

Numerical Analysis

A dynamic optimization problem related to organic aerosols

Neal R. Amundson^a, Alexandre Caboussat^{a,1}, Jiwen He^{a,1},
Chantal Landry^b, John H. Seinfeld^c

^a Department of Mathematics, University of Houston, Houston, TX 77204, USA

^b Institute of Analysis and Scientific Computing, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

^c Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

Received 14 February 2007; accepted 27 February 2007

Available online 3 April 2007

Presented by Roland Glowinski

Abstract

A model that rigorously computes the gas–particle partitioning and liquid–liquid equilibrium for organic atmospheric aerosol particles is presented. The dynamics of the mass transfers between the particle and the gas phase are modeled with differential equations and are coupled with a constrained optimization problem for the thermodynamic equilibrium inside the particle. The nonlinear system composed by the first order optimality conditions coupled with the discretized differential equations is solved with an interior-point method and a Newton method. The resulting linear system is decoupled with sequential quadratic programming techniques. Numerical results and comparisons of time scales show the accuracy and efficiency of our algorithm. **To cite this article:** *N.R. Amundson et al., C. R. Acad. Sci. Paris, Ser. I 344 (2007).*

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

Un problème d'optimisation dynamique lié à la modélisation d'aérosols organiques. Nous proposons un modèle pour le calcul de l'équilibre thermodynamique et la séparation de phases entre une particule et la phase gazeuse. La dynamique des transferts de masse entre particule et phase gazeuse est caractérisée par un système d'équations différentielles couplées avec un problème d'optimisation décrivant l'équilibre interne de la particule. Les conditions de premier ordre et une discrétisation implicite des équations différentielles forment un système d'équations non linéaires qui est traité avec une méthode de point intérieur couplée à une itération de Newton. Des résultats numériques et une comparaison des temps caractéristiques montrent la précision et l'efficacité de notre algorithme. **Pour citer cet article :** *N.R. Amundson et al., C. R. Acad. Sci. Paris, Ser. I 344 (2007).*

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

The modeling of the dynamics of organic-containing aerosol particles is a crucial step in the simulation of atmospheric processes [6]. Currently available computational methods rely on a priori assumptions and split *hydrophobic* and *hydrophilic* components, through a *phase lock* that does not allow all organic components to partition into all possible phases.

E-mail addresses: amundson@uh.edu (N.R. Amundson), caboussat@math.uh.edu (A. Caboussat), jiwenhe@math.uh.edu (J. He), chantal.landry@epfl.ch (C. Landry), seinfeld@caltech.edu (J.H. Seinfeld).

¹ Supported by the United States Environmental Protection Agency Grant X-83234201.

In this note, a computational model for the dynamics and mass transfer between an aerosol particle and the gas phase is presented. It does not rely on any a priori assumptions and computes accurately the gas–particle partitioning, and guarantees the conservation of the total mass. The numerical method relies on a primal–dual interior–point method for the minimization of the Gibbs free energy that is described in [1,2] and is coupled with an implicit first order time discretization scheme for the computation of the fluxes. A sequential quadratic programming approach allows to solve accurately and efficiently the nonlinear problem at each time step.

We first describe the model for the thermodynamic equilibrium in the particle and the mass transfer dynamics between the particle and the gas. Let n_s denote the total number of substances in the gas–particle system, $\mathbf{c} = (c_i)_{i=1}^{n_s} \in \mathbb{R}^{n_s}$ be the substance–abundance concentration vector in unit of moles of the substances in the bulk gas phase and $\mathbf{b}^{\text{tot}} = (b_i^{\text{tot}})_{i=1}^{n_s} \in \mathbb{R}^{n_s}$ be the concentration vector of the same substances in the complete gas–particle system. The concentrations in the particle are therefore given by $\mathbf{b}(t) = \mathbf{b}^{\text{tot}} - \mathbf{c}(t)$.

For one particle of radius $r(t) > 0$ at fixed temperature T and pressure, the gas–particle partitioning for a given substance–abundance vector $\mathbf{b}^{\text{tot}} > \mathbf{0}$ is driven by the rate of change of the concentrations \mathbf{c} :

$$\frac{d}{dt} \mathbf{c}(t) = -\varphi(r) N(r) (\mathbf{c}(t) - \mathbf{c}^{\text{surf}}(t) \eta(r)), \quad (1)$$

where $\varphi(r)$ is the mass transfer rate, $N(r) = N$ is the number density (assumed to remain constant in order to mimic a population of N identical particles), $\mathbf{c}^{\text{surf}}(t) = (c_i^{\text{surf}})_{i=1}^{n_s}$ is the gas concentration vector at the particle surface and $\eta(r)$ is the *Kelvin effect* due to the curvature of the surface of the particle. More precisely, the mass transfer rate is the diagonal matrix given by

