

Modeling and Computation of Thermodynamic Equilibrium and Mass Transfer for Organic Aerosol Particles ^{*}

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^{*} Project supported by the U. S. Environmental Public Agency Grant X-83234201.



Motivations

Modeling of the physical and chemical state of atmospheric aerosol particles.

- *"The chemical and physical properties of aerosols are needed to estimate and predict direct and indirect climate forcing", [IPCC: Third Assessment Report (2001)].*
- Influences for climate forcing, especially in terms of radiation balance and cloud formation.
- At present: limited knowledge of aerosol composition and transformation and high uncertainty on their environmental effects.
- Current aerosol models do not predict accurately the phase state and the growth phenomena of atmospheric aerosols.



Perspectives

- **UHAERO project**: modeling of the thermodynamics and dynamics for inorganic aerosols, organic aerosols and mixtures of inorganic and organic species.
- Tentative to consider general chemical composition of aerosols, instead of separating the aerosols into different types (water, inorganics, dust, organics, trace gases, etc.)
- Computational model for the thermodynamics and crystallization of inorganic aerosols [*Atmos. Chem. Phys.*, 6, 975–992, (2006)].
- Generalization to mixtures of organic and inorganic aerosols.



Organic Particles

- Focus on organic particles to model phase separation in liquid-liquid equilibrium and gas-particle partitioning (no solid salts, no chemical reactions).
- Provide an efficient and accurate mathematical framework for the computation of liquid-liquid equilibria, without introducing *a priori* assumptions
- In current models, the phase separation is often neglected and replaced by a *phase lock* mechanism that splits hydrophilic and hydrophobic organic components.
- However, the influence of organics on crystallization is known as *salt-in - salt-out effect*.



Outline

- Modeling

- Thermodynamic liquid-liquid equilibrium inside one organic particle.
- Mass transfer for gas-particle partitioning.

- Computation

- Phase separation inside the particle as a minimum of energy,
- Mass transfer as a system of differential equations.

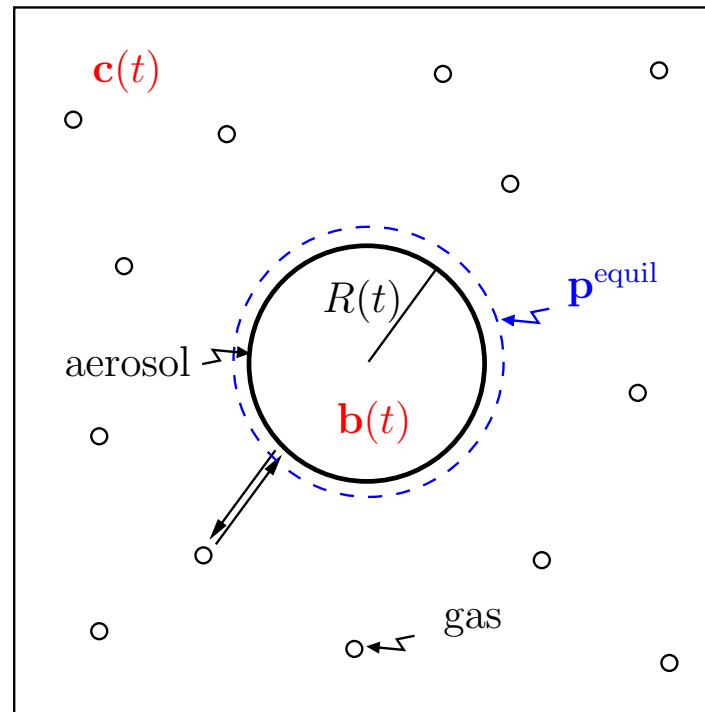
- Numerical Results

- Illustration for a three components system, *e.g.* water, hexacosanol and pinic acid.



Model Setup

- One single aerosol particle



- We want to find the concentration vectors $\mathbf{b}(t)$ in the aerosol particle and $\mathbf{c}(t)$ in the bulk gas, as well as the equilibrium state (phase separation) inside the particle.



Modeling the Dynamics

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:

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

where R is the radius of the particle, \mathbf{h} is the mass transfer rate, \mathbf{N} is the *number density*, p^{equil} is the surface pressure and η is the *Kelvin constant* for curvature effects.

