Primal-Dual Interior-Point Methods for Thermodynamic Phase Calculations

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Motivations

- Aerosol particles have effects on human health, visibility reduction, acid rain, alteration of the earth's radiation balance, cloud formation, climate warming.
- Modeling of the physical and chemical state of atmospheric organic aerosol particles.
- Thermodynamics of a particle (global minimization of the Gibbs free energy) treated with a primal-dual interior-point method
- Gas-particle partitioning modeled by an additional term in the objective function and a sequential quadratic programming approach to decouple the different scales.

Phase Equilibrium

$$
\begin{aligned}
\min_{\mathbf{n}_\alpha} \quad & \sum_{\alpha=1}^{P} g(\mathbf{n}_\alpha) \\
\text{s. t.} \quad & \sum_{\alpha=1}^{P} \mathbf{n}_\alpha = \mathbf{b}, \\
& \mathbf{n}_\alpha \geq 0, \quad \alpha = 1, \ldots, P.
\end{aligned}
$$

- $\mathbf{n}_\alpha$ is the chemical concentration in the phase α.
- Split $\mathbf{n}_\alpha = y_\alpha \mathbf{x}_\alpha$, where $\mathbf{x}_\alpha \in \mathbb{R}^N$ virtual mole-fraction compositions and $y_\alpha \in \mathbb{R}$ total amount of moles in each phase.
- The number of phases P existing at the equilibrium is not known a priori, but a result of the equilibrium computation.
- The function g is homogeneous of degree one.

Phase Equilibrium

$$
\begin{aligned}
\min_{y_\alpha \mathbf{x}_\alpha} \quad & \sum_{\alpha=1}^{P} y_\alpha g(\mathbf{x}_\alpha) \\
\text{s. t.} \quad & \sum_{\alpha=1}^{P} y_\alpha \mathbf{x}_\alpha = \mathbf{b}, \\
& y_\alpha \geq 0, \quad \alpha = 1, \dots, P. \\
& \mathbf{e}^T \mathbf{x}_\alpha = 1, \quad \mathbf{x}_\alpha > 0, \quad \alpha = 1, \dots, N+1.
\end{aligned}
$$

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- Split $\mathbf{n}_\alpha = y_\alpha \mathbf{x}_\alpha$, where $\mathbf{x}_\alpha \in \mathbb{R}^N$ virtual mole-fraction compositions and $y_\alpha \in \mathbb{R}$ total amount of moles in each phase.
- The number of phases P existing at the equilibrium is not known a priori, but a result of the equilibrium computation.
- Projection on the equality constraints $\mathbf{e}^T \mathbf{x}_\alpha = 1$.

Global Optimization Problem

$$
\begin{aligned}
\min_{y_\alpha, \mathbf{z}_\alpha} \quad & \sum_{\alpha=1}^{P} y_\alpha f(\mathbf{z}_\alpha) \\
\text{s. t.} \quad & \sum_{\alpha=1}^{P} y_\alpha \mathbf{z}_\alpha = \mathbf{b}, \quad \sum_{\alpha=1}^{P} y_\alpha = 1, \\
& y_\alpha \geq 0, \qquad \alpha = 1, \ldots, P, \\
& \mathbf{z}_\alpha \in \mathrm{int}(\Delta_N), \quad \alpha = 1, \ldots, P.
\end{aligned}
$$

- $\mathbf{z}_\alpha \in \mathbb{R}^N$ virtual mole-fraction compositions.
- $y_\alpha \in \mathbb{R}$ total amount of moles in each phase. It allows to track of the existence of the phase α.
- $\Delta_N = \mathrm{conv}\{\mathbf{0}, \mathbf{e}_1, \cdots, \mathbf{e}_N\}$ is a N-simplex in $\mathbb{R}^N$.

Convex Hull

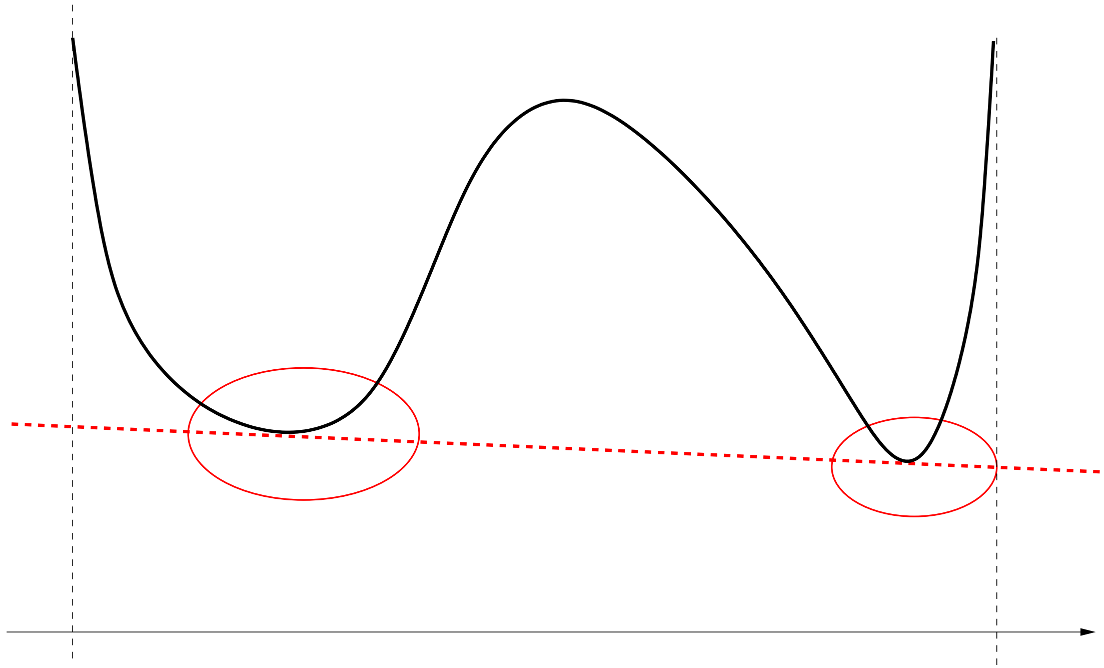
- Convex hull of a function $f : \mathbb{R}^N \mapsto \mathbb{R}$: $\mathrm{conv} f$ is the greatest convex function majored by f.

