

# Modeling of Phase Equilibrium and Mass Transfer for Organic Aerosol Particles\*

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# Motivations

- Modeling and computation 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 on climate forcing, water content, radiation balance, activation, cloud formation, etc.
- Current aerosol models do not always predict accurately the phase state and the growth phenomena of atmospheric aerosols.
- **UHAERO project**: modeling of the thermodynamics and dynamics for inorganic aerosols, organic aerosols and mixtures of inorganic and organic species.



# Perspectives

- Consider general chemical composition of aerosols, instead of separating the aerosols into different types (water, inorganics, dust, organics, trace gases, etc.)
  - (1) Computational model for the thermodynamics and crystallization of **inorganic aerosols** [*Atmos. Chem. Phys.*, 6, (2006)].
  - (2) Computational model for the thermodynamics of **inorganic aerosols and dicarboxylic acids**.
  - (3) **Computational model for phase separation of organic aerosols**.
  - (4) Generalization to **mixtures of organic and inorganic aerosols**.



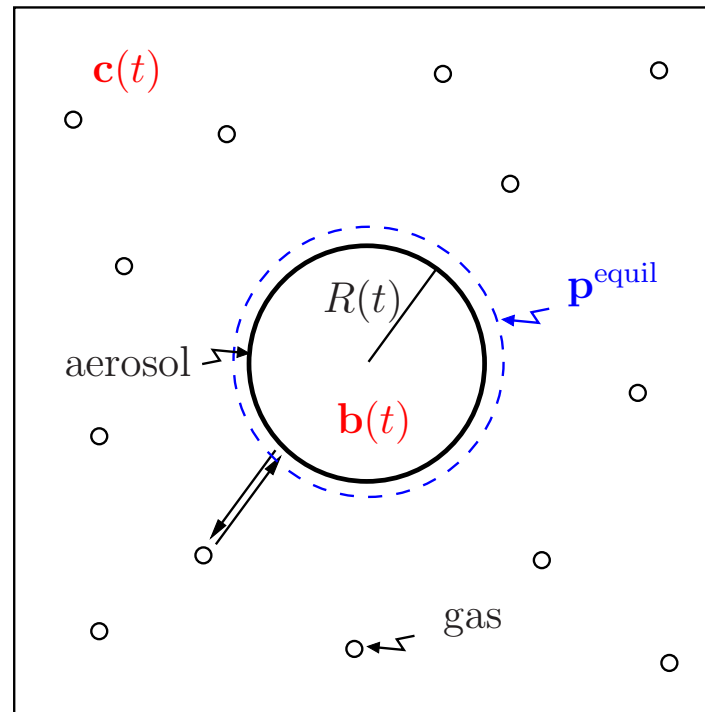
# Organic Particles

- Phase separation, liquid-liquid equilibrium, and gas-particle partitioning.
- No solid salts, no chemical reactions.
- Efficient and accurate mathematical framework, without introduction of *a priori* assumptions.
- Replacement of the *phase lock* mechanism that splits hydrophilic and hydrophobic organic components with the computation of phase equilibrium.



# 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 Thermodynamics

For given temperature  $T$  and pressure  $P$ , solve a **phase liquid-liquid equilibrium problem** inside the aerosol particle for given concentration vector  $\mathbf{b}$ :

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

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

- The number of phases existing at the equilibrium is not known a priori, but is a result of the equilibrium computation.
- The algorithm starts with all phases and selects those that appear at equilibrium.



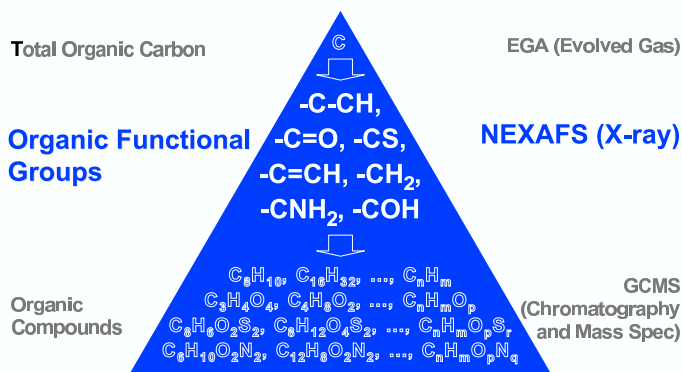
# Modeling the Gibbs Free Energy

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

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

where  $\boldsymbol{\mu}_\alpha^0$  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*.