- The **surface pressure** p^{equil} depends on the internal equilibrium state of the particle



Modeling the Thermodynamics

To determine the surface pressure p^{equil} , solve a **phase equilibrium problem** inside the aerosol particle for given concentration vector \mathbf{b} :

$$\begin{aligned} \min_{\mathbf{n}_\alpha} \quad & G = \sum_{\alpha=1}^p g(\mathbf{n}_\alpha) && \leftarrow \text{Gibbs free energy,} \\ \text{s. t.} \quad & \sum_{\alpha=1}^p \mathbf{n}_\alpha = \mathbf{b}(t), && \leftarrow \text{Mass conservation,} \\ & \mathbf{n}_\alpha \geq \mathbf{0}, \quad \alpha = 1, \dots, p. && \leftarrow \text{Positive concentrations,} \end{aligned}$$

where \mathbf{n}_α is the concentration vector in the phase α .

- The number of phases existing at the equilibrium is not known a priori, but is a result of the equilibrium computation.



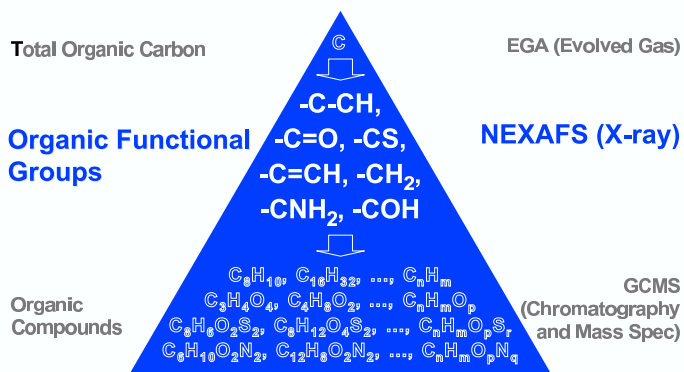
Modeling the Gibbs Free Energy

- The Gibbs free energy is expressed in terms of *chemical potentials* $g(\mathbf{n}_\alpha) = \mathbf{n}_\alpha^T \mu_\alpha(\mathbf{n}_\alpha)$, where

$$\mu_\alpha(\mathbf{n}) = \mu_\alpha^0 + \mathcal{R}T \ln a_\alpha(\mathbf{n}),$$

where μ_α^0 is a constant chemical potential and $a_\alpha(\mathbf{x})$ is the **activity function**.

Organic Measurements



The **UNIFAC model** ([Fredenslund, Gmeling, Rasmussen, 1979 & 1982]) for organic aerosols is used to describe the activity coefficients and relies on the concept of *group contributions*.



Solving the Thermodynamics

- Introduction of a log-barrier penalty function to replace the inequality constraints (simplified formulation):

$$\begin{aligned} \min_{\mathbf{n}_\alpha} \quad & \sum_{\alpha=1}^p g(\mathbf{n}_\alpha) - \nu \sum_{\alpha=1}^p \ln(\mathbf{e}^T \mathbf{n}_\alpha) \\ \text{s. t.} \quad & \sum_{\alpha=1}^p \mathbf{n}_\alpha = \mathbf{b}, \\ & \mathbf{n}_\alpha \geq 0, \quad \alpha = 1, \dots, p. \end{aligned}$$

- ν is a penalty parameter, which tends to zero.
- The phase α disappears when $\mathbf{e}^T \mathbf{n}_\alpha \simeq 0$.
- All phases exist at the beginning and then are selected by the algorithm.



Modeling the Particle Growth

- The surface pressure is derived from the internal equilibrium state of the particle

$$p^{\text{equil}}(\mathbf{b}) = p_{\text{vapor}} \exp \left(-\nabla g \left(\frac{\mathbf{n}_\alpha}{\mathbf{e}^T \mathbf{n}_\alpha} \right) \right).$$

- The radius of the particle $R(t)$ is computed by the equation of conservation of mass in the (spherical) particle:

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

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



Modeling Issues

- The **phase lock is eliminated** and all organic compounds can partition from the gas phase to all the liquid phases.
- The **existing phases at equilibrium** are automatically selected by the algorithm.
- The **mass conservation** in the gas-particle system is guaranteed.

Assumptions (to be relaxed in the future):

- The curvature effects (Kelvin effect) are neglected for large particles.
- The particle is assumed to be spherical. The size is described by the radius.



