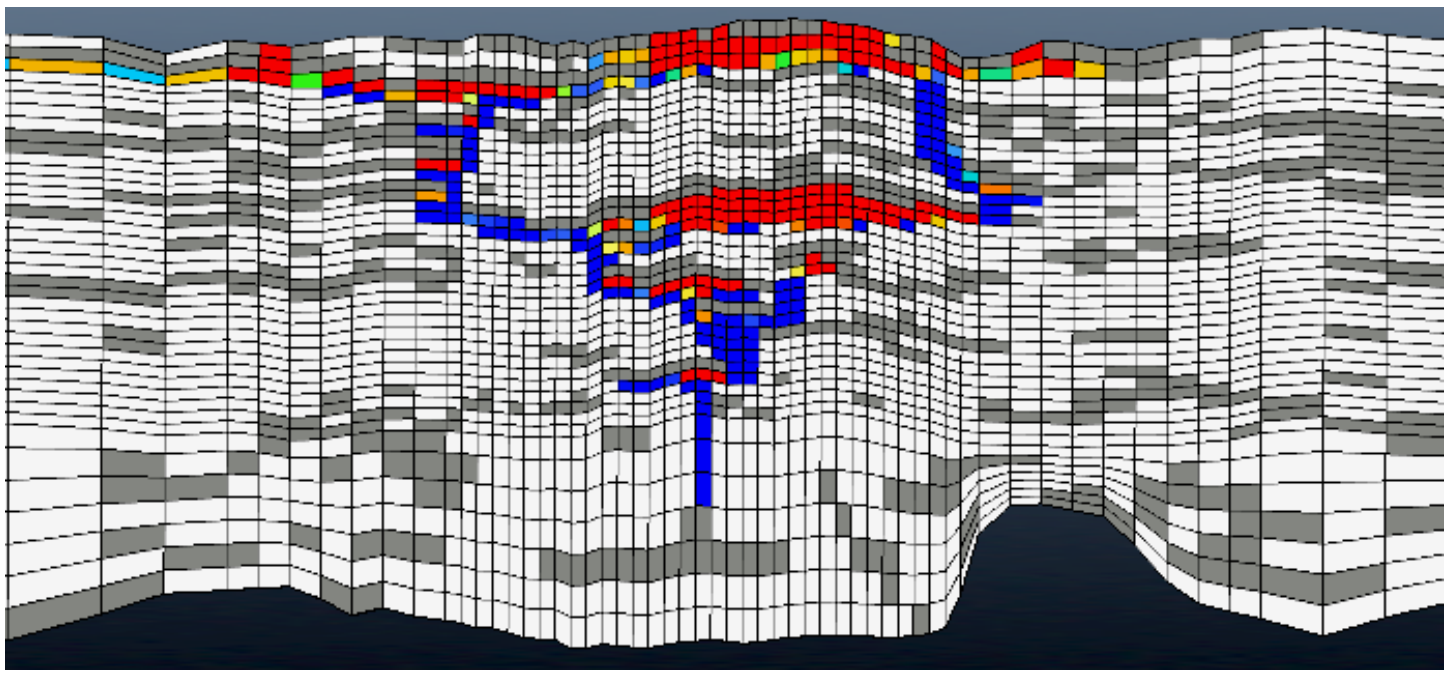
Subsurface CO_2 sequestration

- "Slow" flow of reactive CO_2 in a porous medium
- Possibility of phase change for the fluid (liquid – gas)
- Chemical equilibrium in the liquid phase (ionic liquid)
- Interactions with the solid porous matrix (precipitation – dissolution)
- ▷ To be computed at each time step and in each cell during reactive transport simulations

$\Rightarrow$ **Need of fast and robust solvers**



Chemical speciation example

- Water dissociation and evaporation:

$$
\begin{aligned}
&2 \textbf{ phases} && \mathcal{P} = \{\ell, g\} \\
&2 \textbf{ reactions} && \mathcal{R} = \{\mathrm{H_2O}(\ell) = \mathrm{H^+} + \mathrm{OH^-}, \mathrm{H_2O}(\ell) = \mathrm{H_2O(g)}\} \\
&2 \textbf{ elements} && \mathcal{E} = \{\mathrm{H},\ \mathrm{O}\} \\
&4 \textbf{ species} && \mathcal{S} = \{\mathrm{H^+},\ \mathrm{OH^-},\ \mathrm{H_2O}(\ell),\ \mathrm{H_2O(g)}\}
\end{aligned}
$$