# Modeling the 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:

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

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

where  $R = R(t)$  is the radius of the particle,  $\mathbf{h}$  is the mass transfer rate,  $\mathbf{N}$  is the *number density*,  $\eta$  is the *Kelvin constant* for curvature effects, and  $\mathcal{R}$  is the constant of ideal gases.

- **Coupling** via **the surface pressure**  $p^{\text{equil}}(\mathbf{b}(t))$  of the particle.



# Modeling the Particle Growth

- The **surface pressure** depends on the internal equilibrium state ( $\mathbf{n}_\alpha, \alpha = 1, \dots, p$ ) of the particle and is derived from

$$p^{\text{equil}}(\mathbf{b}) = p_{\text{vapor}} \exp \left( -\frac{1}{\mathbf{e}^T \mathbf{n}_\alpha} \nabla g \left( \frac{\mathbf{n}_\alpha}{\mathbf{e}^T \mathbf{n}_\alpha} \right) \right),$$

where  $p_{\text{vapor}}$  is the vapor pressure.

- The **radius of the particle**  $R(t)$  is computed by 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  $\rho_i$  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 (all phases exist at the beginning).
- The mass conservation in the gas-particle system is guaranteed.
  
- The curvature effects (Kelvin effect) are neglected.
- The particle is assumed to be spherical.



