



## Numerical Analysis

# Numerical method for a dynamic optimization problem arising in the modeling of a population of aerosol particles

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### Abstract

A model coupling differential equations and a sequence of constrained optimization problems is proposed for the simulation of the evolution of a population of particles at equilibrium interacting through a common medium.

The first order optimality conditions of the optimization problems relaxed with barrier functions are coupled with the differential equations into a system of differential-algebraic equations that is discretized in time with an implicit first order scheme. The resulting system of nonlinear algebraic equations is solved at each time step with an interior-point/Newton method. The Newton system is block-structured and solved with Schur complement techniques, in order to take advantage of its sparsity. Application to the dynamics of a population of organic atmospheric aerosol particles is given to illustrate the evolution of particles of different sizes. *To cite this article: A. Caboussat, A. Leonard, C. R. Acad. Sci. Paris, Ser. I 346 (2008).*

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### Résumé

**Une méthode numérique pour un problème d'optimisation dynamique lié à une population de particules.** Nous proposons un modèle pour le calcul de l'évolution d'une population de particules. Ce modèle couple un système d'équations différentielles et une séquence de problèmes d'optimisation sous contraintes.

Les conditions de premier ordre de chacun des problèmes d'optimisation et une discrétisation implicite des équations différentielles forment un système d'équations non linéaires qui est traité avec une méthode de point intérieur, couplé à une itération de Newton. Le système linéaire correspondant a une structure par blocs. Une méthode de résolution directe basée sur le complément de Schur prend en compte la structure creuse de la matrice et permet de découpler les différentes particules du système. Des résultats numériques pour une population de particules organiques montrent l'évolution de particules de différentes tailles. *Pour citer cet article : A. Caboussat, A. Leonard, C. R. Acad. Sci. Paris, Ser. I 346 (2008).*

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The modeling of the dynamics of aerosol particles is a crucial step in the simulation of atmospheric processes [8,9]. The case of pure organic-containing particles is treated here.

A computational model for the mass-conservative dynamics of a population of particles in the gas phase is presented. The numerical method relies on a primal-dual interior-point method for the minimization of the Gibbs free

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energy in each particle [1], coupled with an implicit first order time discretization scheme for the computation of the fluxes [2]. A direct decomposition method allows the efficient resolution of large, sparse Newton systems. The decomposition relies on block LU decompositions and a Schur complement approach that is known to be efficient for block-structured linear systems.

The model presented here couples the thermodynamic equilibrium in each particle and the dynamics between the particles and the gas, at fixed temperature and pressure. Let  $N$  denote the number of particles in the system and  $n_s$  the number of substances in the gas-particle system. Let  $T$  be a given final time; for  $t \in (0, T)$ , let  $\mathbf{c}_0(t) = (c_{0,j})_{j=1}^{n_s} \in \mathbb{R}^{n_s}$  be the concentration vector in unit of moles of the substances in the bulk gas phase and  $\mathbf{c}_i(t) = (c_{i,j})_{j=1}^{n_s} \in \mathbb{R}^{n_s}$  be the concentration vector of these same substances in the particle number  $i$ ,  $i = 1, \dots, N$ . Let  $r_i(t) > 0$  be the radius of particle  $i$  at time  $t \in (0, T)$ .

The internal composition of each particle  $i$ ,  $i = 1, \dots, N$ , at each time  $t \in (0, T)$ , for given feed vector  $\mathbf{c}_i(t)$  is the solution of the constrained optimization problem arising from the minimization of the Gibbs free energy [1,8]:

$$\min_{(\mathbf{x}_\alpha^i, \mathbf{y}_\alpha^i)} \sum_{\alpha=1}^{P_i} y_\alpha^i g_i(\mathbf{x}_\alpha^i), \quad \text{s.t.} \quad \mathbf{x}_\alpha^i > 0, \quad \mathbf{e}^T \mathbf{x}_\alpha^i = 1, \quad y_\alpha^i \geq 0, \quad \alpha = 1, \dots, P_i, \quad \text{and} \quad \sum_{\alpha=1}^{P_i} y_\alpha^i \mathbf{x}_\alpha^i = \mathbf{c}_i(t), \quad (1)$$

