Modeling and Computation of Thermodynamics and Dynamics of Organic Aerosol Particles

The UHAERO model

Alexandre Caboussat

Department of Mathematics, University of Houston
Houston, TX 77204-3008, USA

caboussat@math.uh.edu
http://math.uh.edu/∼caboussat

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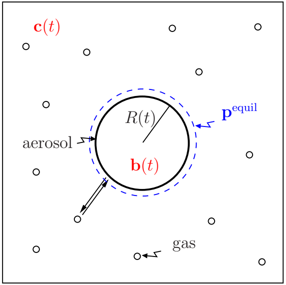
Motivations and Framework

- Modeling and computation of the physical state and chemical composition of atmospheric aerosol particles.
- Thermodynamic (liquid-liquid) equilibrium and gas-particle partitioning of **organic** particles.
- Phase separations/no solid salts, no chemical reactions.
- No *a priori* assumptions (phase lock).
- Efficient and accurate mathematical and computational framework.



Outline

- Introduction and Motivations
- Thermodynamics of Organic Particles
- Dynamics of Organic Particles
- Current Work: Several Organic Particles
- Conclusions

Thermodynamic Equilibrium

- Global optimization problem for the modeling of phase separation into different liquid phases.

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

- $\mathbf{n}_\alpha \in \mathbb{R}^{N+1}$ is the chemical concentration in the phase α.
- Split $\mathbf{n}_\alpha = y_\alpha \mathbf{x}_\alpha$, where y_α is the total number of moles in phase α and $\mathbf{x}_\alpha$ is the mole-fraction (g is homogeneous of degree one).

Thermodynamic Equilibrium

- Global optimization problem for the modeling of phase separation into different liquid phases.

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

- y_α is the total number of moles in phase α and $\mathbf{x}_\alpha$ is the (normalized) mole-fraction.
- The Gibbs free energy g and activity coefficients are modeled by the UNIFAC model.

Numerical Algorithm : Interior-Point Method

- Log/Barrier Penalty parameter for the treatment of the inequality constraints $y_\alpha \geq 0$.

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

Numerical Algorithm : Interior-Point Method

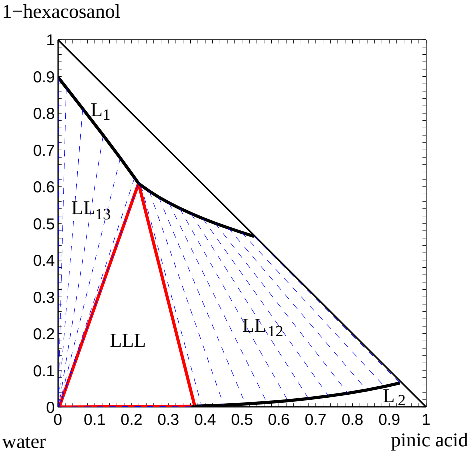
- Log/Barrier Penalty parameter for the treatment of the inequality constraints $y_\alpha \geq 0$.

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

- First order optimality conditions.
- Resolution of nonlinear systems with Newton's method for decreasing values of $\nu \rightarrow 0$.

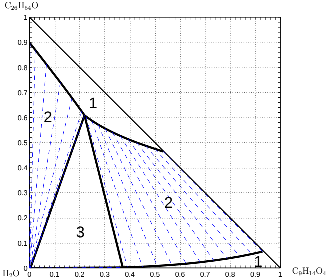
Water/1-Hexacosanol/Pinic Acid System

- Phase diagram.



- Equilibrium state can be composed by up to 3 liquid phases.

Computational Efficiency



- For one grid point, the number of iterations is approximately 25.
- For the (triangular) phase diagram with 100 $\times$ 100 grid points, the CPU time is 2.9 s.

- Scaling w.r.t. the number of organics.

# Organics	# Iterations	CPU time
3	25	0.024
4	40	0.0369
18	41	0.1799

Dynamics and Gas-Particle Partitioning

For given temperature T and pressure P, find the concentration vectors $\mathbf{b}(t)$ in the aerosol particle and $\mathbf{c}(t)$ in the bulk gas:

$$\frac{d}{dt}\mathbf{c}(t) = -\mathbf{h}(R)\left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T}p^{\text{equil}}(\mathbf{b}(t))\eta(\mathbf{b},R)\right)$$

$$\frac{d}{dt}\mathbf{b}(t) = \mathbf{h}(R)\left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T}p^{\text{equil}}(\mathbf{b}(t))\eta(\mathbf{b},R)\right)$$

where $R = R(t)$ is the radius of the particle, $\mathbf{h}$ is the mass transfer rate, η is the *Kelvin constant* for curvature effects, $\mathcal{R}$ is the constant of ideal gases, and $p^{\text{equil}}(\mathbf{b}(t))$ is the surface pressure of the particle.