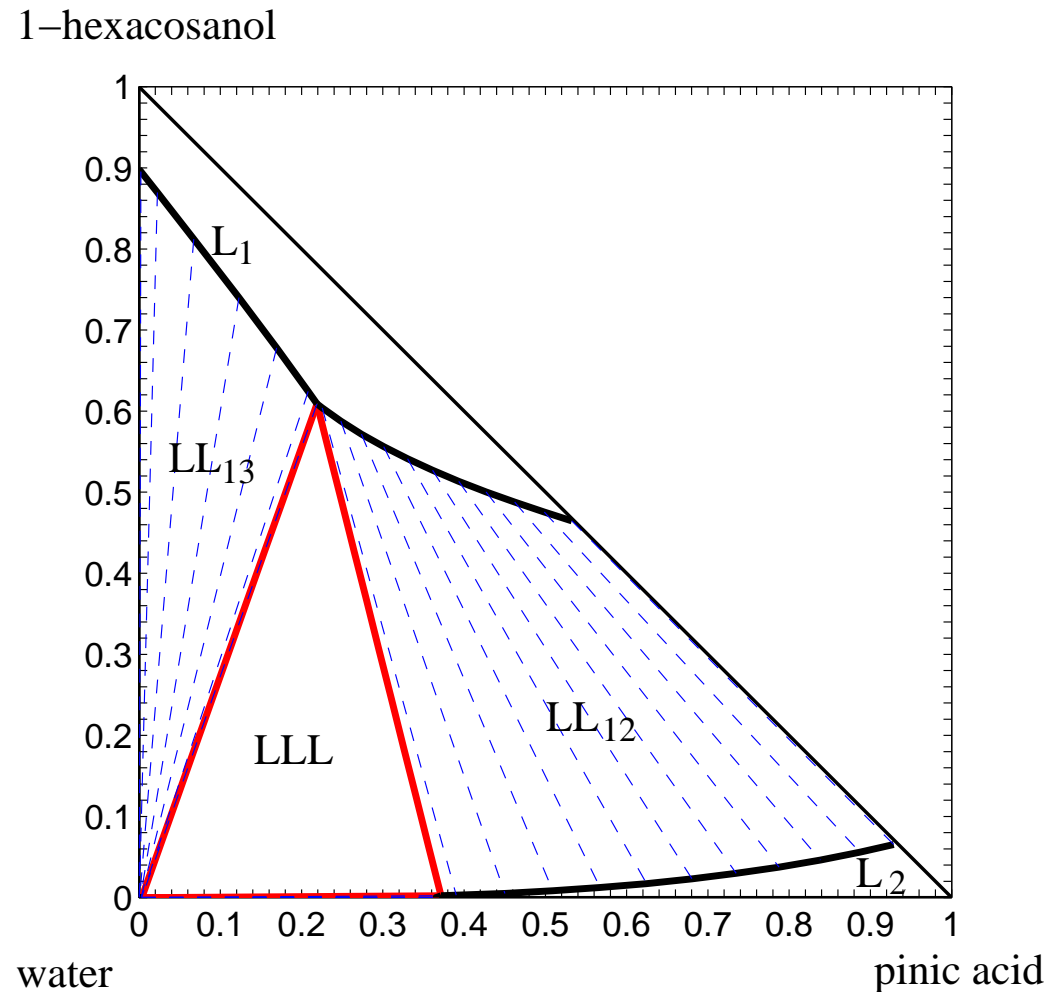
# Computational Issues

- 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 compute the gas-particle partitioning.
- Flexibility of the method (black-box algorithm)
  - Current Work: Web interface.
  - Future: Open-source code.



# Water/1-Hexacosanol/Pinic Acid System

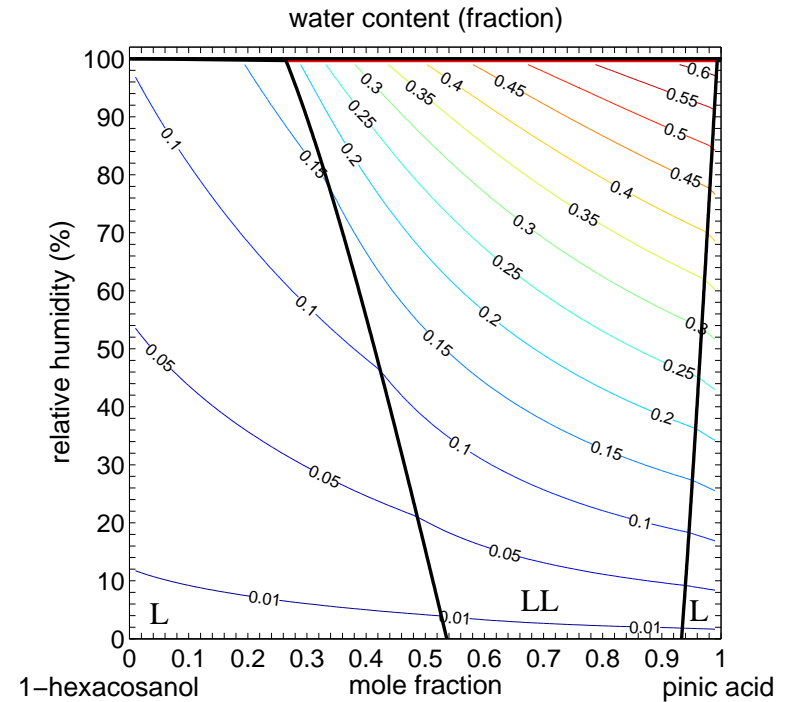
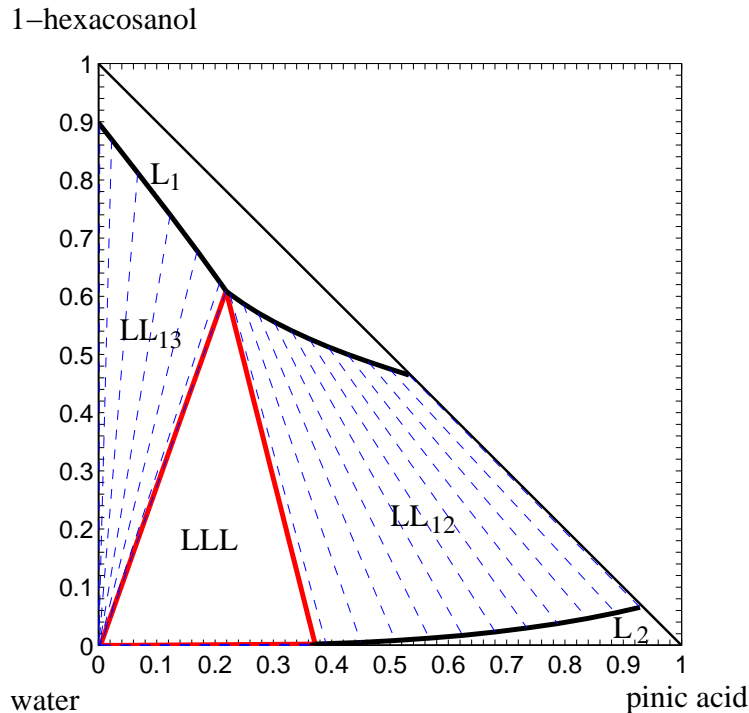
- Phase diagram.