$$(\mathrm{conv} f)(\mathbf{b}) = \inf \left\{ \sum_{\alpha=1}^{P} y_\alpha \, f(\mathbf{z}_\alpha) \middle| \; \sum_{\alpha=1}^{P} y_\alpha \mathbf{z}_\alpha = \mathbf{b}, y_\alpha \geq 0, \; \sum_{\alpha=1}^{P} y_\alpha = 1 \right\}.$$

- **Carathéodory's Theorem:** For a set $C \neq \emptyset$ in $\mathbb{R}^N$, every point of $\mathrm{conv}(C)$ belongs to some simplex with vertices in C and thus can be expressed as a convex combination of $N+1$ points of C (not necessarily different). When C is connected, N points suffice.

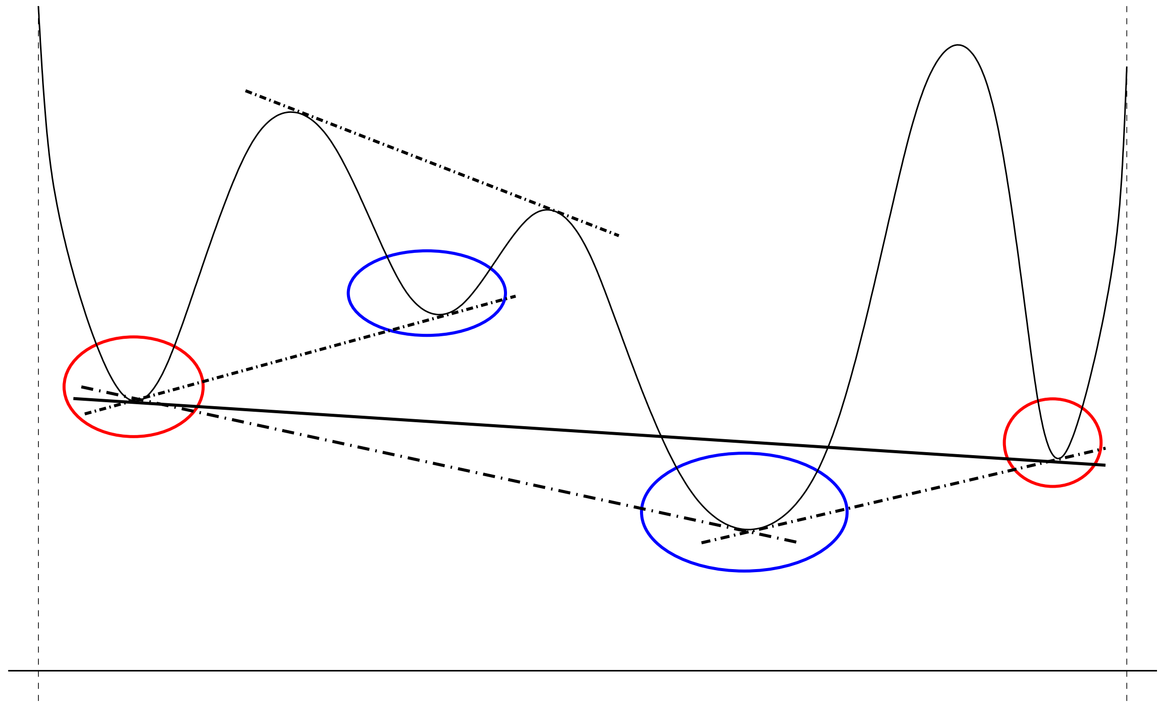
$$(\mathrm{conv} f)(\mathbf{b}) = \inf \left\{ \sum_{\alpha=1}^{N+1} y_\alpha \, f(\mathbf{z}_\alpha) \middle| \; \sum_{\alpha=1}^{N+1} y_\alpha \mathbf{z}_\alpha = \mathbf{b}, y_\alpha \geq 0, \; \sum_{\alpha=1}^{N+1} y_\alpha = 1 \right\}.$$

Properties of the Energy Function



- Regularity of the energy function: $f \in C^\infty(\mathrm{int}\Delta_N) \cap C^0\left(\overline{\Delta_N}\right)$.
- $\forall \mathbf{x}_0 \in \partial\Delta_N, \quad \forall w$ proper $\lim_{\mathbf{x}\to\mathbf{x}_0} \nabla f \cdot w = -\infty$.
- Each vertex of the N-simplex Δ_N (pure components) belongs to a connected convex region of f.
- Determination of a tangent plane to the energy function.

Properties of the Energy Function



- No *isolated connected convex regions* (for global optimum).
- The function f is strictly convex in a neighborhood of a solution (for uniqueness).

Some Results on the Convex Hull

- Application of results from [Rabier, Griewank (1992)].
- The feed $\mathbf{b}$ can be decomposed into a stable phase splitting:

$$\mathbf{b} = \sum_{\alpha=1}^{P} y_\alpha \mathbf{z}_\alpha, \quad \mathbf{z}_\alpha \in \text{int}(\Delta_N), \quad \alpha = 1, \ldots, P.$$

The convex hull is continuously differentiable on int(Δ_N).

