Modeling of Organic Effects on Aerosols Growth ⋆

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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)].
- At present: limited knowledge of aerosol composition and transformation, high uncertainty on their environmental effects (gas-aerosol-cloud-climate interactions).
- Current aerosol models often fail to predict the phase state and composition and the multistage growth phenomena of atmospheric aerosols.

Organic Particles

- Focus on organic particles to model phase separation in liquid-liquid equilibrium and gas-particle partitioning (no solid salts).
- The phase separation is often neglected and replaced by a *phase lock* mecanism that splits hydrophilic and hydrophobic organic components and does not allow any mixing between the two parts.
- However, the influence of organics on crystallization is well-known as *salt-in - salt-out effect*. The presence of organic components influences the formation of salts.

Outline

- Modeling
  - Thermodynamic equilibrium inside one organic particle.
  - Mass transfers for gas-particle partitioning.
- Computation
  - Phase separation inside the particle, liquid-liquid equilibrium,
  - Mass transfer between the particles and the gas phase.
- Numerical Results
  - Illustration for a three components system, *e.g.* water, hexacosanol and pinic acid.

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:

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

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 $\mathbf{b}$:

$$\begin{array}{lll} \min & G = \displaystyle\sum_{\alpha=1}^{\pi} g(\mathbf{n}_\alpha) & \longleftarrow \text{Gibbs free energy,} \\ \text{s. t.} & \displaystyle\sum_{\alpha=1}^{\pi} \mathbf{n}_\alpha = \mathbf{b}, & \longleftarrow \text{Mass conservation,} \\ & \mathbf{n}_\alpha \geq \mathbf{0}, \quad \alpha = 1, \ldots, \pi. & \longleftarrow \text{Positive concentrations,} \end{array}$$

where $\mathbf{n}_\alpha$ is the concentration vector in the phase α.

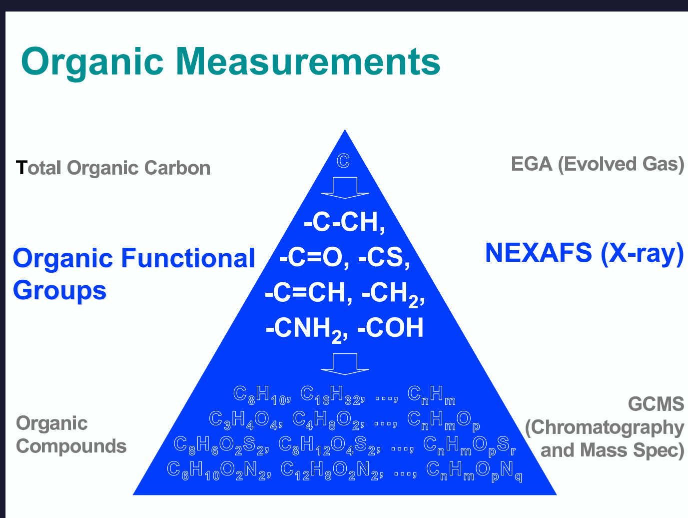
- The number of phases existing at the equilibrium is not known a priori, but is a result of the equilibrium computation.

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

$$\boldsymbol{\mu}_\alpha(\mathbf{n}) = \boldsymbol{\mu}_\alpha^0 + RT \ln \boldsymbol{a}_\alpha(\mathbf{n}),$$

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



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

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 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 mass conservation in the gas-particle system is guaranteed.
- The curvature effects (Kelvin effect) are neglected for large particles.
- The density of the particle is approximated from the density of the components.

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.

Computational Method

- Accuracy of the computations = Accuracy of the Energy model
- 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, with a *Newton's method* applied to the *KKT system of equations* augmented with a log/barrier penalty term.
  - Extension with sequential quadratic programming techniques to model the phase changes, dynamics between the gas phase and particle phases and aerosols growth.