 Equilibrium state can be composed by up to three liquid phases.

# Water Content and Relative Humidity

- Representation of water content and relative humidity:



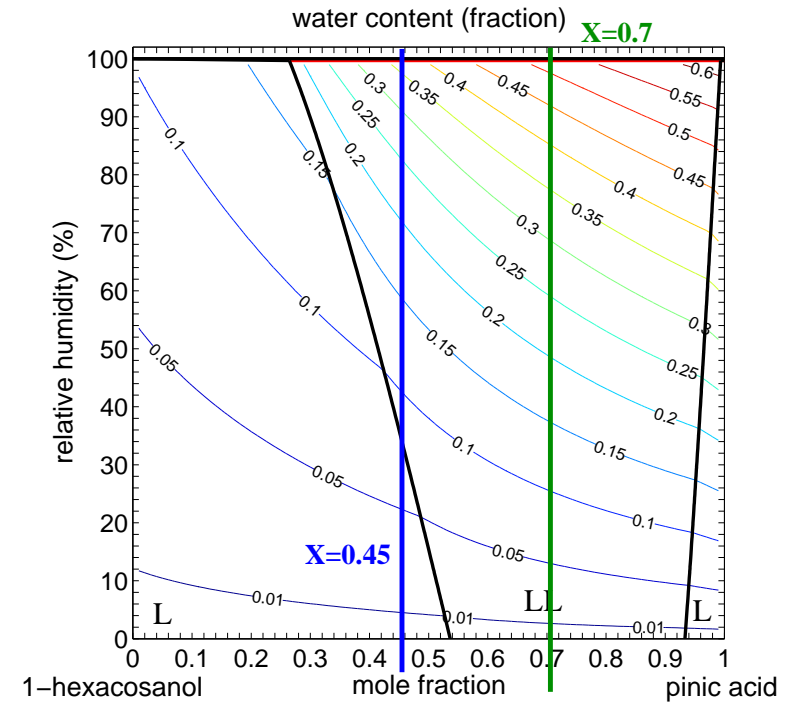
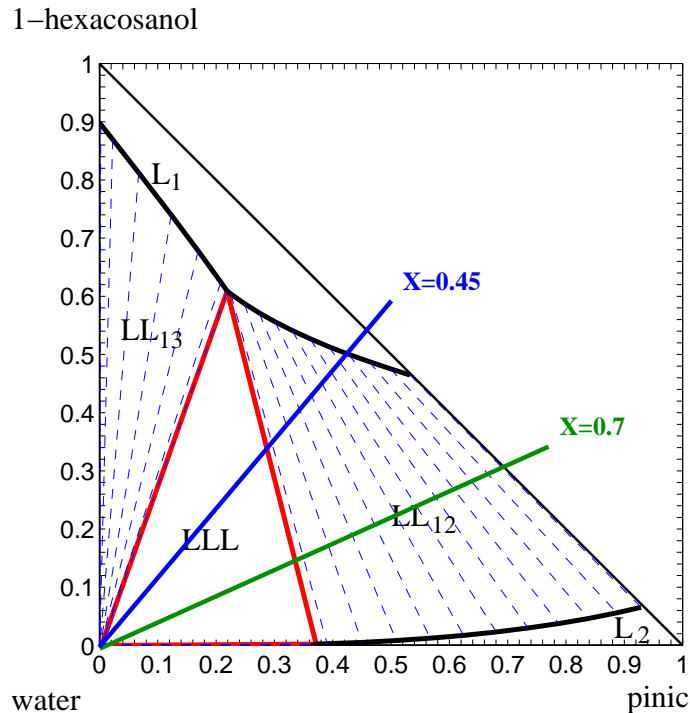
$$\text{ratio} = \frac{\text{mole fraction of pinic acid}}{\text{mole fraction of pinic acid} + \text{mole fraction of 1-hexacosanol}}$$

- Phase changes and water content modifications for increasing RH.