- The following relations hold for all $(k, m) = 1, \ldots, P$:

$$\begin{aligned} \nabla f(\mathbf{z}_k) &= \nabla f(\mathbf{z}_m) \\ f(\mathbf{z}_k) - \nabla f(\mathbf{z}_k) \cdot \mathbf{z}_k &= f(\mathbf{z}_m) - \nabla f(\mathbf{z}_m) \cdot \mathbf{z}_m \end{aligned}$$

Moreover the tangent plane $\Theta(\mathbf{z}) = f(\mathbf{z}_1) + \nabla f(\mathbf{z}_1) \cdot (\mathbf{z} - \mathbf{z}_1)$ is tangent to f at all active vertices and always below the graph of f.

Acknowledgments: A. Anantharanam, Ecole Polytechnique de Paris

An Interior-Point Method

- Introduction of a log-barrier penalty function to relax the inequality constraints.

$$\begin{aligned}
\min_{y_\alpha, \mathbf{z}_\alpha} \quad & \sum_{\alpha=1}^{N+1} y_\alpha f(\mathbf{z}_\alpha) \\
\text{s. t.} \quad & \sum_{\alpha=1}^{N+1} y_\alpha \mathbf{z}_\alpha = \mathbf{b}, \quad \sum_{\alpha=1}^{N+1} y_\alpha = 1, \\
& \mathbf{z}_\alpha \in \operatorname{int}(\Delta_N), \quad \alpha = 1, \ldots, N+1. \\
& y_\alpha \geq 0, \qquad \alpha = 1, \ldots, N+1,
\end{aligned}$$

- ν is a penalty parameter, which tends to zero.
- The phase α disappears when $y_\alpha \simeq 0$.
- Initial guess with $N+1$ vertices and deletion of extra vertices until convergence is reached.

An Interior-Point Method

- Introduction of a log-barrier penalty function to relax the inequality constraints.

$$\min_{y_\alpha, \mathbf{z}_\alpha} \quad \sum_{\alpha=1}^{N+1} y_\alpha f(\mathbf{z}_\alpha) - \nu \sum_{\alpha=1}^{N+1} \ln(y_\alpha)$$

$$\text{s. t.} \quad \sum_{\alpha=1}^{N+1} y_\alpha \mathbf{z}_\alpha = \mathbf{b}, \quad \sum_{\alpha=1}^{N+1} y_\alpha = 1,$$

$$\mathbf{z}_\alpha \in \operatorname{int}(\Delta_N), \quad \alpha = 1, \ldots, N+1.$$

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Karush-Kuhn-Tucker Conditions

- KKT conditions (stationary points of the Lagrangian):

$$
\begin{aligned}
y_\alpha \left(\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta} \right) &= 0, \quad \alpha = 1, \ldots, N+1, \\
f(\mathbf{z}_\alpha) + \boldsymbol{\eta}^T \mathbf{z}_\alpha - \frac{\nu}{y_\alpha} + \theta &= 0, \quad \alpha = 1, \ldots, N+1, \\
\sum_{\alpha=1}^{N+1} y_\alpha \mathbf{x}_\alpha - \mathbf{b} &= 0, \quad \sum_{\alpha=1}^{N+1} y_\alpha - 1 = 0.
\end{aligned}
$$

- KKT System (Newton method):

$$
\begin{pmatrix}
y_\alpha \nabla^2 f(\mathbf{z}_\alpha) & \nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta} & y_\alpha & 0 \\
(\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta})^T & \frac{\nu}{y_\alpha^2} & \mathbf{z}_\alpha^T & \mathbf{e} \\
y_\alpha^T & \mathbf{z}_\alpha & 0 & 0 \\
0 & \mathbf{e}^T & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\mathbf{p}_{\mathbf{z}} \\ \mathbf{p}_y \\ \mathbf{p}_{\boldsymbol{\eta}} \\ \mathbf{p}_\theta
\end{pmatrix}
=
\begin{pmatrix}
\mathbf{b}_{\mathbf{z}} \\ \mathbf{b}_y \\ \mathbf{b}_{\boldsymbol{\eta}} \\ \mathbf{b}_\theta
\end{pmatrix}
$$

Global Optimum vs Local Optimum

- $(y_\alpha, \mathbf{z}_\alpha)$ is a global minimum if and only if $(y_\alpha, \mathbf{z}_\alpha, \boldsymbol{\eta}, \theta)$ is a KKT point with $\mathbf{z}_\alpha \in \Delta_n$ such that $\nabla^2 f(\mathbf{z}_\alpha) > 0$ and $y_\alpha > 0$.
- A feasible point $(y_\alpha, \mathbf{z}_\alpha)$ is a global minimum if and only if it is a KKT point and

$$f(\mathbf{z}) \geq \Theta(\mathbf{z}) \quad \forall \mathbf{z} \in \Delta_n,$$

where $\Theta(\mathbf{z})$ is the hyperplane associated with the KKT point.

Computational Issues

- KKT systems for chemical systems are usually ill-conditioned.
- Direct decomposition techniques of the block-structured system (range-space + null-space).
- Control of the inertia of the matrices arising in the resolution.
- Numerically coupled with active sets procedure.

Assumptions:

- The Hessian $\nabla^2 f(\mathbf{z}_\alpha)$ has to remain positive definite (*second order conditions*)
- The iterates $\mathbf{z}_1, \mathbf{z}_2, \ldots, \mathbf{z}_{N+1}$ remain linearly independent (*linear independent constraint qualification*).

Computational Issues

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- Numerically coupled with active sets procedure.