$$\varphi(r) = 4\pi D_i r \frac{1}{\lambda/(\alpha_i r) + 1},$$

where D_i is the gas–phase molecular diffusivity of species i , λ is the air mean free path and α_i is the accommodation coefficient of the particle species i . Initial concentrations $\mathbf{c}(0)$ are prescribed. The internal composition of the aerosol is the solution of the constrained optimization problem arising from the minimization of the Gibbs free energy [1,6]:

$$\min_{(\mathbf{x}_\alpha, y_\alpha)} \sum_{\alpha=1}^P y_\alpha g(\mathbf{x}_\alpha), \quad \text{s.t.} \quad \mathbf{x}_\alpha > \mathbf{0}, \quad \mathbf{e}^T \mathbf{x}_\alpha = 1, \quad y_\alpha \geq 0, \quad \alpha = 1, \dots, P, \quad \text{and} \quad \sum_{\alpha=1}^P y_\alpha \mathbf{x}_\alpha = \mathbf{b}^{\text{tot}} - \mathbf{c}(t), \quad (2)$$

where $\mathbf{e}^T = (1, \dots, 1)$, P is the number of possible aerosol phases, $(\mathbf{x}_\alpha)_{\alpha=1}^P$ is the mole–fraction concentration vector in phase α , $(y_\alpha)_{\alpha=1}^P$ is the total number of moles in phase α . The function g is the molar Gibbs free energy function. It is modeled by the UNIFAC model, based on the concept of group contributions. The surface equilibrium concentration, $\mathbf{c}^{\text{surf}}(t)$, depends on the composition and phase state of the aerosol $(y_\alpha, \mathbf{x}_\alpha)_{\alpha=1}^P$. The relation between the internal composition of the particle and the mass fluxes is strongly nonlinear. Following the mass action laws, the surface equilibrium concentration vector $\mathbf{c}^{\text{surf}}(t)$ is given by

$$\mathbf{c}^{\text{surf}}(t) = \frac{1}{RT} p_{\text{vapor}} \exp(\nabla g(\mathbf{x}_\alpha)),$$

for all $\alpha = 1, \dots, P$ such that $y_\alpha > 0$, where $R = 8.20575 \times 10^{-5}$ [J K⁻¹ l⁻¹] is the gas constant and p_{vapor} is the vapor pressure.

The minimization problem (2) expresses the liquid–liquid equilibrium inside an aerosol particle composed of organic species, subject to mass balance constraints. Depending on the atmospheric conditions, the equilibrium state consists of one or several liquid phases, which number is a priori unknown. Once the concentrations are known, the radius of the particle is computed by

$$\frac{4}{3} \pi N r(t)^3 = \sum_{i=1}^{n_s} \frac{(b_i^{\text{tot}} - c_i(t)) m_{c,i}}{\rho_i},$$

where $\mathbf{m}_c = (m_{c,i})_{i=1}^{n_s}$ is the molecular weight vector of the components set and ρ_i is the density of each individual chemical components in the particle. For simplicity, the Kelvin effects are neglected here ($\eta(r) = 1$).

The inequality constraints in (2) are relaxed with a log/barrier formulation with a penalty parameter $\nu > 0$. By replacing (2) by its first order optimality conditions, a system of differential-algebraic equations of index 1 [4] is obtained:

$$\begin{aligned} \frac{d}{dt} \mathbf{c}(t) &= -\varphi(r) N(r) (\mathbf{c}(t) - \mathbf{c}^{\text{surf}}(t)), \\ y_\alpha (\nabla g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}) + \zeta_\alpha \mathbf{e} &= \mathbf{0}, \quad g(\mathbf{x}_\alpha) + \boldsymbol{\lambda}^T \mathbf{x}_\alpha - \nu/y_\alpha = 0, \\ \sum_{\alpha=1}^P y_\alpha \mathbf{x}_\alpha &= \mathbf{b}^{\text{tot}} - \mathbf{c}, \quad \mathbf{e}^T \mathbf{x}_\alpha = 1, \quad \mathbf{x}_\alpha, y_\alpha > 0, \quad \alpha = 1, \dots, P. \end{aligned} \quad (3)$$