Computational Method

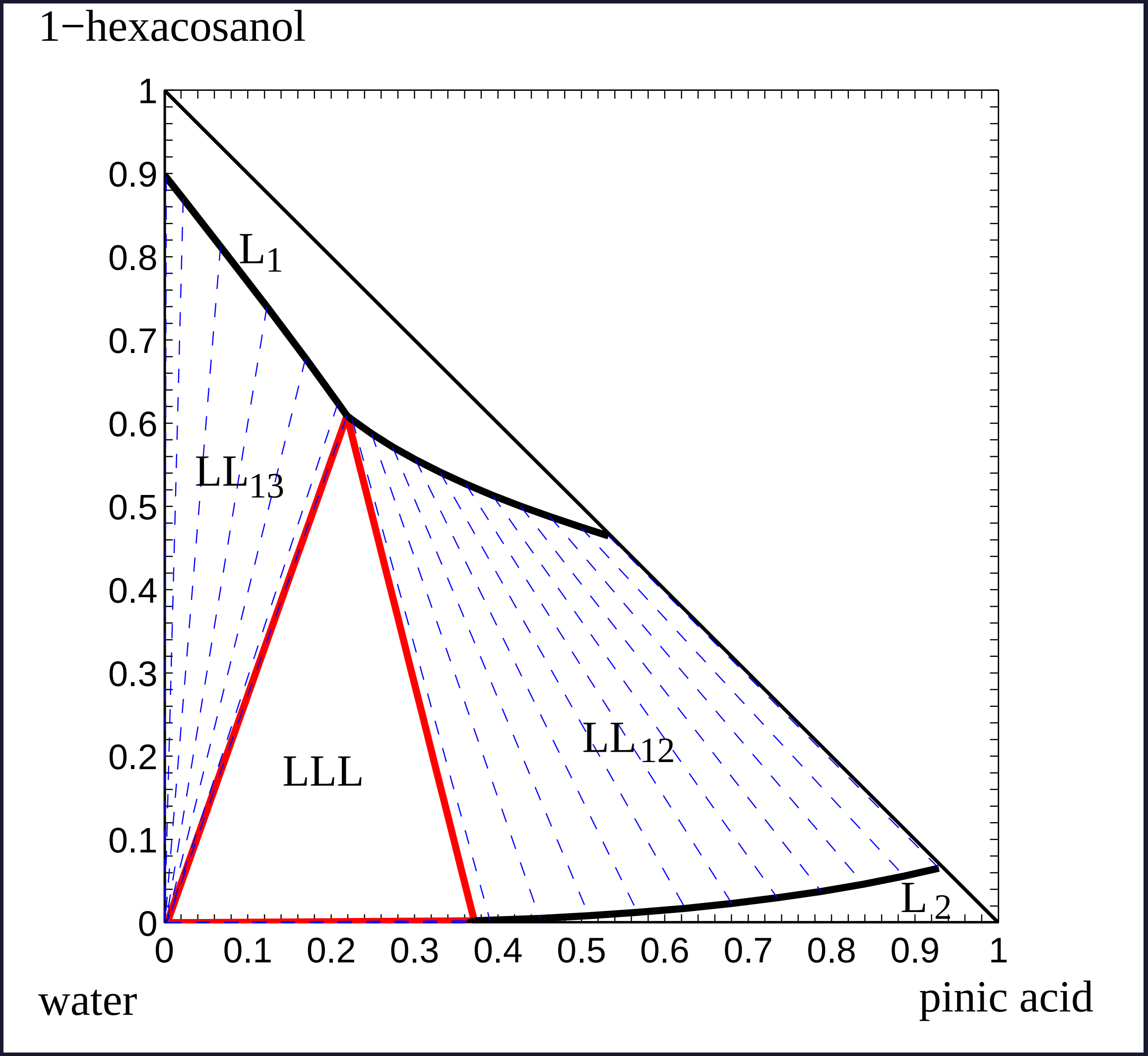
- Accuracy of the computations = Accuracy of the Energy model
- Cost of the Computation = Cost of the Energy model evaluation + Cost of the numerics
- Flexibility of the Method (Black-Box Algorithm)