Algorithm:

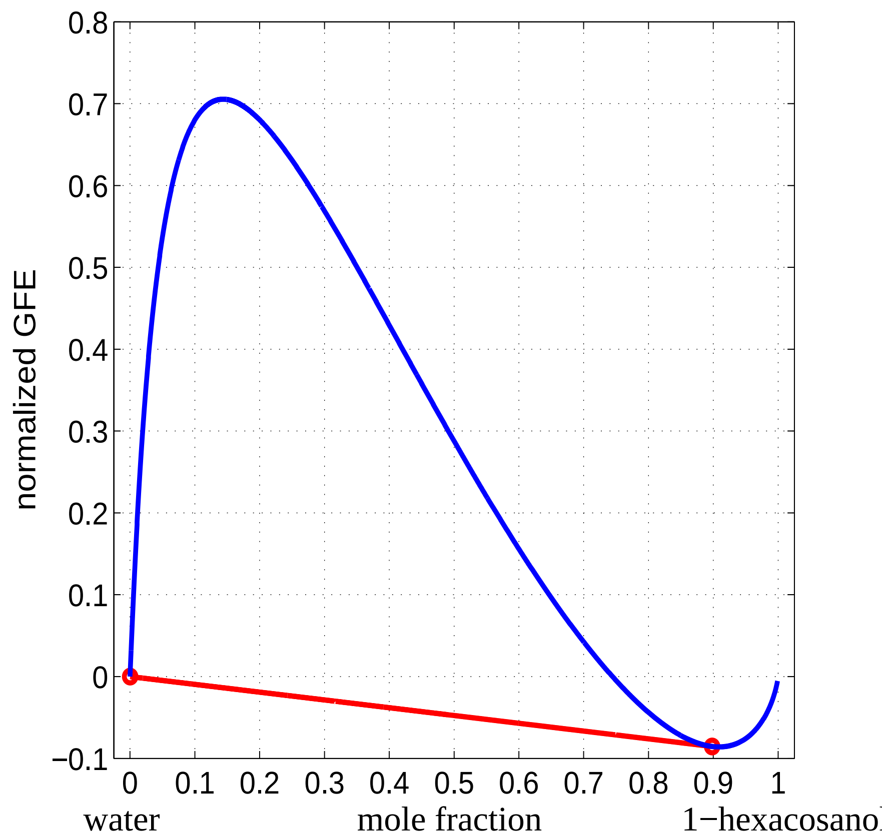
- Initialization of the primal and dual variables. Initialization of the penalty parameter ν.
- Resolution of the KKT system to obtain a descent direction.
- Update the penalty parameter ν and compute next iterate.

Key Issue:

- Initialization of $\mathbf{z}_\alpha$ in order to guarantee the second order conditions during the whole algorithm.

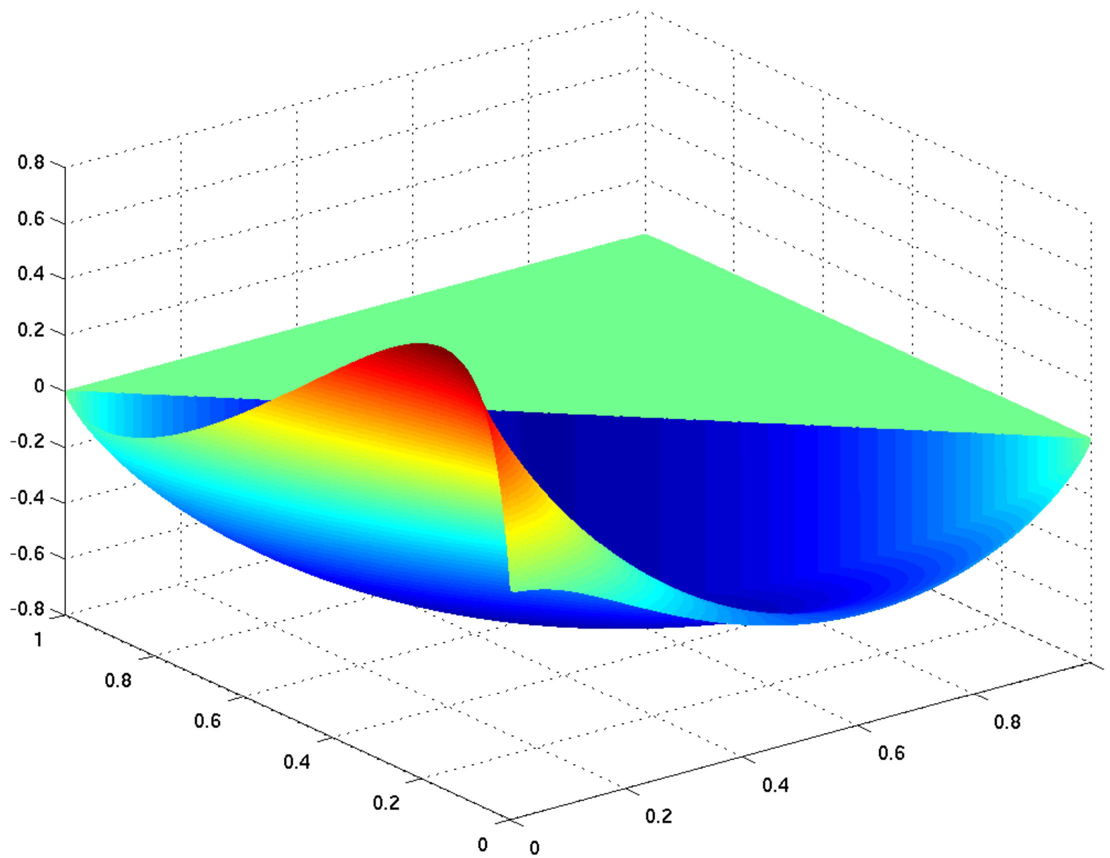
Results in One Dimension

- Energy is defined on the $(0, 1)$ segment. Both extremities of the segment are in a convex region by assumption.
- Convex Hull:



Results in Two Dimensions

- Non-convex energy Function:

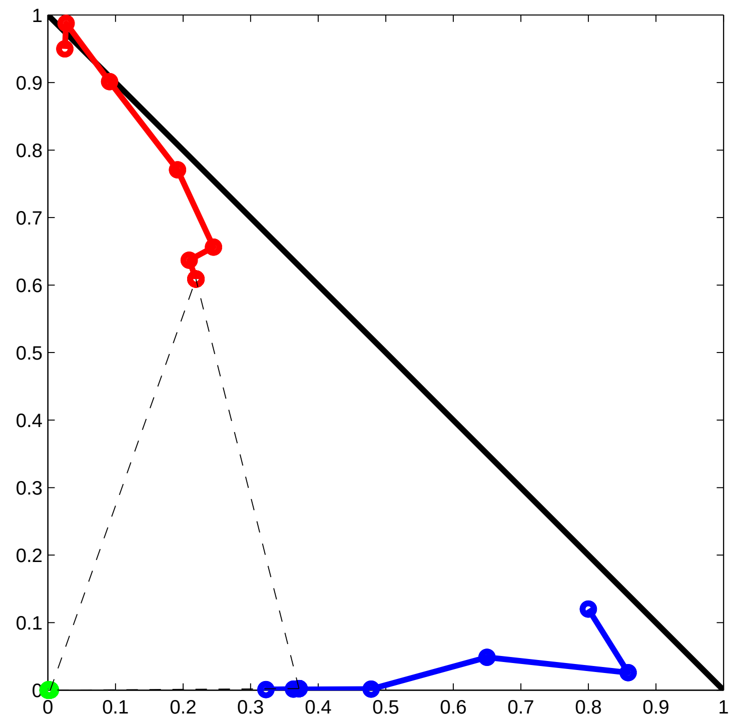


- Determination of a tangent plane.

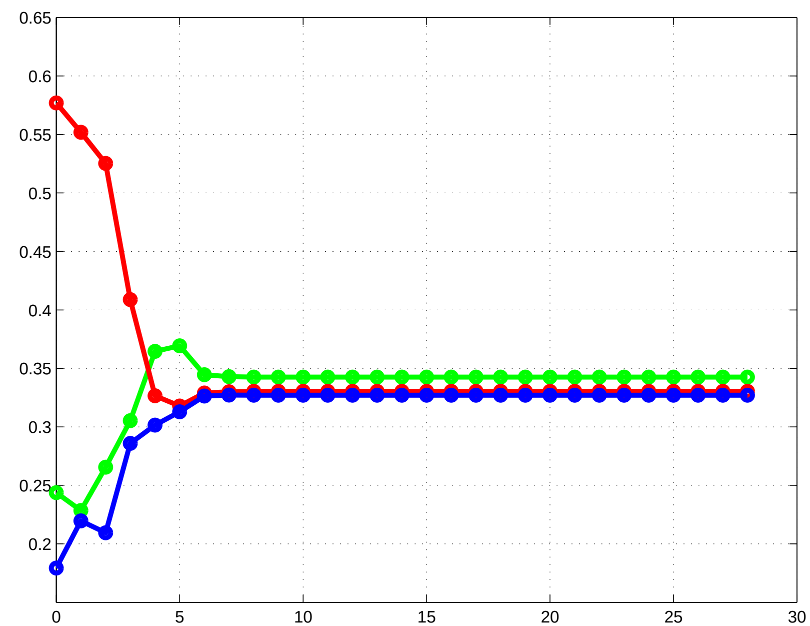
Convergence of Phase Simplexes

- Convergence towards three active vertices:

Vertices $\mathbf{z}_\alpha$

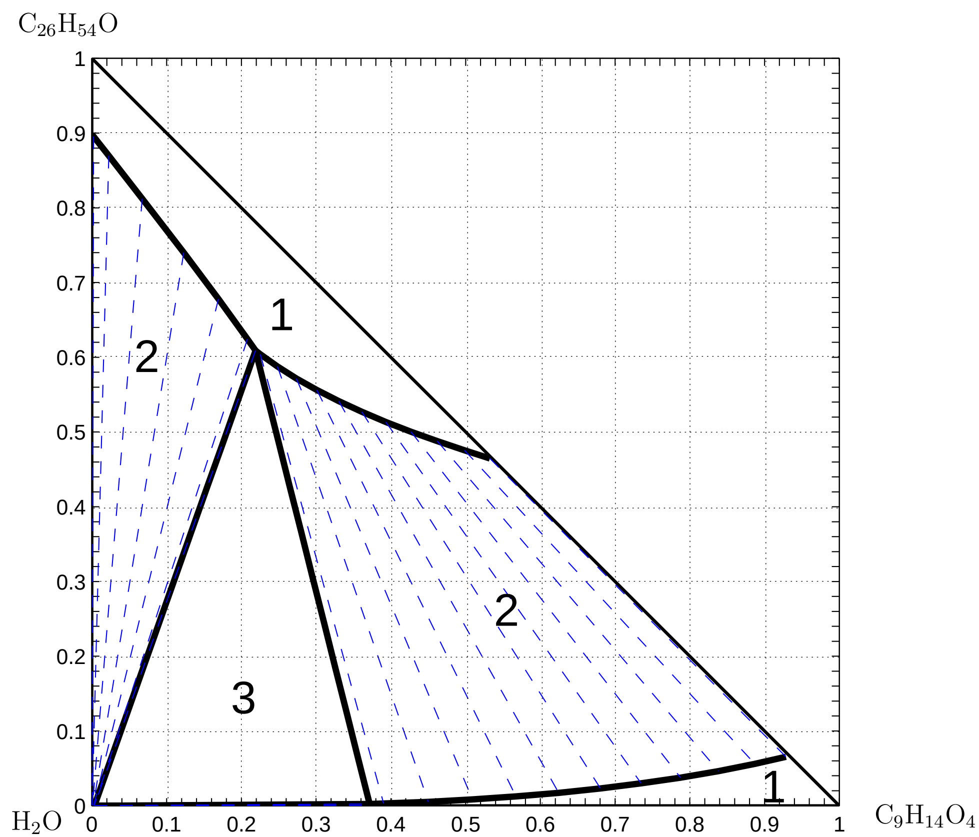


Barycentric Coordinates y_α



- Particular choice of initial guess (near the vertices) and numerical parameters to avoid local minima.