# Water Content and Relative Humidity

- Representation of water content and relative humidity:

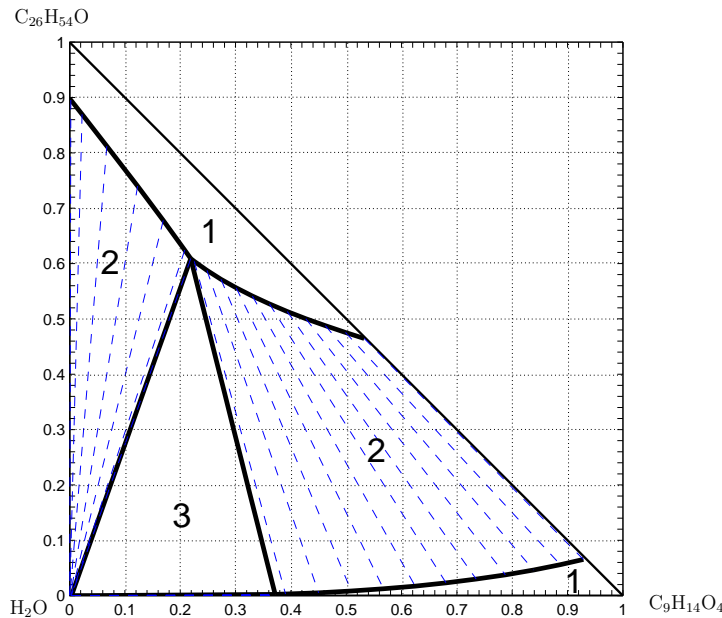


$$\text{ratio} = \frac{\text{mole fraction of pinic acid}}{\text{mole fraction of pinic acid} + \text{mole fraction of 1-hexacosanol}}$$

- Phase changes and water content modifications for increasing RH.



# Computational Efficiency



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

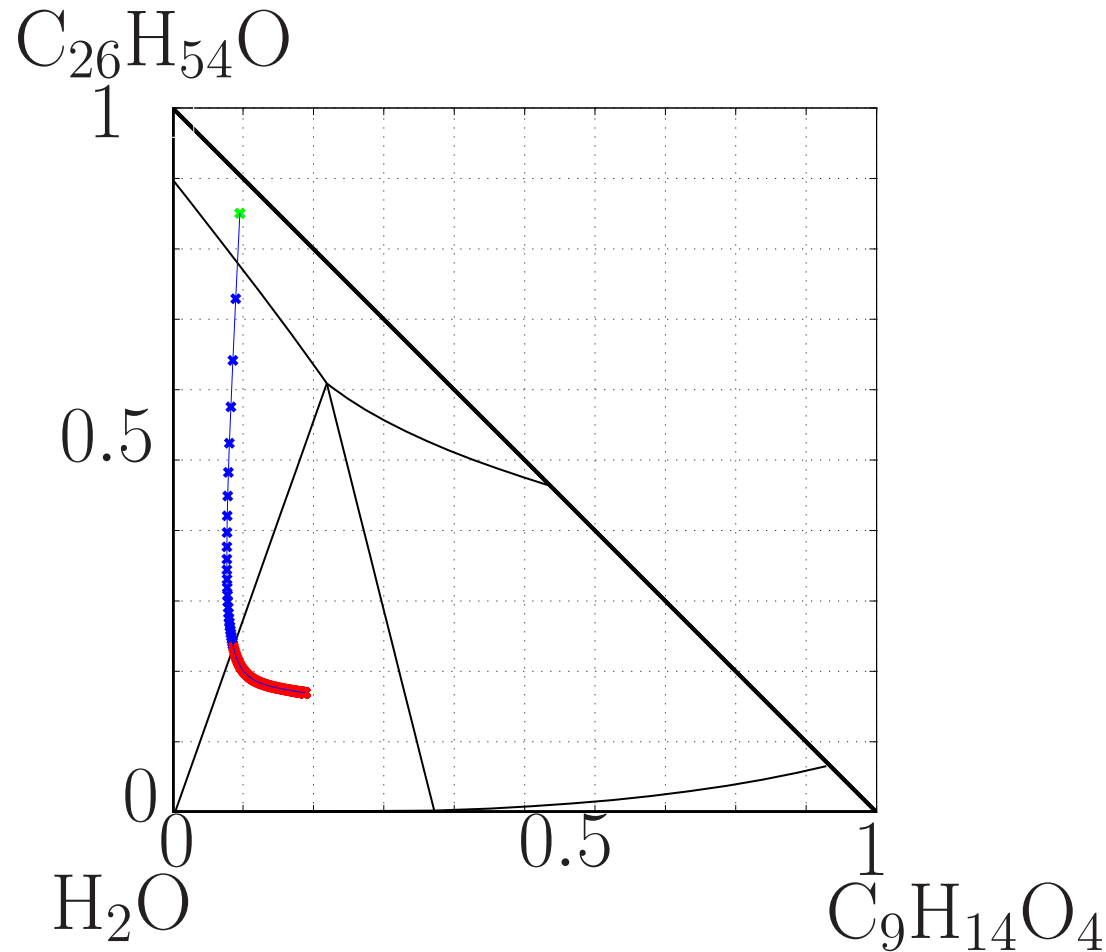
- Insertion in 3D global models is totally reasonable.
- Current work (with S. Clegg, Univ. East Anglia) : systems up to 18 organic components.