- **Formula** and **stoichiometric** matrices:

$$
\mathbf{A} = \begin{array}{c} \\ \\ \end{array}
\begin{array}{c}
\begin{array}{cccc} \mathrm{H^+} & \mathrm{OH^-} & \mathrm{H_2O}(\ell) & \mathrm{H_2O(g)} \end{array} \\
\begin{bmatrix} 1 & 1 & 2 & 2 \\ 0 & 1 & 1 & 1 \end{bmatrix}
\end{array}
\qquad
\mathbf{S} = \begin{bmatrix} 1 & 0 \\ 1 & 0 \\ -1 & -1 \\ 0 & 1 \end{bmatrix}
\qquad
\mathbf{AS} = \mathbf{0}
$$

- **Unknowns** and **constraints**:

$$
\mathbf{n} = [n_{\mathrm{H^+}},\ n_{\mathrm{OH^-}},\ n_{\mathrm{H_2O}(\ell)},\ n_{\mathrm{H_2O(g)}}]^T
\qquad
\mathbf{b} = [\mathrm{b_H},\ \mathrm{b_O}]^T
$$

- Elements conservation:

$$
\mathbf{An} = \mathbf{b}
$$

Chemical equilibrium: the multiphase case

- N_{Sp} species in N_{Ph} phases:

$$\sigma : i \in \{1, \dots, N_{Sp}\} \mapsto \alpha \in \{1, \dots, N_{Ph}\}$$

- **Gibbs free energy**:

$$G(\mathbf{n}) := \sum_{\alpha=1}^{N_{Ph}} G_\alpha(\mathbf{n}^\alpha) \quad \text{where} \quad G_\alpha(\mathbf{n}^\alpha) = \sum_{i \in \sigma^{-1}(\alpha)} n_i \mu_i(\mathbf{n}^\alpha)$$

- **Chemical potential**:

$$\mu_i(\mathbf{n}^\alpha) := \mu_i^\circ + RT \ln x_i(\mathbf{n}^\alpha)$$

- **Mole fraction**:

$$x_i(\mathbf{n}^\alpha) := \frac{n_i}{\sum_{j \in \sigma^{-1}(\alpha)} n_j}$$

Chemical equilibrium problem

- **Gibbs energy minimization**:

$$\min_{\mathbf{An}=\mathbf{b}} \sum_{\alpha=1}^{N_{Ph}} \mathcal{G}_\alpha(\mathbf{n}^\alpha) \quad \text{with} \quad \mathcal{G}_\alpha(\mathbf{n}^\alpha) := \begin{cases} G_\alpha(\mathbf{n}^\alpha) & \text{if } \mathbf{n}^\alpha \geq \mathbf{0} \\ +\infty & \text{otherwise} \end{cases}$$

- **Euler-Lagrange equations**:

$$\begin{aligned} \mathbf{An} - \mathbf{b} &= \mathbf{0}, \\ \mathbf{S}^T \boldsymbol{\mu} &= \mathbf{0}, \\ \boldsymbol{\mu} &= (\boldsymbol{\mu}^\alpha)_{\alpha=1,\ldots,N_{Ph}} \\ \boldsymbol{\mu}^\alpha &\in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha) \end{aligned}$$

where

$$\boldsymbol{\mu}^\alpha \in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha) \;\Leftrightarrow\; \mathcal{G}_\alpha(\mathbf{m}^\alpha) \geq \mathcal{G}_\alpha(\mathbf{n}^\alpha) + \langle \boldsymbol{\mu}^\alpha, \mathbf{m}^\alpha - \mathbf{n}^\alpha \rangle, \; \forall \mathbf{m}^\alpha \in \mathbb{R}^{\#\sigma^{-1}(\alpha)}$$

Chemical equilibrium problem

- **Gibbs energy minimization**:

$$\min_{\mathbf{An}=\mathbf{b}} \sum_{\alpha=1}^{N_{Ph}} \mathcal{G}_\alpha(\mathbf{n}^\alpha) \quad \text{with} \quad \mathcal{G}_\alpha(\mathbf{n}^\alpha) := \begin{cases} G_\alpha(\mathbf{n}^\alpha) & \text{if } \mathbf{n}^\alpha \geq \mathbf{0} \\ +\infty & \text{otherwise} \end{cases}$$

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Extended mole frations [*Lauser et al.* 2011, *Vu et al.* 2021]