Convex Hull and Active Constraints



- Computational cost: 20 s. for $\frac{1}{2}100 \times 100$ grid points, 25 iterations in average (tolerance $= 10^{-7}$).

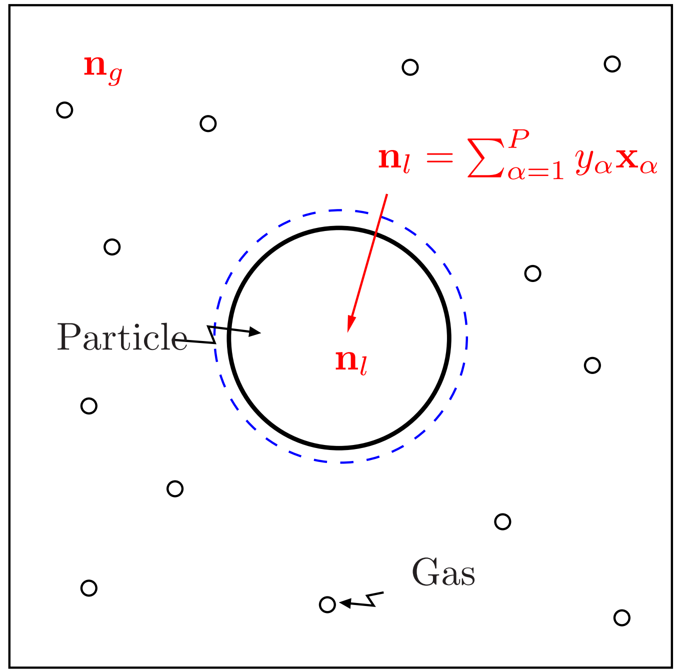
Acknowledgments: C. Landry, Graduate Student, EPFL, Switzerland

Results in Higher Dimensions

Size $N+1$	# Iterations	CPU time
3	25	0.024
4	40	0.0369
18	41	0.1799

Gas-Particle Partitioning

- Single aerosol particle:



- Find the equilibrium state of the particle and the repartition between solid, liquid and gas phases.
- Find the gas-particle partitioning/thermodynamics of the system gas+particle.

Energy Model

$$\min_{y_\alpha, \mathbf{x}_\alpha, \mathbf{n}_g} \quad \sum_{\alpha=1}^{P} y_\alpha g(\mathbf{x}_\alpha) + \mathbf{n}_g^T \boldsymbol{\mu}_g(\mathbf{n}_g)$$

$$\text{s. t.} \quad \sum_{\alpha=1}^{P} y_\alpha \mathbf{x}_\alpha + \mathbf{n}_g = \tilde{\mathbf{b}},$$

$$y_\alpha \geq 0, \quad \mathbf{e}^T \mathbf{x}_\alpha = 1, \quad \mathbf{x}_\alpha > \mathbf{0}, \quad \alpha = 1, \ldots, P,$$

$$\mathbf{n}_g > 0.$$

- $\mathbf{n}_g$ are the concentrations in the gas, supposed to be positive.
- $\boldsymbol{\mu}_g = \boldsymbol{\mu}_g(\mathbf{n}_g) = \ln\left(\mathbf{n}_g \frac{\mathrm{R}T}{p_{\mathrm{vapor}}}\right)$ is chemical potentials vector.

Global Optimization Problem

- Projected optimization problem:

$$
\begin{aligned}
\min_{y_\alpha, \mathbf{z}_\alpha, \mathbf{n}_g} \quad & \sum_{\alpha=1}^{P} y_\alpha f(\mathbf{z}_\alpha) + \mathbf{n}_g^T \boldsymbol{\mu}_g(\mathbf{n}_g) \\
\text{s. t.} \quad & \sum_{\alpha=1}^{P} y_\alpha \mathbf{z}_\alpha + \mathcal{P}\mathbf{n}_g = \mathbf{b}, \quad \sum_{\alpha=1}^{P} y_\alpha + \mathbf{e}^T \mathbf{n}_g = \tilde{b}, \\
& y_\alpha \geq 0, \qquad \alpha = 1, \ldots, P, \\
& \mathbf{z}_\alpha \in \mathrm{int}(\Delta_N), \quad \alpha = 1, \ldots, P, \\
& \mathbf{n}_g > 0.
\end{aligned}
$$

where $\mathcal{P} : \mathbb{R}^{n+1} \to \mathbb{R}^n$ is the projection on $\mathbf{e}^T \mathbf{x} = 1$.

- **Result:** The extended problem admits a unique global minimizer (additional term is convex).

Interior-Point Method and KKT Conditions

- Interior-point method and first-order conditions:

$$\begin{aligned}
&\boldsymbol{\mu}_g(\mathbf{n}_g) + \boldsymbol{\lambda} = \mathbf{0}, \\
&y_\alpha\big(\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta}\big) = \mathbf{0}, && \alpha = 1, \ldots, P, \\
&f(\mathbf{z}_\alpha) + \boldsymbol{\eta}^T \mathbf{z}_\alpha + \theta - \frac{\nu}{y_\alpha} = 0, && \alpha = 1, \ldots, P, \\
&\sum_{\alpha=1}^{P} y_\alpha \mathbf{z}_\alpha + \mathcal{P}\mathbf{n}_g = \mathbf{b}, \\
&\sum_{\alpha=1}^{P} y_\alpha + \mathbf{e}^T \mathbf{n}_g = \tilde{b}.
\end{aligned}$$

- **Result:** $(y_\alpha, \mathbf{z}_\alpha, \mathbf{n}_g)$ is a global minimum if and only if $(y_\alpha, \mathbf{z}_\alpha, \mathbf{n}_g, \boldsymbol{\eta}, \theta)$ is a KKT point with $\mathbf{z}_\alpha \in \Delta_n$ such that $\nabla^2 f(\mathbf{z}_\alpha) > 0$ and $y_\alpha > 0$.
- KKT system is obtained by using one Newton iteration at each iteration of the interior-point method.