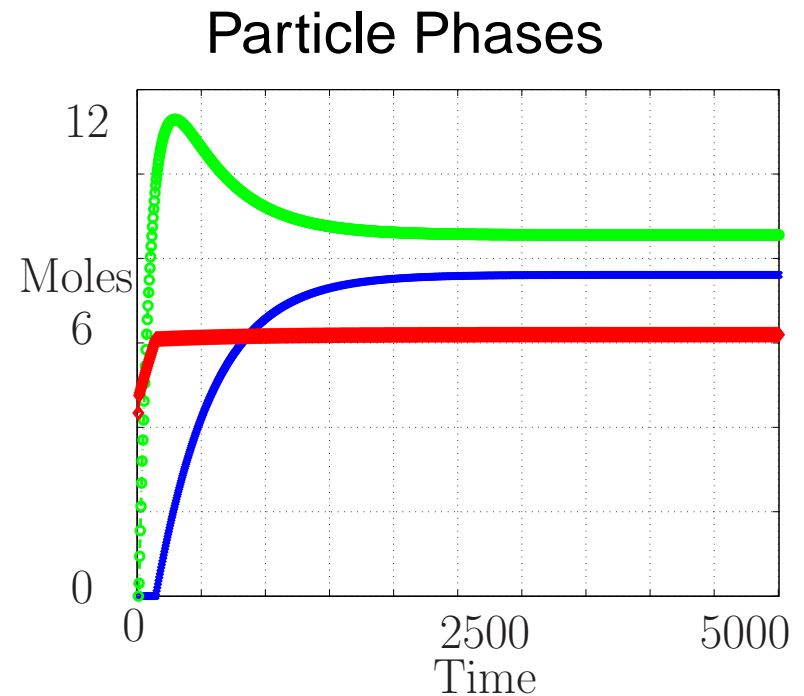
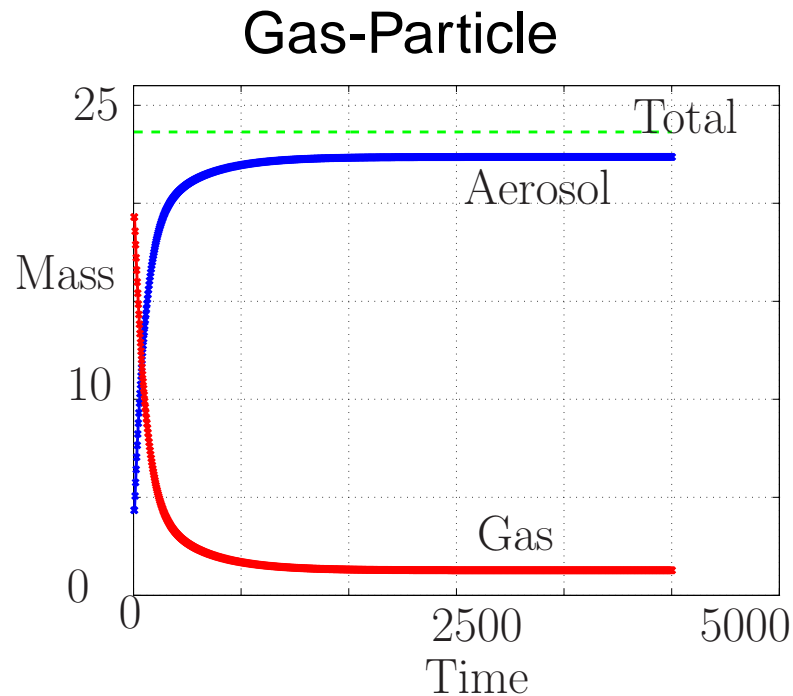
*Acknowledgments: Pictures by C. Landry, EPFL, Switzerland*