- ***Proposition***. $\boldsymbol{\mu}^\alpha \in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha) \Leftrightarrow \exists (s_\alpha, r_\alpha, \boldsymbol{\xi}^\alpha)$ such that

$$\mu_i = \mu_i^0 + RT \ln \xi_i \quad \text{et} \quad n_i = s_\alpha \xi_i, \quad (\forall i)$$

satisfying

$$\sum_{i \in \sigma^{-1}(\alpha)} \xi_i + r_\alpha = 1$$

$$s_\alpha r_\alpha = 0, \quad s_\alpha, r_\alpha \geq 0$$

- Present phase:

$$s_\alpha > 0, \, r_\alpha = 0 \quad \text{et} \quad \xi_i = \frac{n_i}{s_\alpha} = x_i(\mathbf{n}^\alpha)$$

- Absent phase:

$$s_\alpha = 0, \, r_\alpha \geq 0 \quad \text{et} \quad \sum_{i \in \sigma^{-1}(\alpha)} \xi_i \leq 1$$

Extended mole frations [*Lauser et al.* 2011, *Vu et al.* 2021]

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Multiphase chemical equilibrium problem

- **Unified formulation**:

$$
\begin{aligned}
\mathbf{An} - \mathbf{b} &= \mathbf{0} \\
\mathbf{S}^T \boldsymbol{\mu} &= \mathbf{0} \\
\boldsymbol{\mu} &= (\boldsymbol{\mu}^\alpha)_{\alpha=1,\dots,N_{Ph}} \\
\boldsymbol{\mu}^\alpha &\in \partial \mathcal{G}_\alpha(\mathbf{n}^\alpha)
\end{aligned}
\quad \Leftrightarrow \quad
\begin{aligned}
\sum_{\alpha=1}^{N_{Ph}} s_\alpha \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha - \mathbf{b} &= 0 \\
\mathbf{S}^T [\boldsymbol{\mu}^\circ/(RT) + \ln \boldsymbol{\xi}] &= \mathbf{0} \\
\textstyle\sum_i \xi_i + r_\alpha - 1 = 0, &\quad (\forall \alpha) \\
s_\alpha r_\alpha = 0, &\quad (\forall \alpha) \\
s_\alpha \geq 0,\ r_\alpha \geq 0, &\quad (\forall \alpha)
\end{aligned}
$$

- Dimension : $|\mathcal{S}| + 2|\mathcal{P}|$

Multiphase chemical equilibrium problem

- Equations:

$$\sum_{\alpha=1}^{N_{Ph}} s_\alpha \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha - \mathbf{b} = 0$$

$$\mathbf{S}^T[\boldsymbol{\mu}^\circ/(RT) + \ln \boldsymbol{\xi}] = \mathbf{0}$$

$$\textstyle\sum_i \xi_i + r_\alpha - 1 = 0, \qquad (\forall \alpha)$$

$$s_\alpha r_\alpha = 0, \qquad (\forall \alpha)$$

$$s_\alpha \geq 0,\ r_\alpha \geq 0, \qquad (\forall \alpha)$$

- Two difficulties:
  - Nonlinear terms:

$$\ln \xi_i$$

  - Complementarity problem:

$$s_\alpha r_\alpha = 0,$$

$$s_\alpha \geq 0,\ r_\alpha \geq 0$$

Classical resolution by Newton

- Residual:

$$\mathcal{F}(\boldsymbol{\xi}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} \sum_\alpha s_\alpha \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha - \mathbf{b} \\ \mathbf{S}^T[\mu^\circ/(\mathrm{RT}) + \ln \boldsymbol{\xi}] \\ [\mathbf{1}_\alpha^T \boldsymbol{\xi} + r_\alpha - 1]_\alpha \\ \vdots \end{bmatrix}$$

- Jacobian:

$$J_\alpha(\boldsymbol{\xi}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} s_\alpha \mathbf{A}^\alpha & \mathbf{A}^\alpha \boldsymbol{\xi}^\alpha & \mathbf{0} \\ \mathbf{S}^{T,\alpha} \mathrm{diag}\left\{\frac{1}{\boldsymbol{\xi}^\alpha}\right\} & \mathbf{0} & \mathbf{0} \\ \mathbf{1}_\alpha^T & 0 & 1 \end{bmatrix}$$

- Issues:
  - $1/\xi_i$ **blows up** when $\xi_i \to 0$.
  - **Does not preserve the positivity** of $\boldsymbol{\xi}$.
  - **Orders of magnitude** of $\boldsymbol{\xi}$.