Computational Method

- Accuracy of the computations = Accuracy of the energy model
 - Error due to the numerics is the rounding error.
 - No a priori information on the equilibrium state.
- Cost of the computation = Cost of the energy model evaluation + Cost of the numerics
 - Determination of the thermodynamic equilibrium with a *primal-dual interior-point method*.
 - Extension with *sequential quadratic programming techniques* to model the dynamics for the gas-particle partitioning.
- Flexibility of the method (black-box algorithm)
 - Current Work: Web interface to allow remote computations with personal parameters.
 - Future: Open-source code.



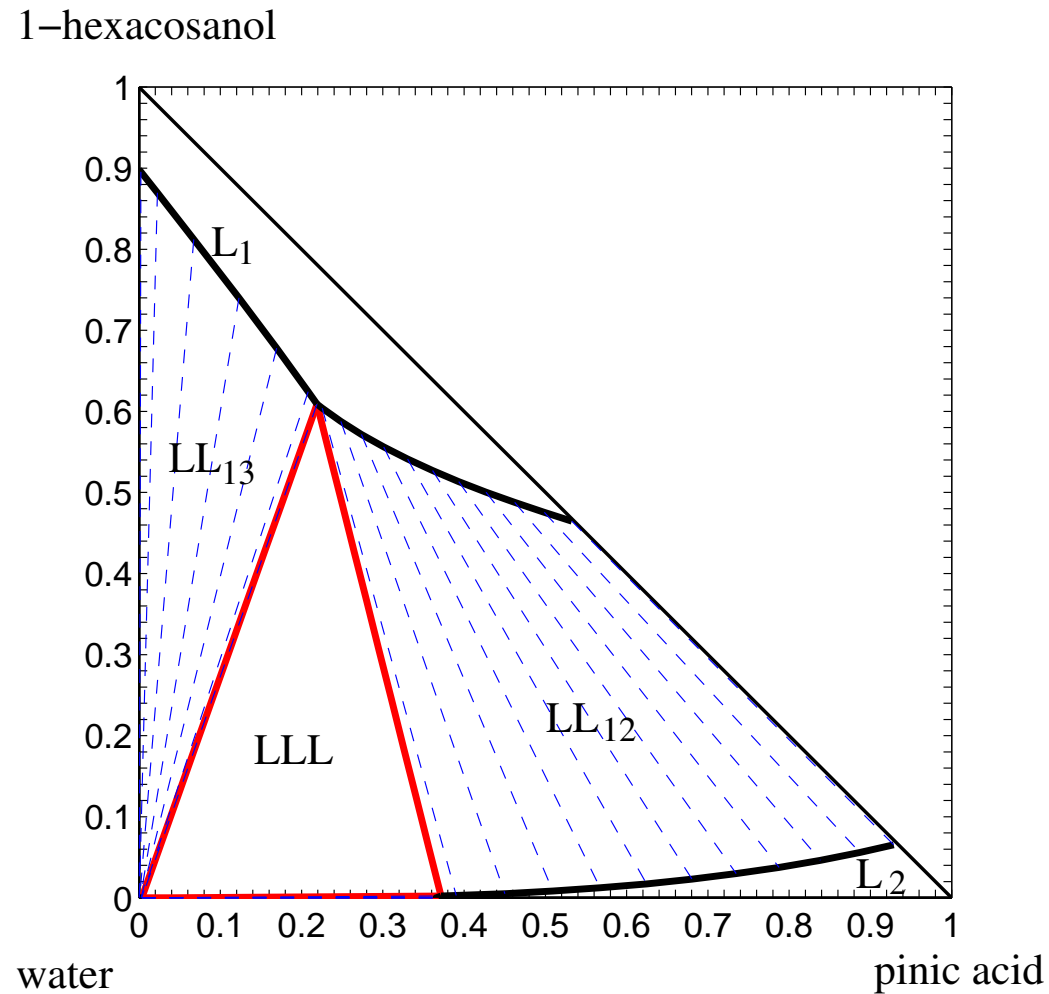
Water-Hexacosanol-Pinic Acid System

- Composition :
 - 1-hexacosanol (1 CH₃, 25 CH₂, 1 OH)
 - pinic acid (2 CH₃, 2 CH₂, 2 CH, 1 C, 2 COOH)
 - water (1 H₂O)
- Equilibrium state can be composed by up to three liquid phases, depending on the particle composition (mixing)
- Results for
 - (i) the thermodynamic equilibrium;
 - (ii) the gas-phase partitioning.
- Current work (with S. Clegg, Univ. East Anglia) : systems up to 18 components.