Initialization Techniques

- Geometric properties of the energy function f: the variables $\mathbf{z}_\alpha$ are initialized in a neighborhood $\mathcal{N}$ of the vertices of Δ_n such that the function f is convex on $\Delta_n \cap \mathcal{N}$.
- The variables y_α are the barycentric coordinates of $\mathbf{b}$ in terms of $\mathbf{z}_\alpha$ and $\boldsymbol{\lambda}$ are obtained in a least-squares sense.
- Interior-point method to obtain a solution for $\boldsymbol{\mu}_g = \mathbf{n}_g = 0$.
- Define $\mathbf{n}_g$ with

$$\boldsymbol{\mu}_g(\mathbf{n}_g) = \ln \frac{\mathbf{n}_g \mathrm{R} T}{p_{\text{vapor}}} = -\boldsymbol{\lambda}.$$

- Scale the liquid quantities by:

$$\mathbf{n}_g + \beta^0 \sum_{\alpha=1}^{P} y_\alpha \mathbf{x}_\alpha = \mathbf{b}.$$

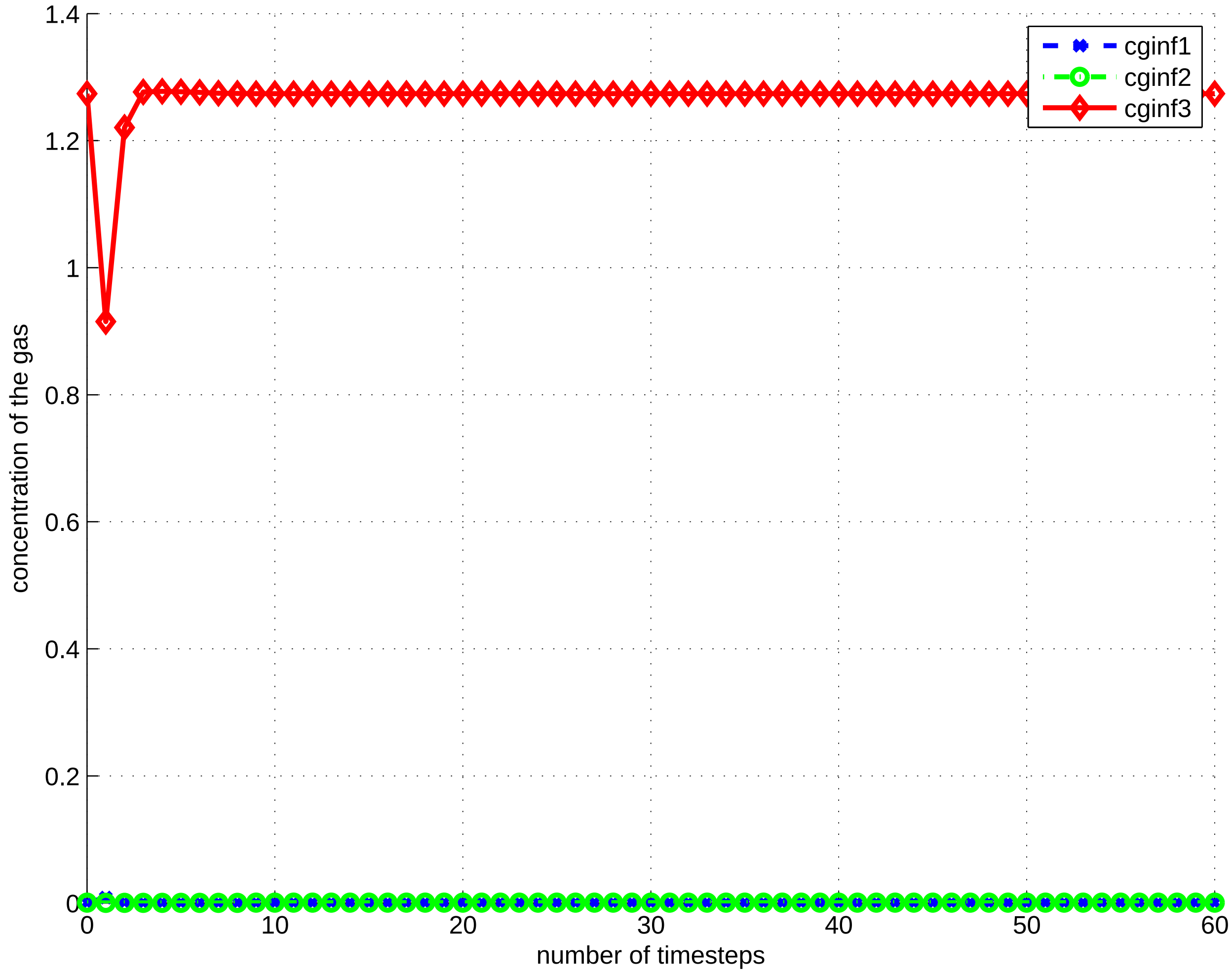
Extended KKT System

$$\begin{bmatrix} \mathbf{H_b} & 0 & 0 & \mathbf{I} & \mathbf{e} \\ 0 & y_\alpha \nabla^2 f(\mathbf{z}_\alpha) & \nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta} & y_\alpha & 0 \\ 0 & (\nabla f(\mathbf{z}_\alpha) + \boldsymbol{\eta})^T & \dfrac{\nu}{y_\alpha^2} & \mathbf{z}_\alpha^T & \mathbf{e} \\ \mathbf{I} & y_\alpha^T & \mathbf{z}_\alpha & 0 & 0 \\ \mathbf{e}^T & 0 & \mathbf{e}^T & 0 & 0 \end{bmatrix} \begin{bmatrix} \mathbf{p_b} \\ \mathbf{p_z} \\ \mathbf{p}_y \\ \mathbf{p}_{\boldsymbol{\eta}} \\ \mathbf{p}_\theta \end{bmatrix} = \begin{bmatrix} \mathbf{r_b} \\ \mathbf{r_z} \\ \mathbf{r}_y \\ \mathbf{r}_{\boldsymbol{\eta}} \\ \mathbf{r}_\theta \end{bmatrix}$$