# Gas-Particle Partitioning

- Trajectory of the feed vector  $\mathbf{b}(t)$  (the mixing inside the particle) and tracking of the phase separations:



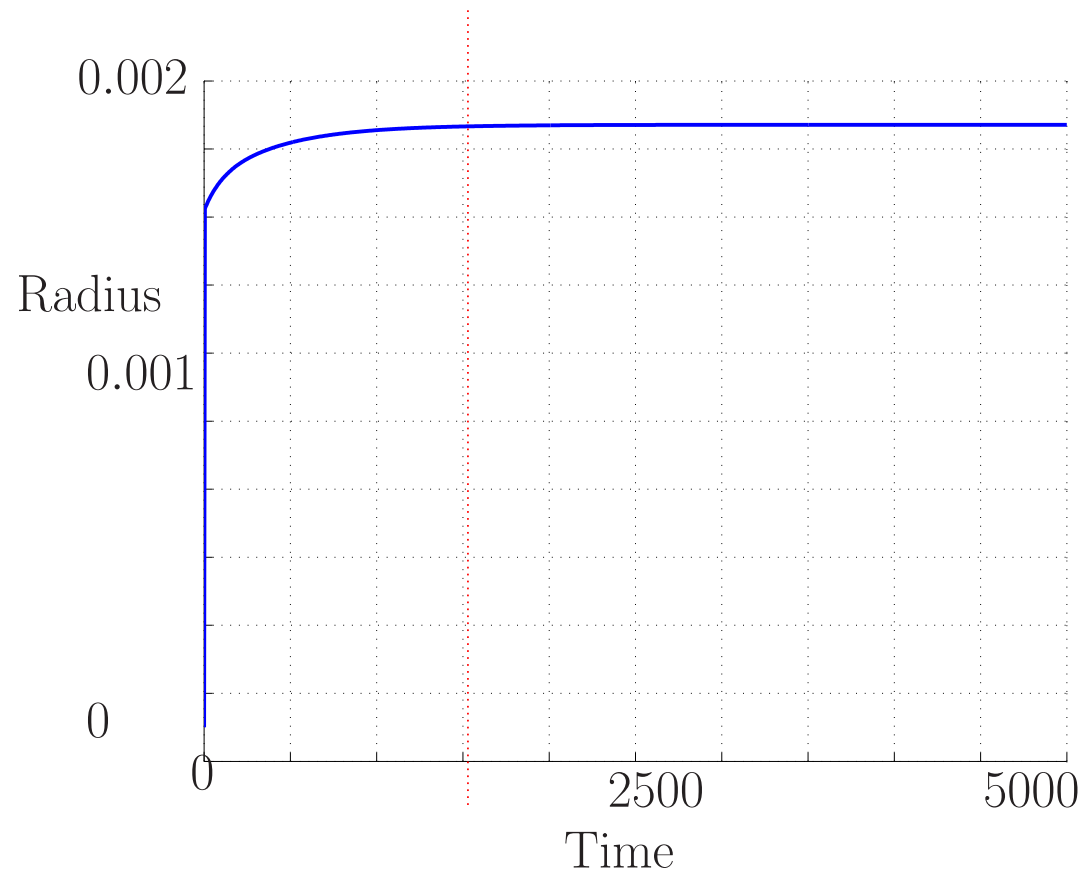
# Mass Conservation



- Mass conservation in the gas-particle system.
- Mass conservation inside the particle.