Phase Diagram

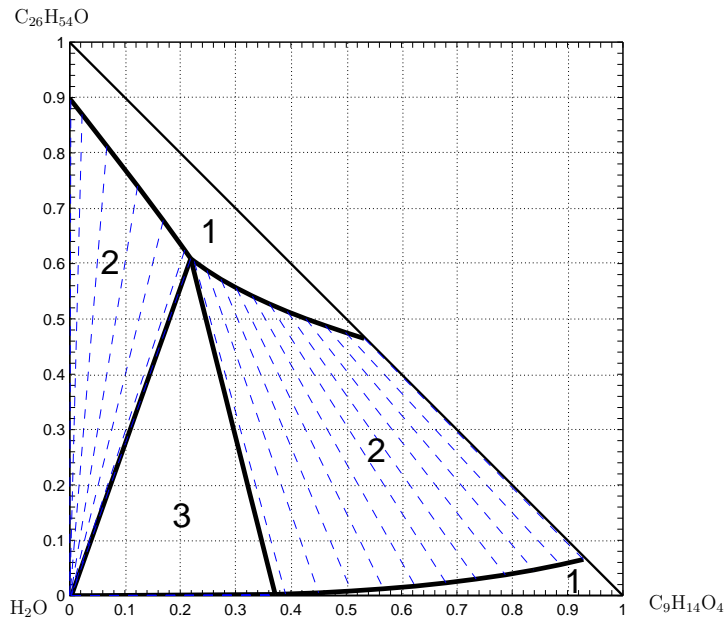
- Reconstruction of the phase diagram.



Pictures by C. Landry, EPFL, Switzerland



Computational Efficiency



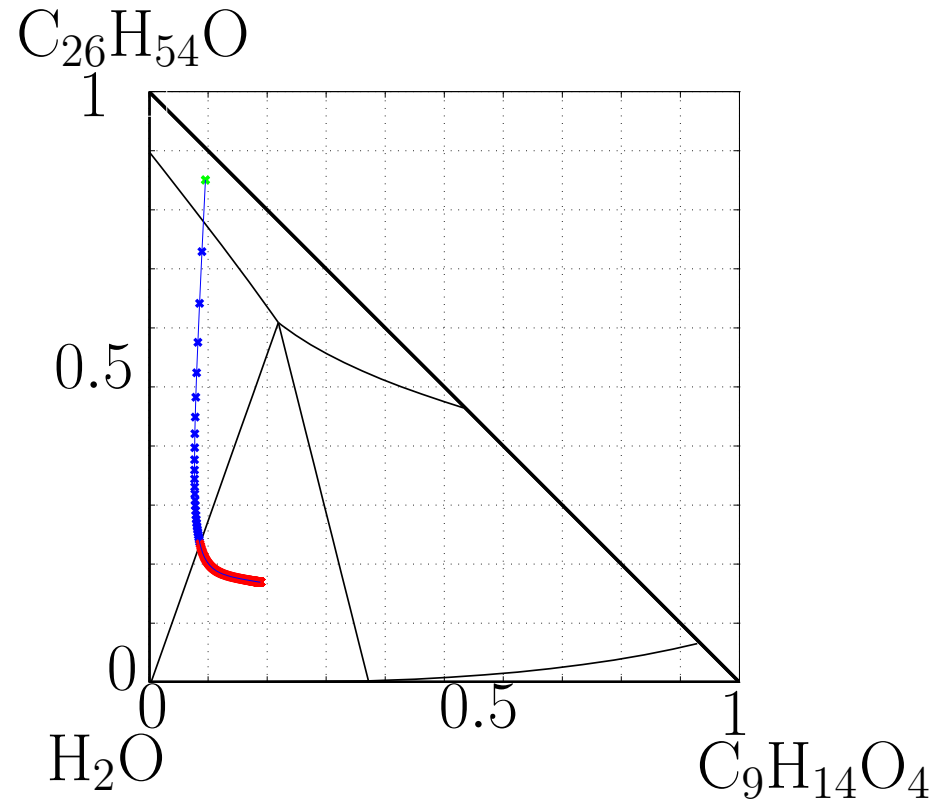
- For one grid point, the number of iterations is approximately 20.
- For the (triangular) phase diagram with 100×100 grid points, the CPU time is 2.9 s.