- $\mathbf{H_b}$ is positive definite.
- Design of decomposition methods for the Newton system with control of the inertia.
  - Schur complement techniques induce modifications of the lower right matrix.
  - Sequential quadratic programming techniques.

Numerical Results

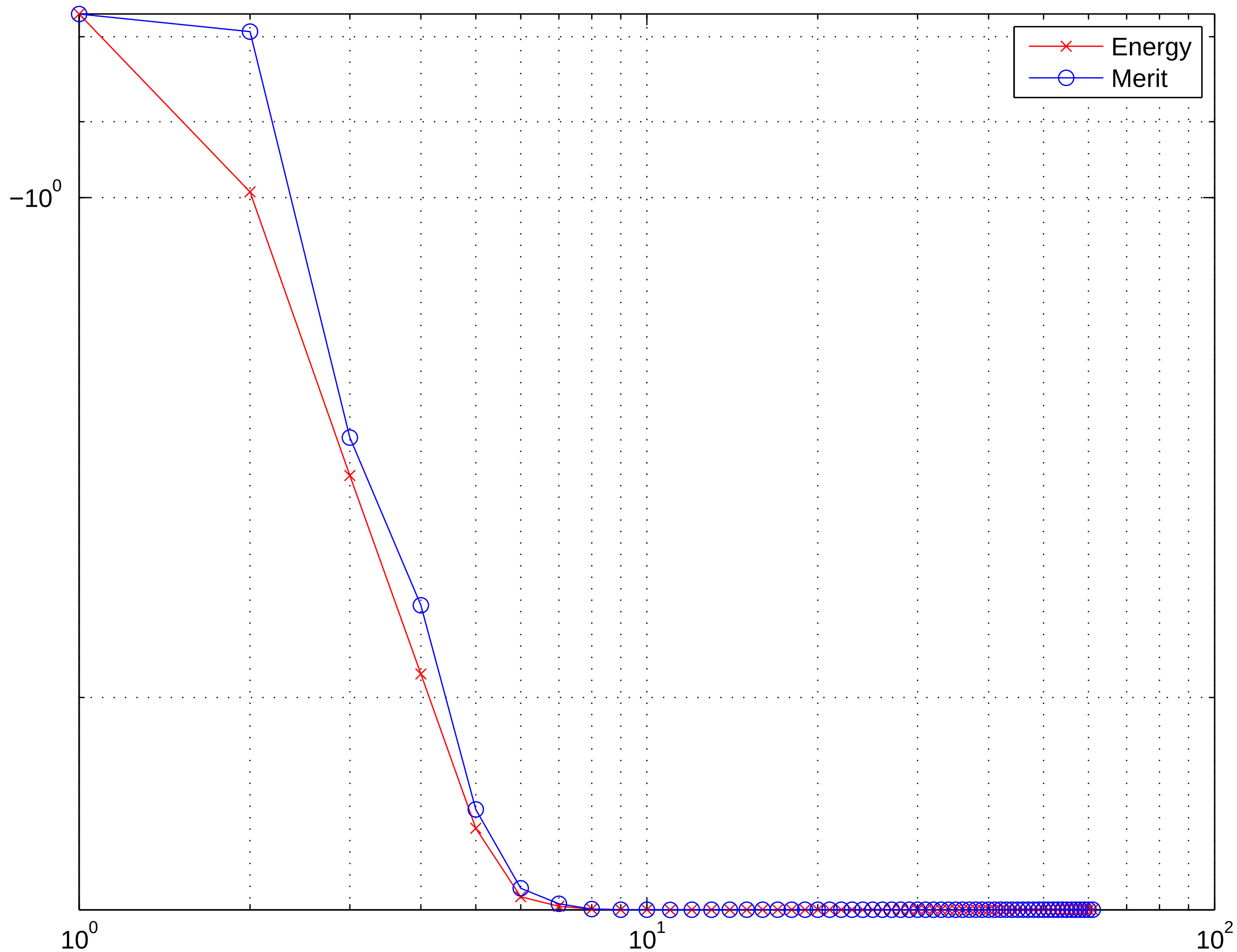
- Gas-Partitioning for one given $\mathbf{b}$:



Concentrations $\mathbf{n}_g$

Numerical Results

- Gas-Partitioning for one given b:



Merit function and objective function

Numerical Results (2)

- Sensitivity with respect to the size of the system.

Size $N+1$	# Iterations (init.)	# Iterations	CPU time
2	16	2	0.06
4	31	30	0.19
8	33	29	0.45
18	31	45	0.66

- Increase of the number of iterations.
- Increase of CPU time mainly due to the size of the linear systems.

Current and Future Work

1. Determination of the convex hull of a finite family of different energy functions (mixtures of aerosols).
2. Dynamic optimization (coupling with differential equations, time detection of activation/deactivation of constraints).
3. Dynamic optimization with a sequence of optimization problems (population of particles).
4. Extension to the determination of the convex hull with multiple local minima.