Water-Hexacosanol-Pinic Acid System

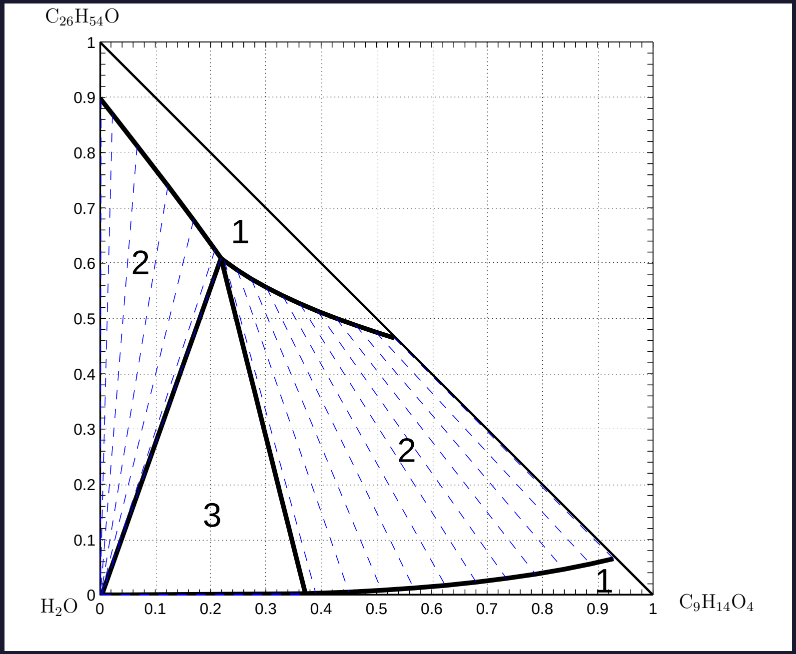
- Composition :
  - 1-hexacosanol (1 CH_3, 25 CH_2, 1 OH)
  - pinic acid (2 CH_3, 2 CH_2, 2 CH, 1 C, 2 COOH)
  - water (1 H_2O)
- Equilibrium state can be composed by up to three liquid phases, depending on the particle composition (mixing)
- Results for
  (i) the thermodynamic equilibrium;
  (ii) the gas-phase partitioning.

Phase Diagram

- Reconstruction of the phase diagram.