The log trick

- Modified residual:

$$\mathbf{y} = \ln \boldsymbol{\xi} \quad \Rightarrow \quad \mathcal{F}(\mathbf{y}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} \sum_\alpha s_\alpha \mathbf{A}^\alpha \exp \mathbf{y}^\alpha - \mathbf{b} \\ \mathbf{S}^T [\mu^\circ / (\mathrm{RT}) + \mathbf{y}] \\ [\mathbf{1}_\alpha^T \exp \mathbf{y}^\alpha + r_\alpha - 1]_\alpha \\ \vdots \end{bmatrix}$$

- Jacobian:

$$J_\alpha(\mathbf{y}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} s_\alpha \mathbf{A}^\alpha \mathrm{diag}\{\exp \mathbf{y}^\alpha\} & \mathbf{A}^\alpha \exp \mathbf{y}^\alpha & \mathbf{0} \\ \mathbf{S}^{T,\alpha} & \mathbf{0} & \mathbf{0} \\ \mathbf{1}_\alpha^T \mathrm{diag}\{\exp \mathbf{y}^\alpha\} & 0 & 1 \end{bmatrix}$$

- Issue: $\exp y_i$ blows up when $y_i \to \infty$.

Basic idea [*Brenner & Cancès* 2017, *Bassetto & al.* 2021]

- Parametrization of the graph:

$$\mathbf{Y}(\boldsymbol{\tau}) = \ln \mathbf{X}(\boldsymbol{\tau})$$

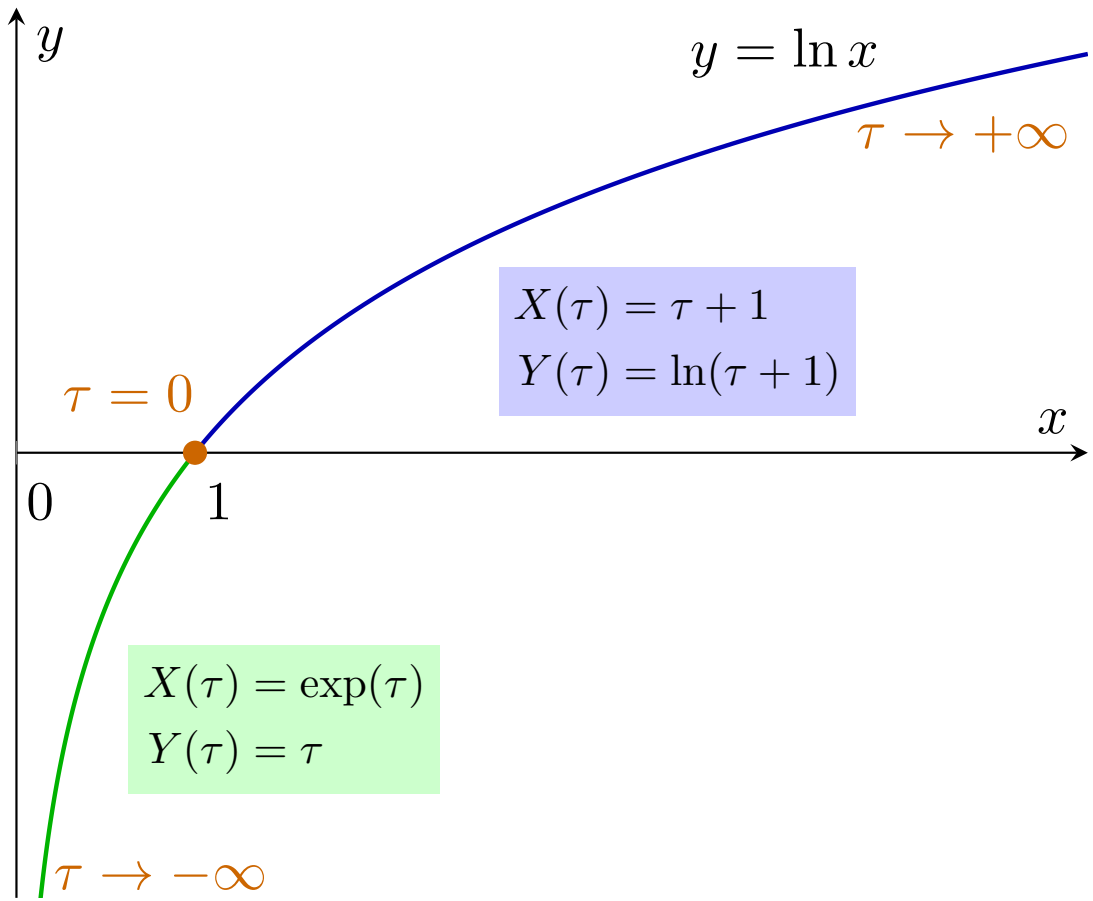
- Residual:

$$\mathcal{F}(\boldsymbol{\tau}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} \sum_\alpha s_\alpha \mathbf{A}^\alpha \mathbf{X}(\boldsymbol{\tau}^\alpha) - \mathbf{b} \\ \mathbf{S}^T [\mu^\circ/(\mathrm{RT}) + \mathbf{Y}(\boldsymbol{\tau})] \\ [\mathbf{1}_\alpha^T \mathbf{X}(\boldsymbol{\tau}^\alpha) + r_\alpha - 1]_\alpha \\ \vdots \end{bmatrix}$$

- Jacobian:

$$J_\alpha(\boldsymbol{\tau}, \boldsymbol{s}, \boldsymbol{r}) = \begin{bmatrix} s_\alpha \mathbf{A}^\alpha \mathrm{diag}\{\mathbf{X}'(\boldsymbol{\tau}^\alpha)\} & \mathbf{A}^\alpha \mathbf{X}(\boldsymbol{\tau}^\alpha) & \mathbf{0} \\ \mathbf{S}^{T,\alpha} \mathrm{diag}\{\mathbf{Y}'(\boldsymbol{\tau}^\alpha)\} & \mathbf{0} & \mathbf{0} \\ \mathbf{1}_\alpha^T \mathrm{diag}\{\mathbf{X}'(\boldsymbol{\tau}^\alpha)\} & 0 & 1 \end{bmatrix}$$

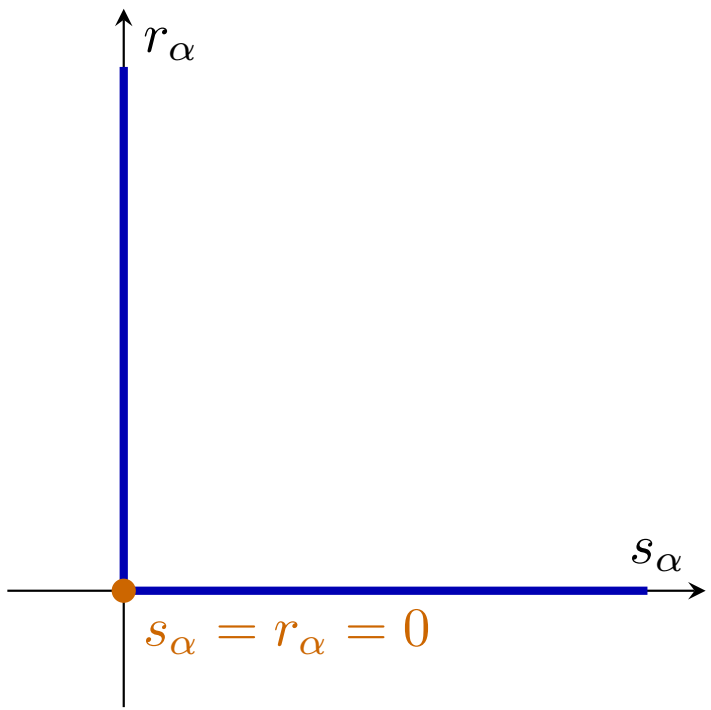
The switch function [Jonval, Ben Gharbia, Cancès, Faney & Tran 2025]



Complementarity problem

- The complementarity problem:

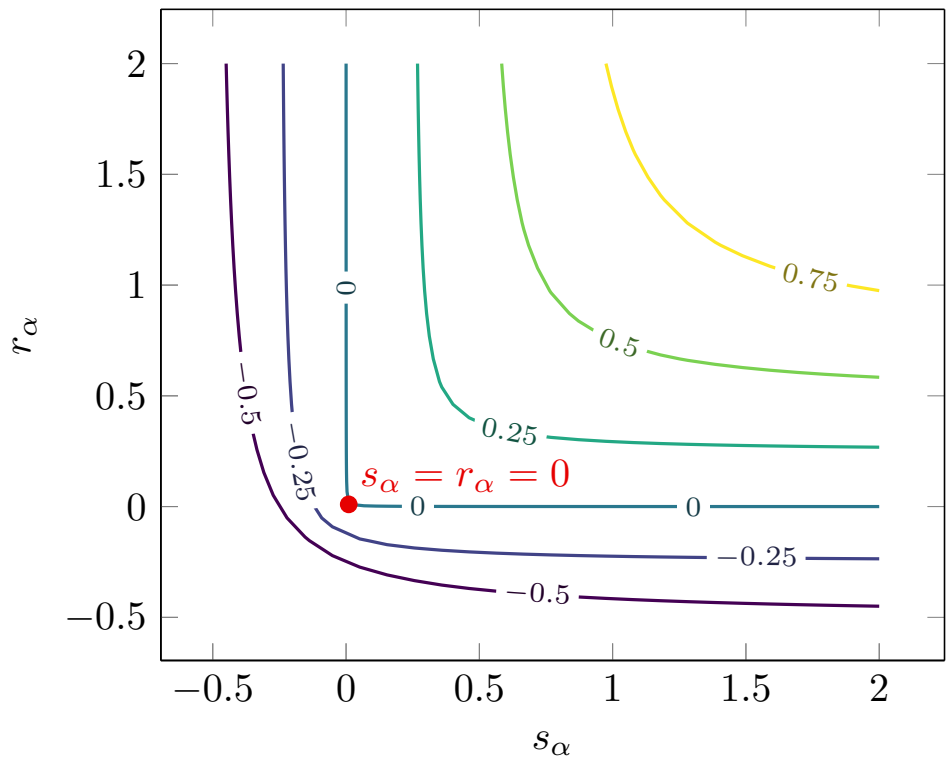
$$s_\alpha r_\alpha = 0 \quad \text{and} \quad s_\alpha,\, r_\alpha \geq 0.$$



Semi-smooth methods

- Complementarity function:

$$\Psi(s_\alpha, r_\alpha) = 0 \quad \Leftrightarrow \quad s_\alpha r_\alpha = 0 \text{ et } s_\alpha \geq 0,\ r_\alpha \geq 0.$$



$$\Psi_{\text{FB}} = s_\alpha + r_\alpha - \sqrt{s_\alpha^2 + r_\alpha^2}$$

Interior points method

- Smoothing of the complementarity:

$$s_\alpha r_\alpha = \nu^{(k)}$$

- Sequence tending to zero:

$$\nu^{(k+1)} = \Theta(\nu^{(k)})$$

- Maintaining positivity:

$$\mathbf{s}^{(k+1)} = \mathbf{s}^{(k)} + \beta_{\mathbf{s}}^{(k)} \boldsymbol{\delta}\mathbf{s}^{(k)}$$
$$\mathbf{r}^{(k+1)} = \mathbf{r}^{(k)} + \beta_{\mathbf{r}}^{(k)} \boldsymbol{\delta}\mathbf{r}^{(k)}$$

Complementarity parametrization

- Parametrization:

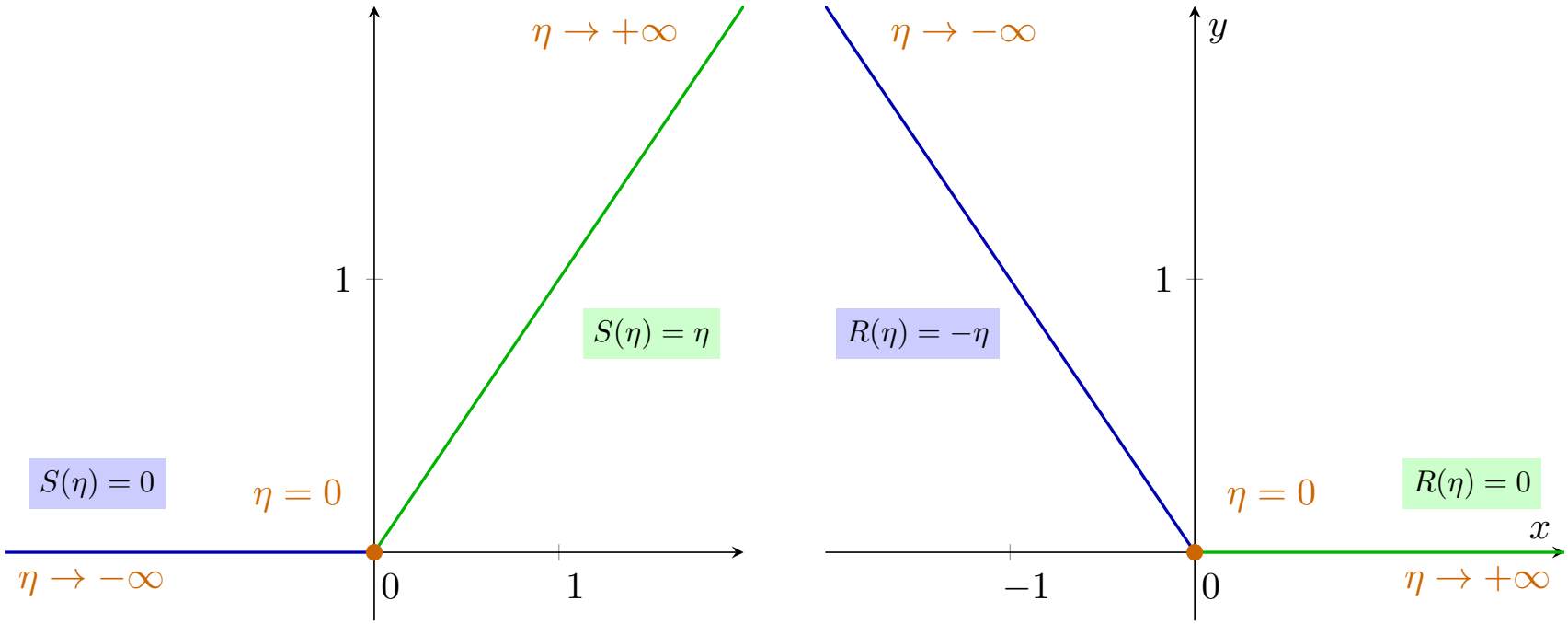
$$S(\eta)R(\eta) = 0$$

- Residual:

$$\sum_{\alpha=1}^{N_{Ph}} S(\boldsymbol{\eta}^\alpha)\mathbf{A}^\alpha\boldsymbol{\xi}^\alpha - \mathbf{b} = 0,$$
$$\mathbf{S}^T[\boldsymbol{\mu}^\circ/(RT) + \ln\boldsymbol{\xi}] = \mathbf{0},$$
$$\textstyle\sum_i \xi_i + R(\boldsymbol{\eta}^\alpha) - 1 = 0, \quad (\forall\alpha)$$

- Dimension: $|\mathcal{S}| + |\mathcal{P}|$

Complementarity parametrization functions



- Line search:

$$\boldsymbol{\eta}^{(k+1)} = \boldsymbol{\eta}^{(k)} + \beta_{\boldsymbol{\eta}}^{(k)} \delta\boldsymbol{\eta}^{(k)}$$

Numerical results

- log-trick *vs.* Parametrization
- Complementarity parametrization *vs.* FB function *vs.* IPM
- Tolerance for the Newton algorithm: 10^{-10}
- Test case:
  - **SiO2**:
    $$|\mathcal{S}| = 5, \quad |\mathcal{E}| = 3, \quad |\mathcal{R}| = 2, \quad |\mathcal{P}| = 2$$
  - **Multiphase seawater**:
    $$|\mathcal{S}| = 72, \quad |\mathcal{E}| = 13, \quad |\mathcal{R}| = 59, \quad |\mathcal{P}| = 22$$

Results for SiO2

- **A** : present mineral phase ($s_{\text{mineral}} > 0$)
- **B** : absent but stable mineral phase ($r_{\text{mineral}} = s_{\text{mineral}} = 0$)
- **C** : absent mineral phase ($r_{\text{mineral}} > 0$)

Log formulation	**Complementarity**	**Configuration**		
		A	**B**	**C**
Log trick	**param**	7	7	10
	FB	8	7	15
	IPM	9	52	12
Param	**param**	5	5	10
	FB	7	6	14
	IPM	9	52	12

Multiphase seawater

- Variation in oxygen quantity:

$\mathbf{b_O}$	**Nb of phases**		
	aqueous	**mineral**	**gazeous**
55	1	1	0
15	1	2	0
5	1	3	0
1	1	5	0
0.5	1	5	1

Table: Number of present phases

Results of multiphase seawater

Log formulation	**Complementarity**	**Oxygen quantity**				
		55	**15**	**5**	**1**	**0.5**
Log	**param**	21	26	46	27	×
	FB	91	×	×	×	×
	IPM	×	×	×	×	×
Param	**param**	27	31	36	29	31
	FB	70	67	65	52	63
	IPM	×	×	×	×	55