- Insertion in 3D global models is totally reasonable.
- High accuracy (tolerance $\simeq 10^{-13}$) and no a priori assumptions on the behavior of the system.



Gas-Particle Partitioning

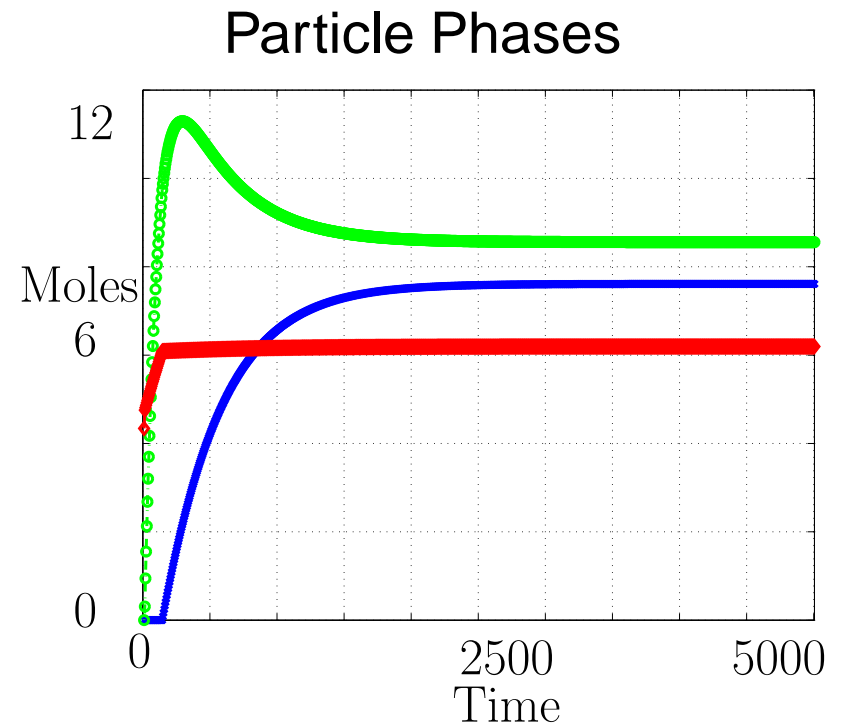
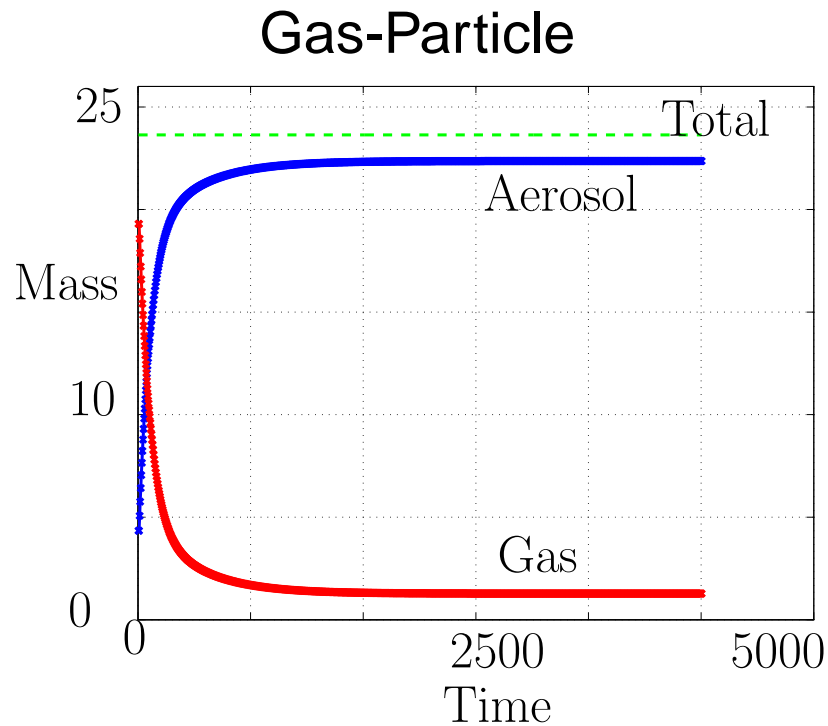
- Trajectory of the feed vector \mathbf{b} (mixing inside the particle):



- Convergence towards a stationary solution inside the particle.
- Tracking of the phase separations.