Computational Efficiency

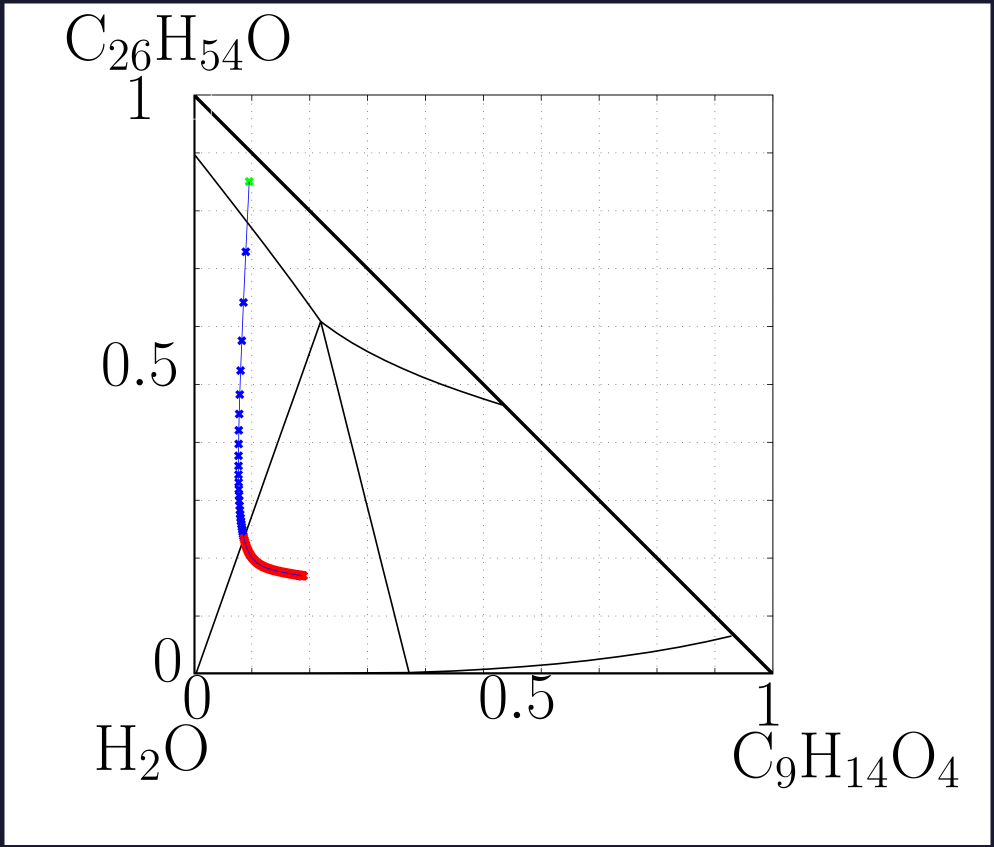


- For one grid point, the number of iterations is approximately 20-30 .
- For the (triangular) phase diagram with 100×100 grid points, the CPU time is 2.9 s.

- Insertion in 3D global models is totally reasonable.
- High accuracy and no a priori assumptions on the behavior of the system.