Dynamics and Growth

- Surface pressure depends on the internal equilibrium state.

$$p^{\text{equil}}(\mathbf{b}) = p_{\text{vapor}} \exp\left(\nabla g\left(\mathbf{x}_\alpha\right)\right)$$

  where p_{vapor} is the vapor pressure.

- Radius of the particle $R(t)$ (for spherical particles).

$$\underbrace{\frac{4}{3}\pi R(t)^3}_{\text{Volume}} = \underbrace{\sum_{i=1}^{n_s} \frac{\mathbf{b}_i(t)\mathbf{m}_{c,i}}{\rho_i}}_{\text{Approximated ratio Mass/density}}$$

  where $\mathbf{m}_c$ the molecular weight vector of the components set and ρ_i is the density of the component i.

- Assumption: $\eta(\mathbf{b}, R) = 1$ (no Kelvin effect).

Time Discretization

- Coupled problem (mass conservation $\mathbf{b}(t) + \mathbf{c}(t) = \mathbf{b}^{tot}$).

$$
\begin{aligned}
\frac{d}{dt}\mathbf{c}(t) &= -\mathbf{h}(R)\left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T} p_{\text{vapor}} \exp\left(\nabla g\left(\mathbf{x}_\alpha\right)\right)\right) \\
\frac{d}{dt}\mathbf{b}(t) &= \mathbf{h}(R)\left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T} p_{\text{vapor}} \exp\left(\nabla g\left(\mathbf{x}_\alpha\right)\right)\right) \\
\min_{y_\alpha(t), \mathbf{x}_\alpha(t)} & \sum_{\alpha=1}^{N+1} y_\alpha(t) g(\mathbf{x}_\alpha(t)) - \nu \sum_{\alpha=1}^{N+1} \ln(y_\alpha(t)) \\
\text{s. t.} & \sum_{\alpha=1}^{N+1} y_\alpha(t)\mathbf{x}_\alpha(t) = \mathbf{b}(t) \\
& \mathbf{e}^T\mathbf{x}_\alpha(t) - 1 = 0, \quad \mathbf{x}_\alpha(t) > 0, \quad \alpha = 1, \ldots, N+1.
\end{aligned}
$$

Time Discretization

- Coupled problem (mass conservation $\mathbf{b}(t) + \mathbf{c}(t) = \mathbf{b}^{tot}$).

$$\frac{d}{dt}\mathbf{b}(t) = \mathbf{h}(R)\left(\mathbf{b}^{tot} - \mathbf{b}(t) - \frac{1}{\mathcal{R}T} p_{\mathrm{vapor}} \exp\left(\nabla g\left(\mathbf{x}_\alpha\right)\right)\right)$$

$$\min_{y_\alpha(t),\mathbf{x}_\alpha(t)} \sum_{\alpha=1}^{N+1} y_\alpha(t) g(\mathbf{x}_\alpha(t)) - \nu \sum_{\alpha=1}^{N+1} \ln(y_\alpha(t))$$

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

$$\mathbf{e}^T \mathbf{x}_\alpha(t) - 1 = 0, \quad \mathbf{x}_\alpha(t) > 0, \quad \alpha = 1, \ldots, N+1.$$

Time Discretization

- Discretization in time with a implicit (one-step) scheme.

$$\frac{\mathbf{b}^{n+1} - \mathbf{b}^{n}}{h} = \mathbf{h}^{n} \left(\mathbf{b}^{tot} - \mathbf{b}^{n+1} - \frac{1}{\mathcal{R}T} p_{\mathrm{vapor}} \exp\left(\nabla g \left(\mathbf{x}_{\alpha}^{n+1} \right) \right) \right)$$

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

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

$$\mathbf{e}^{T} \mathbf{x}_{\alpha}^{n+1} - 1 = 0, \quad \mathbf{x}_{\alpha}^{n+1} > 0, \quad \alpha = 1, \ldots, N+1.$$

- When introducing the first order optimality conditions, extended system of nonlinear equations for fixed ν and Newton method.

Metastable States and Acceleration Techniques

- **Cold-start techniques:** Convergence to the global minimum and accurate detection of active/inactive constraints for a suitable starting point.
- **Warm-start techniques:** Convergence to a local minimum starting from the solution at previous time step.
  - Quadratic/faster convergence in a neighborhood of a KKT point.
  - Possible convergence to a meta-stable state (local attractor).
  - Phase separations/merging can be missed!
- **Tracking techniques:** Automatic detection of the phase separation/merging and accurate computation of the corresponding time and compositions.