# Aerosol Growth : Evolution of the Radius



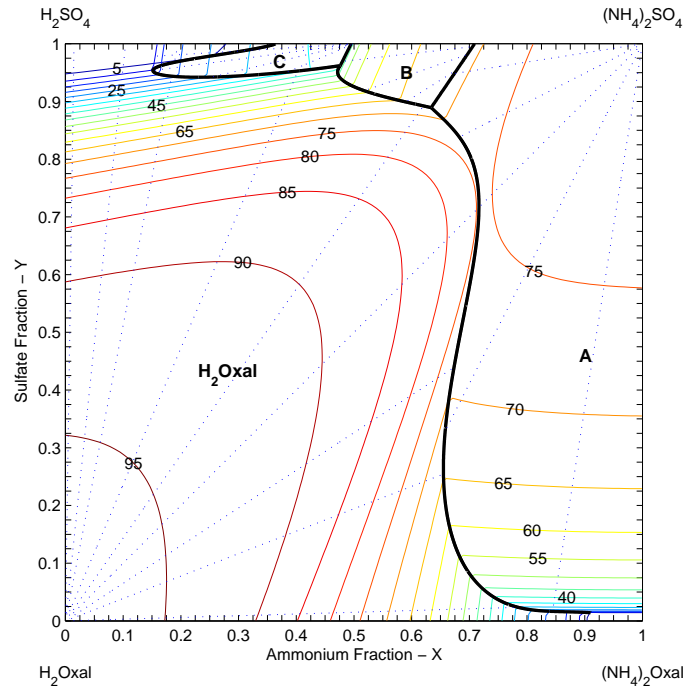
- *Qualitatively*, the characteristic times for gas-particle equilibrium compare well with [Meng, Seinfeld (1996)].



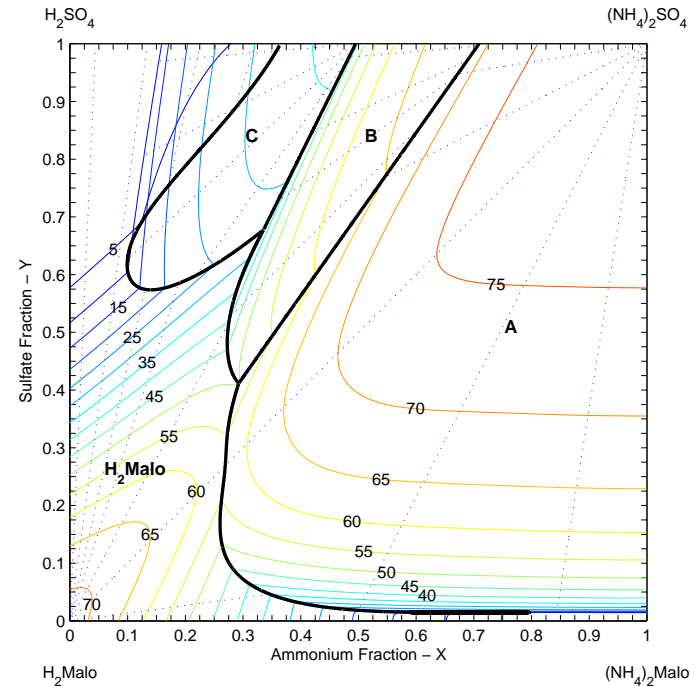
# Inorganic Electrolytes/Dissociated Organics

- Computational model for the thermodynamics of particles with inorganic electrolytes (sulfate and ammonium) and dicarboxylic acids [*IAC Poster (2006)*].

Oxalic acid



Malonic acid



 Oxalic, Malonic, Malic, Glutaric, Maleic, Methyl succinic acids...

# 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.

## Current Work.

- Modeling of mixtures of inorganic electrolytes and dicarboxylic acids.
- Modeling of mixtures of organic and inorganic aerosols.
  - Phase separation and chemical reactions.
  - Extension of the numerical method.
  - Extension of the Gibbs free energy model.



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**ΨAERO**  
Mathematical Modeling, Analysis & Computation

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x} (In) = \frac{1}{2} \int_0^x \beta(x', x - x') n(x') n(x - x') dx' - n \int_0^{\infty} \beta(x, x') n(x') dx'$$
$$\inf \left\{ \sum_{\alpha} y_{\alpha} f(x_{\alpha}), \sum_{\alpha} y_{\alpha} x_{\alpha} = x, \sum_{\alpha} y_{\alpha} = 1 \right\}$$