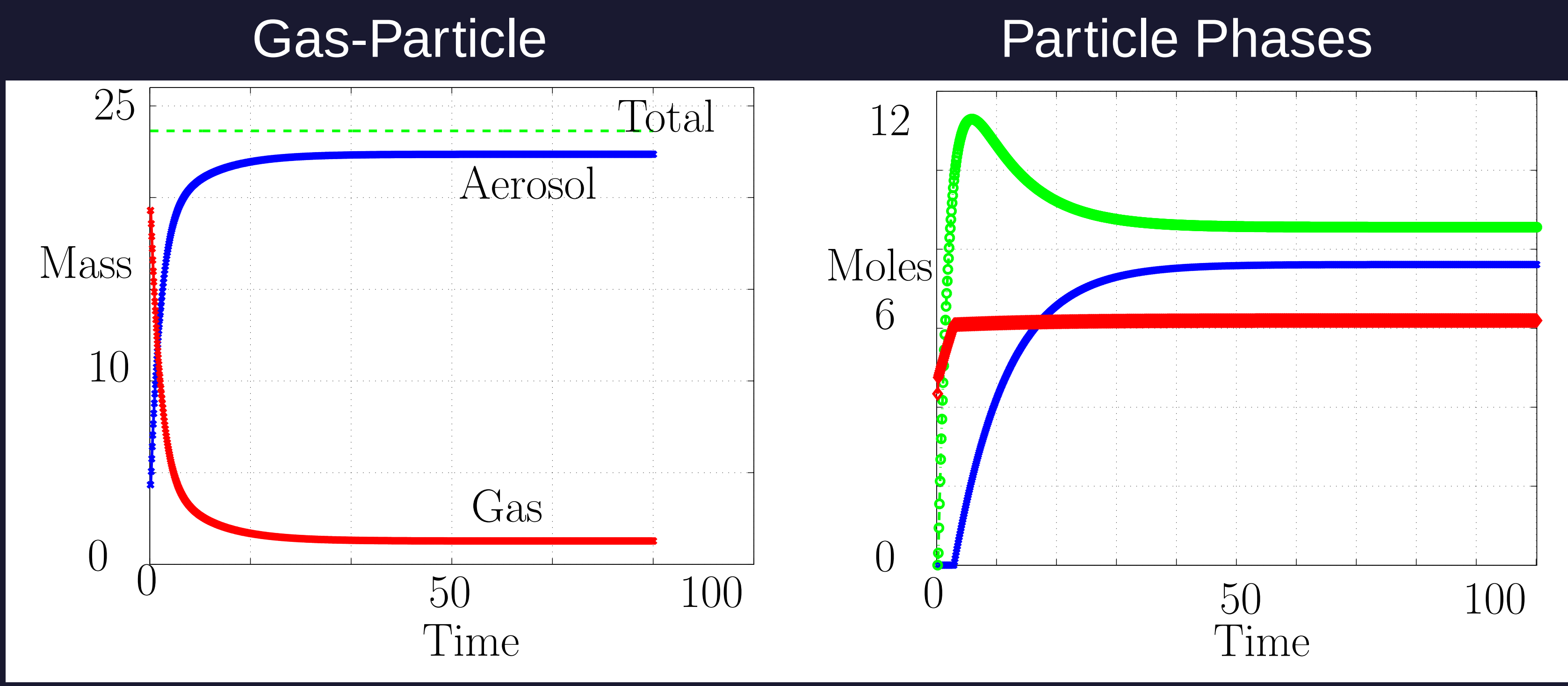
Gas-Particle Partitioning

Trajectory of b



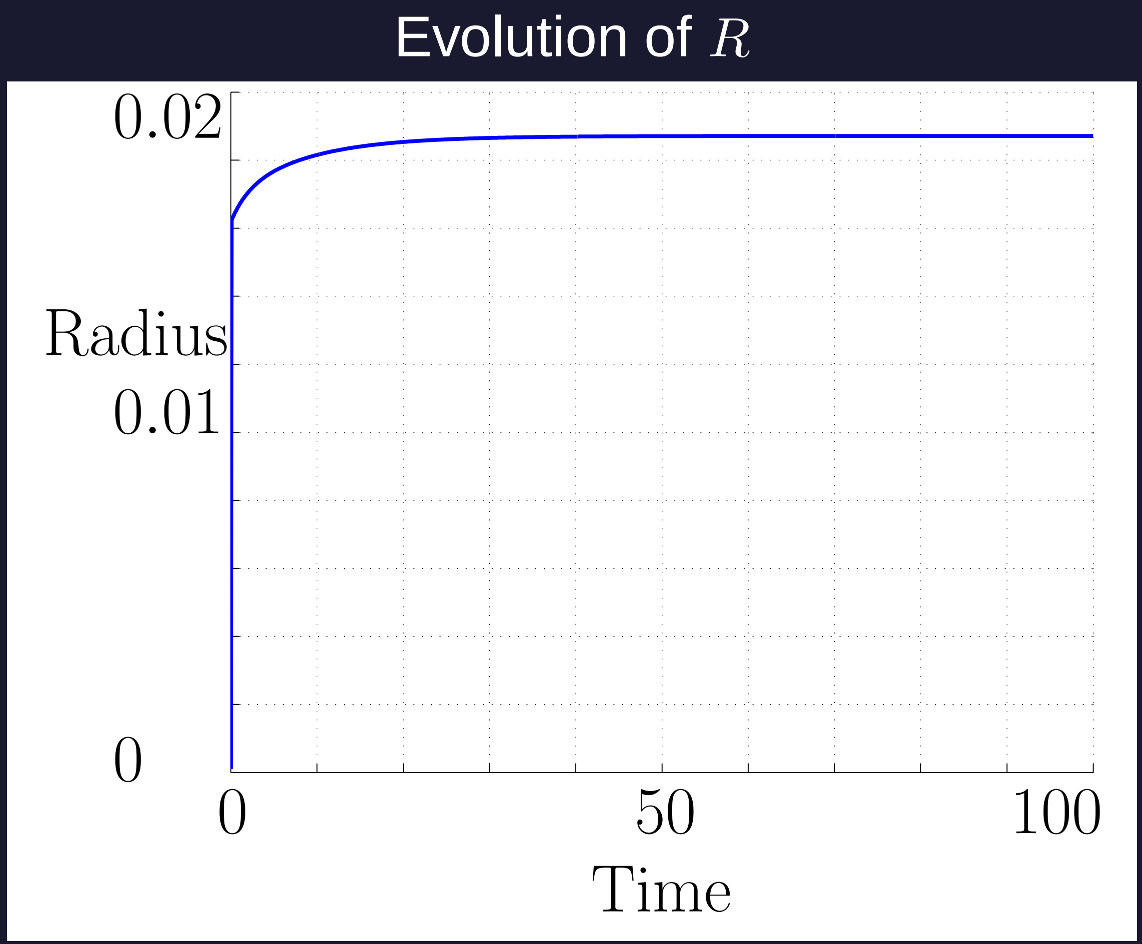
- Tracking of the phase separations.
- Convergence towards a stationary gas-particle equilibrium.

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.
- I. Accuracy of the Computations.
- II. Cost of the Computations.
- III. Flexibility of the Method.

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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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