Let t^0, t^1, \dots be discrete times with $\tau = t^{n+1} - t^n$ and $\mathbf{c}^n, \mathbf{b}^n$ and r^n denote respectively approximations of $\mathbf{c}(t^n)$, $\mathbf{b}(t^n)$ and $r(t^n)$. The system (3) is discretized with a first order Euler implicit time discretization scheme [4] between times t^n and t^{n+1} . An explicit treatment of the radius r is used in (3) due to different characteristic times [6]. At each time t^{n+1} , the phase equilibrium is characterized by the global minimum of the Gibbs free energy of the particle system for a given feed $\mathbf{b}^{n+1} = \mathbf{b}^{\text{tot}} - \mathbf{c}^{n+1}$.

$$\begin{aligned} \frac{\mathbf{c}^{n+1} - \mathbf{c}^n}{\tau} &= -\varphi(r^n) N \left(\mathbf{c}^{n+1} - \frac{1}{RT} p_{\text{vapor}} \exp(\nabla g(\mathbf{x}_\alpha^{n+1})) \right), \\ y_\alpha^{n+1} (\nabla g(\mathbf{x}_\alpha^{n+1}) + \boldsymbol{\lambda}^{n+1}) + \zeta_\alpha^{n+1} \mathbf{e} &= \mathbf{0}, \quad g(\mathbf{x}_\alpha^{n+1}) + (\boldsymbol{\lambda}^{n+1})^T \mathbf{x}_\alpha^{n+1} - \nu/y_\alpha^{n+1} = 0, \\ \sum_{\alpha=1}^{P^{n+1}} y_\alpha^{n+1} \mathbf{x}_\alpha^{n+1} &= \mathbf{b}^{\text{tot}} - \mathbf{c}^{n+1}, \quad \mathbf{e}^T \mathbf{x}_\alpha^{n+1} = 1, \quad \mathbf{x}_\alpha^{n+1}, y_\alpha^{n+1} > 0, \quad \alpha = 1, \dots, P^{n+1}. \end{aligned} \quad (4)$$

The radius of the particle is then updated with the algebraic relation

$$r^{n+1} = \left(\frac{3}{4\pi N} \sum_{i=1}^{n_s} \frac{(b_i^{\text{tot}} - c_i^{n+1}) m_{c,i}}{\rho_i} \right)^{1/3}.$$

At each time step t^{n+1} , a primal-dual interior-point algorithm [1–3] is used for the resolution of the coupled problem. A sequence of solutions to the nonlinear system (4) is obtained for decreasing values of ν [3]. For given ν , the system (4) is solved by a Newton iteration. The resulting linear system is solved with direct methods to compute increments for the particle concentrations and the internal variables and update the corresponding variables. Then ν is decreased until the norm of the residuals is smaller than a given tolerance. The final iterate is set to be the approximated solution $(\mathbf{x}_\alpha^{n+1}, y_\alpha^{n+1}, \boldsymbol{\lambda}^{n+1}, \zeta_\alpha^{n+1}, \mathbf{c}^{n+1})$ for the next time step.

The block-structured Newton system related to (4) is solved with sequential quadratic programming techniques to decouple the differential variables \mathbf{c}^{n+1} from the optimization variables. The techniques presented in [1,2] are used to solve the pure optimization problem and a convex unconstrained minimization problem allows to obtain \mathbf{c}^{n+1} .

We consider the three components system ($n_s = 3$) with 1-hexacosanol ($\text{C}_{26}\text{H}_{54}\text{O}$), pinic acid ($\text{C}_9\text{H}_{14}\text{O}_4$) and water (H_2O) at temperature 298.15 [K] and pressure 1 [atm]. This example of aerosol particles of atmospheric interest admits a maximum of three phases at equilibrium for some particular compositions. The vapor pressures are given by 1.7734×10^{-5} , 2.2545×10^{-5} and 3.13×10^{-2} [atm] for 1-hexacosanol, pinic acid and water respectively, $\alpha = 0.01$ and $\lambda = 0.1 \times 10^{-6}$ [m].

Fig. 1 illustrates the mass transfer between the particle and the gas phase, when $N = 10^8$ [m^{-3}]. A non-equilibrium solution is chosen as a starting point, that is $\mathbf{b}^{\text{tot}} = (3.79, 4.21, 15.63)$ [moles] and $\mathbf{c}^0 = (0.1, 3.8, 15.4)$ [moles]. In this case, (i) the repartition of mass between gas and particle phase is not reached and (ii) the mixing of components inside the particle is not an equilibrium state. The left figure shows the evolution of the normalized particle feed $\mathbf{b}(t) = \mathbf{b}^{\text{tot}} - \mathbf{c}(t)$ in the phase diagram. Each vertex of this two-dimensional simplex (triangle) corresponds to a pure component without mixing, while any point in the interior of the simplex corresponds to a certain mixing of water, pinic acid and 1-hexacosanol. The regions of the simplex where the equilibrium state is composed of P phases, $P = 1, 2, 3$, are separated with solid black lines. Phase separations happen when the particle feed changes of region and crosses the solid black lines. The middle figure shows the total number of moles in each phase (y_α), while the right figure illustrates the radius evolution in function of time.