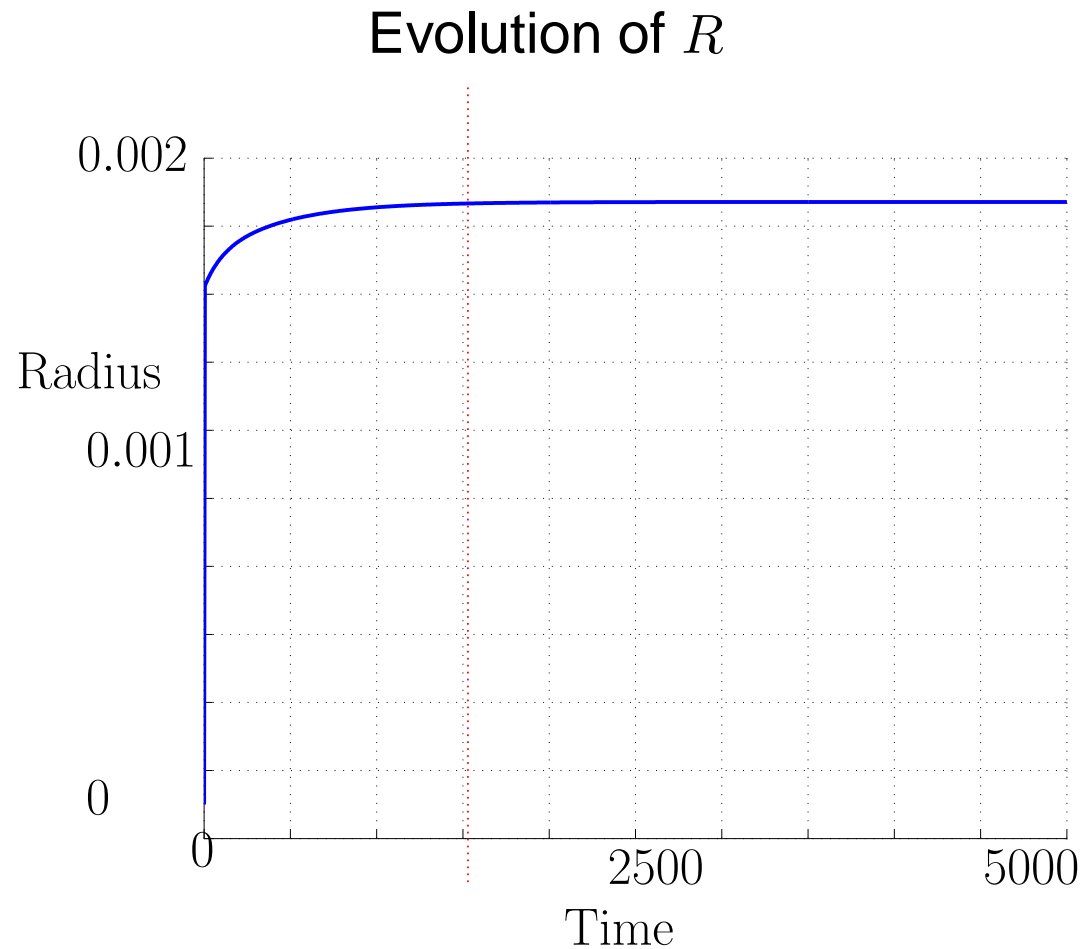
Mass Conservation



- Mass conservation in the gas-particle system and convergence to a stationary solution for the particle phases.



Aerosol Growth



- The characteristic times for gas-particle equilibrium compare well with [Meng, Seinfeld (1996)].



Conclusions

Modeling of organic aerosols.

- Determination of phase separation and gas-particle equilibrium.
- Gibbs free energy given by a UNIFAC model.
- Framework is accurate, efficient and flexible.
- Experimentation with various chemical systems.



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Current Work : Mixtures of organic and inorganic aerosols.

- Phase separation and chemical reactions.
- Extension of the Gibbs free energy model.
- Salt-in - Salt-out phenomenon for salt crystallization.



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