Accurate Tracking of Phase Separation

- Separation/merging of liquid phases corresponds to the activation/deactivation of inequality constraints.
- A vanishing phase is implicitly given by

$$y_\alpha(t) > 0 \rightarrow y_\alpha(t) = 0.$$

- A phase separation is implicitly given by

$$y_\alpha(t) = 0 \rightarrow y_\alpha(t) > 0.$$

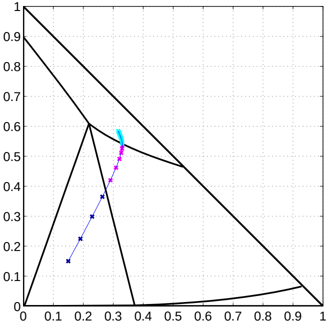
- **Tool.** Truncated Taylor expansion:

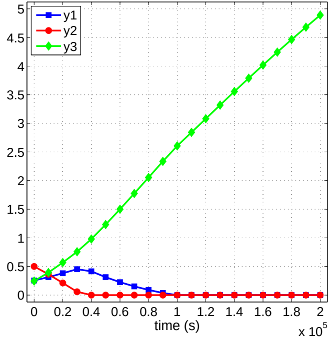
$$0 = y_\alpha(t^n + h^\star) = y_\alpha(t^n) + h^\star \frac{dy_\alpha}{dt}(t^n) + \mathcal{O}((h^\star)^2).$$

$$\Rightarrow \quad h^\star \simeq -\frac{y_\alpha(t^n)}{\frac{dy_\alpha}{dt}(t^n)}.$$

Numerical Results

- Trajectory of the (normalized) feed vector $\mathbf{b}(t)$. Convergence to a stationary solution.

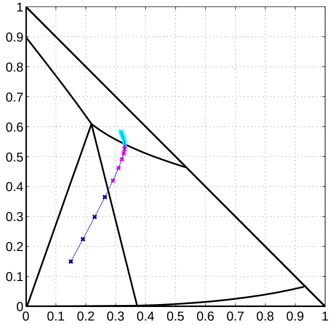


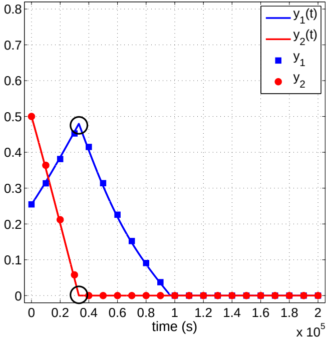


- Detection of the phase separations with cold starts.

Numerical Results

- Trajectory of the (normalized) feed vector $\mathbf{b}(t)$. Convergence to a stationary solution.

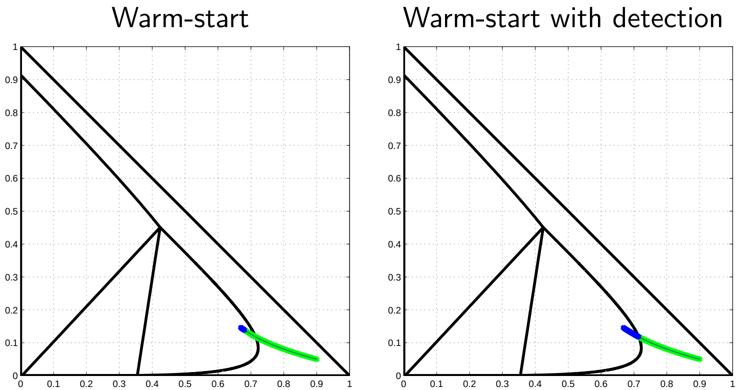




- Detection of the phase separations with cold starts.
- What happens with warm starts ??

Warm-Start and Tracking Results

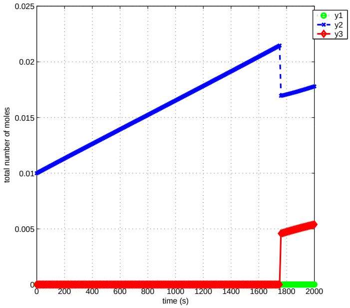
- Warm-start techniques for faster convergence miss the time of activation/deactivation!
- Evolution of $\mathbf{b}(t)$.



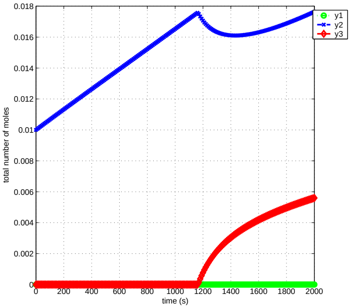
Warm-Start and Tracking Results

- Warm-start techniques for faster convergence miss the time of activation/deactivation!
- Evolution of $y_\alpha(t)$.