Table: Number of iterations

Results of multiphase Seawater

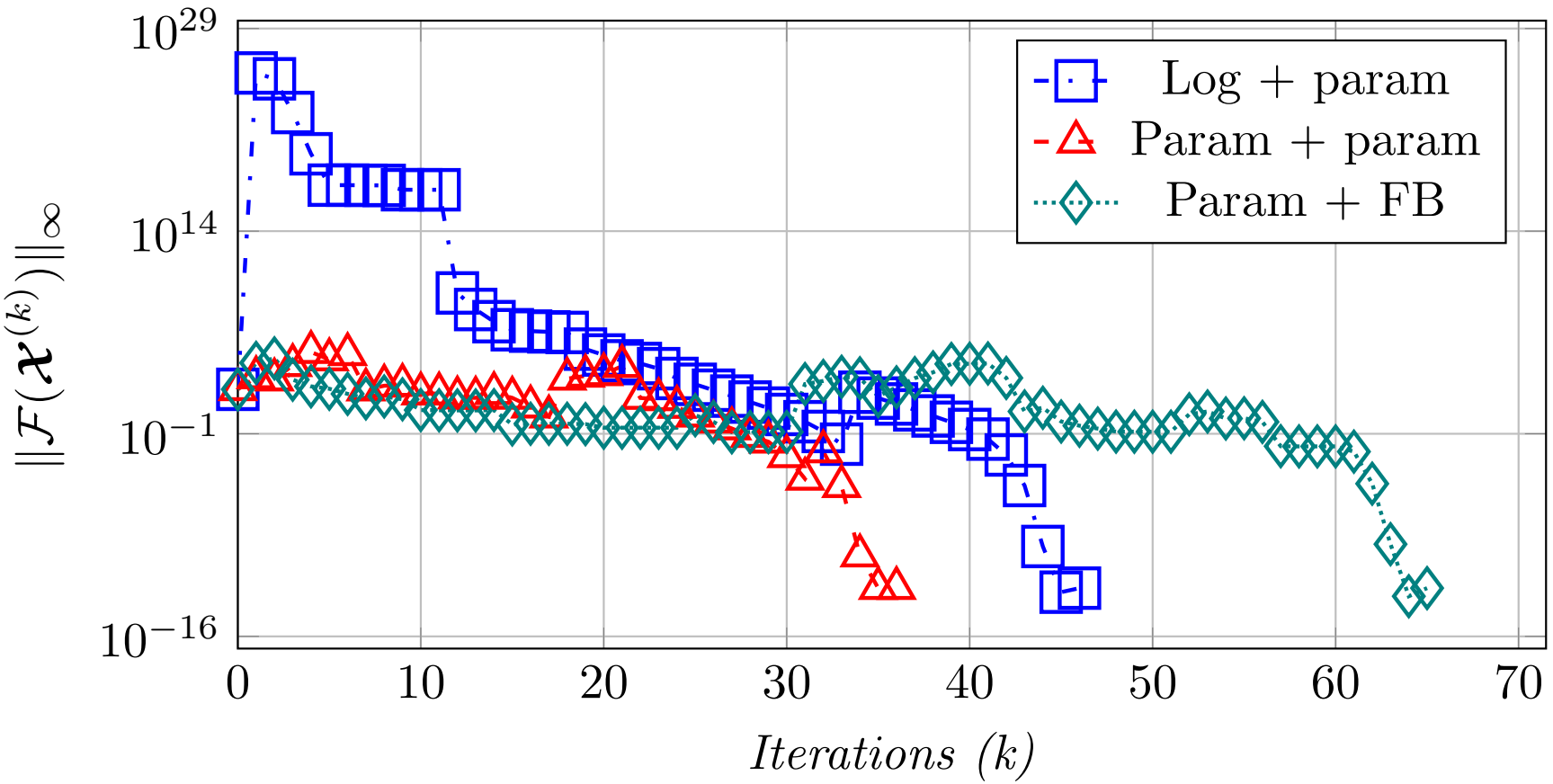


Figure: Residuals evolution $\mathbf{b}_O = 5$.

Conclusion and prospects

- Rigorous derivation of the **unified formulation** for reactive flashes
- **Parametrization for complementarity conditions** looks promizing
- Improved **robustness and efficiency** of Newton's method for difficult multiphase systems

- ▷ Coupling with transport in porous media
- ▷ Beyond ideal activities
- ▷ Extension to isochoric / non-isothermal flashes
- ▷ Acceleration of Newton's method by pre-flattening technics
  $\rightsquigarrow$ PhD thesis of Ngoc Do Quyen Dang (2024-2027)