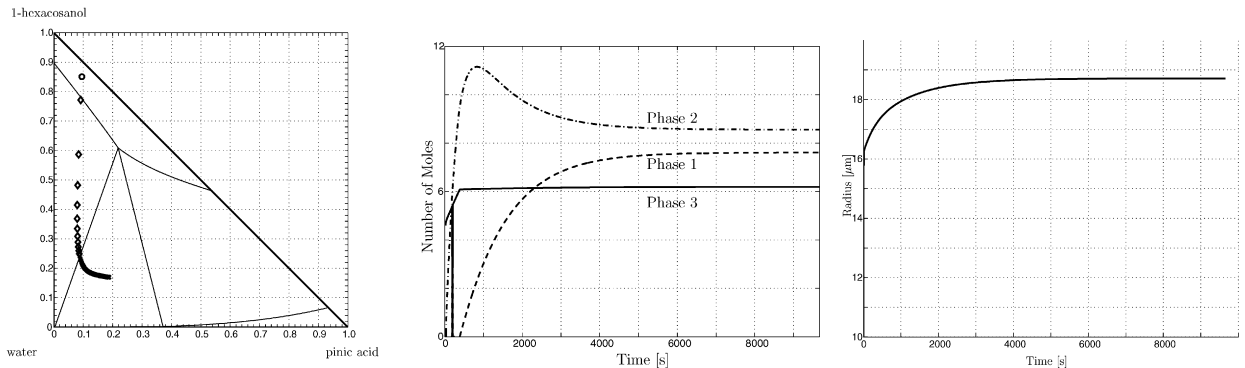


Fig. 1. Dynamics for the three-component system water, pinic acid, 1-hexacosanol. Left: evolution of the concentration vector \mathbf{b} in the phase diagram; middle: convergence of the total number of moles in the phases inside the aerosol particle; and right: aerosol growth and evolution of the radius of the particle.

Table 1

Comparisons of orders of magnitude for characteristic times for various radius and number densities

Number density	Radius [m]	τ_0 [s] [5]	Stationarity time [s]	Radius [m]	τ_0 [s] [5]	Stationarity time [s]
10^7	10^{-6}	2.49×10^4	$\sim 9. \times 10^4$	10^{-7}	2.29×10^6	$\sim 8. \times 10^6$
10^8	10^{-6}	2.49×10^3	$\sim 9. \times 10^3$	10^{-7}	2.29×10^5	$\sim 6. \times 10^5$
10^9	10^{-6}	2.49×10^2	$\sim 8. \times 10^2$	10^{-7}	2.29×10^4	$\sim 5. \times 10^4$

Numerical results are validated by the comparison of the time scales to reach gas–particle equilibrium with [5]. A characteristic time of gas–particle partitioning dynamics is given by $\tau_0 = \frac{1}{\varphi(r)N}$ (under linear assumptions [6]). Table 1 compares the characteristic times computed by our model and those reported in [5] for typical particles of radius of 1 μm and 0.1 μm respectively, suggesting a good agreement in the order of magnitude between those results.

References

- [1] N.R. Amundson, A. Caboussat, J.W. He, J.H. Seinfeld, An optimization problem related to the modeling of atmospheric organic aerosols, C. R. Acad. Sci. Paris, Ser. I 340 (10) (2005) 765–768.
- [2] N.R. Amundson, A. Caboussat, J.W. He, J.H. Seinfeld, Primal-dual interior-point method for an optimization problem related to the modeling of atmospheric organic aerosols, J. Optim. Theory Appl. 130 (3) (2006) 375–407.
- [3] A.V. Fiacco, G.P. McCormick, Nonlinear Programming: Sequential Unconstrained Minimization Techniques, John Wiley and Sons, 1968.
- [4] E. Hairer, G. Wanner, Solving Ordinary Differential Equations II. Stiff and Differential-Algebraic Problems, Springer Series in Comput. Mathematics, vol. 14, Springer-Verlag, 1996.
- [5] Z. Meng, J.H. Seinfeld, Times scales to achieve atmospheric gas–aerosol equilibrium for volatile species, Atmospheric Environment 30 (16) (1996) 2889–2900.
- [6] J.H. Seinfeld, S.N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley, New York, 1998.