Warm-start

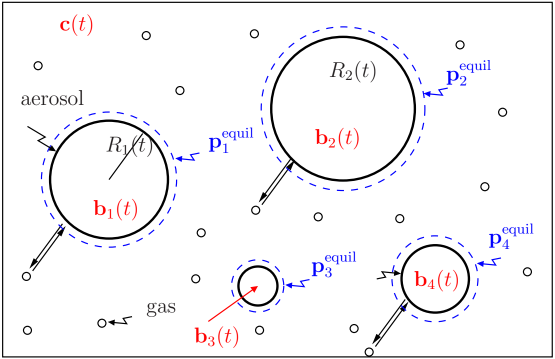


Warm-start with detection



Current Work - Coupling of Several Particles

- Population of M aerosol particles.



- Differences of sizes, reaction speeds, modeling of internal energies.

Modeling with Sequences of Optimization Problems

- Population of M aerosol particles ($i = 1, \ldots, M$).

$$\frac{d}{dt}\mathbf{c}(t) = -\sum_{i=1}^{M} \mathbf{h}(r_i) \left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T} p_{\text{vapor}} \exp\left(\nabla g_i\left(\mathbf{x}_\alpha^i\right)\right)\right), \mathbf{c}(0) = \mathbf{c}_0$$

$$\frac{d}{dt}\mathbf{b}_i(t) = \mathbf{h}(r_i) \left(\mathbf{c}(t) - \frac{1}{\mathcal{R}T} p_{\text{vapor}} \exp\left(\nabla g_i\left(\mathbf{x}_\alpha^i\right)\right)\right), \ \mathbf{b}_i(0) = \mathbf{b}_{0,i}$$

$$\min_{y_\alpha^i, \mathbf{x}_\alpha^i} \sum_{\alpha=1}^{N+1} y_\alpha^i g_i(\mathbf{x}_\alpha^i)$$

$$\text{s. t.} \quad \sum_{\alpha=1}^{N+1} y_\alpha^i \mathbf{x}_\alpha^i = \mathbf{b}_i(t)$$

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

Newton system

- Time discretization, first order optimality conditions and Newton method lead to large block-structured linear systems.

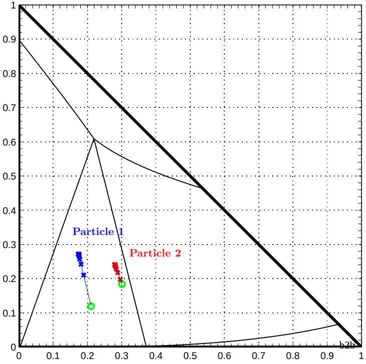
$$
\left[\begin{array}{ccc|ccc|cc|c}
H_1 & 0 & B_1 & 0 & 0 & 0 & \dots & \dots & C_1 \\
0 & O_1 & A_1 & 0 & 0 & 0 & & & 0 \\
E_1 & A_1^T & 0 & 0 & 0 & 0 & & & 0 \\
\hline
0 & 0 & 0 & H_2 & 0 & B_2 & & & C_2 \\
0 & 0 & 0 & 0 & O_2 & A_2 & & & 0 \\
0 & 0 & 0 & E_2 & A_2^T & 0 & & & 0 \\
\hline
\vdots & & & & & & \ddots & & \vdots \\
\vdots & & & & & & & \ddots & \vdots \\
\hline
0 & 0 & D_1 & 0 & 0 & D_2 & \dots & \dots & H_0
\end{array}\right]
\left[\begin{array}{c}
p_{c_1} \\ p_{x_1} \\ p_{\lambda_1} \\ \hline p_{c_2} \\ p_{x_2} \\ p_{\lambda_2} \\ \hline \vdots \\ \vdots \\ \hline p_{c_0}
\end{array}\right]
=
\left[\begin{array}{c}
r_{c_1} \\ r_{x_1} \\ r_{\lambda_1} \\ \hline r_{c_2} \\ r_{x_2} \\ r_{\lambda_2} \\ \hline \vdots \\ \vdots \\ \hline r_{c_0}
\end{array}\right]
$$

- Resolution with *Schur complement techniques.*

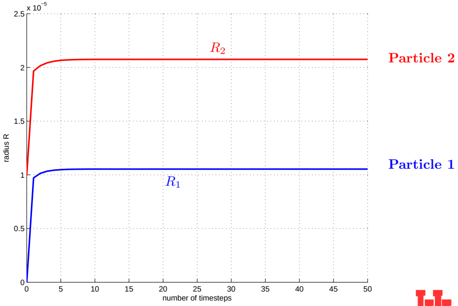
Preliminary Results

- Two particles without metastable states.

Trajectories $\mathbf{b}_i$



Radii R_i



Conclusions and Perspectives

- Thermodynamics of organic particles.
- Dynamics of organic particles.
- Stable vs. meta-stable branches of equilibria.
- (Small) population of organic particles.

- (Large) population of organic particles.
- Multiscale techniques.
- Mixtures of organic and inorganic compounds.
- More accurate methods.

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