where  $\mathbf{e}^T = (1, \dots, 1)$ ,  $P_i$  is the number of possible aerosol phases,  $(\mathbf{x}_\alpha^i)_{\alpha=1}^{P_i}$  are the mole-fraction concentration vectors in phase  $\alpha$ ,  $(y_\alpha^i)_{\alpha=1}^{P_i}$  are the total numbers of moles in each phase  $\alpha$ . The minimization problem (1) expresses the liquid–liquid equilibrium inside an aerosol particle composed of organic species, subject to mass balance constraints. The function  $g_i$  is the molar Gibbs free energy function, modeled in this work by the UNIFAC model for organic species. Depending on the atmospheric conditions, the equilibrium state consists of one or several liquid phases. The number of phases  $P_i$  is *a priori* unknown.

The gradient  $\nabla g_i(\mathbf{x}_\alpha^i(t))$  is constant for all  $\alpha = 1, \dots, P_i$ , such that  $y_\alpha^i > 0$  and denoted by  $\lambda_i(t)$  [1]. The evolution of the concentration vectors  $\mathbf{c}_0(t)$ ,  $\mathbf{c}_i(t)$  is given by the nonlinear ordinary differential equations

$$\begin{aligned} \frac{d}{dt} \mathbf{c}_0(t) &= - \sum_{i=1}^N \varphi(r_i(t)) (\mathbf{c}_0(t) - \Gamma \mathbf{e}^{-\lambda_i(t)}), \quad \mathbf{c}_0(0) = \mathbf{c}_{0,0}, \\ \frac{d}{dt} \mathbf{c}_i(t) &= \varphi(r_i(t)) (\mathbf{c}_0(t) - \Gamma \mathbf{e}^{-\lambda_i(t)}), \quad \mathbf{c}_i(0) = \mathbf{c}_{i,0}, \quad i = 1, \dots, N, \end{aligned} \quad (2)$$

where  $\varphi(r)$  is the mass transfer rate,  $\Gamma$  is a constant depending on vapor pressures and temperature. The *Kelvin effect* due to the curvature of the surface of the particles is neglected. The mass transfer rate is given by  $\varphi(r) = \text{diag}(4\pi D_j r \frac{1}{\lambda_j / (\alpha_j r) + 1})$ , where  $D_j$  is the gas-phase molecular diffusivity of species  $j$ ,  $\lambda$  is the air mean free path and  $\alpha_j$  is the accommodation coefficient of the particle species  $j$ .

Each particle  $i$  is assumed to be spherical, with radius  $r_i$  given by the approximated relation  $\frac{4}{3}\pi r_i(t)^3 = \sum_{k=1}^{n_s} \frac{c_{i,k}(t)m_k}{\rho_k}$ , where  $m_k$  is the molecular weight and  $\rho_k$  is the density of the chemical component  $k$ .

Let  $t^0, t^1, \dots$  be discrete times with  $\tau = t^{n+1} - t^n$  and  $\mathbf{c}_i^n$ ,  $(\mathbf{x}_\alpha^i)^n$ ,  $(y_\alpha^i)^n$ ,  $\lambda_i^n$ ,  $P_i^n$  and  $r_i^n$  denote respectively approximations of  $\mathbf{c}_i(t^n)$ ,  $\mathbf{x}_\alpha^i(t^n)$ ,  $y_\alpha^i(t^n)$ ,  $\lambda_i(t^n)$ ,  $P_i(t^n)$  and  $r_i(t^n)$ . The coupled system (1), (2) is discretized with a first order Euler implicit discretization scheme.

The inequality constraints in (1) are relaxed with a log/barrier term associated to a penalty parameter  $\nu > 0$  [4]. By replacing (1) by its first order optimality conditions, a system of differential-algebraic equations of index 1 is obtained [2,7]. The radii  $r_i$  are discretized explicitly in (2) due to different time scales [8]. The discretization of (1), (2) leads to a system of nonlinear equations:

$$\begin{aligned} \mathbf{c}_0^{n+1} - \mathbf{c}_0^n &= -\tau \sum_{i=1}^N \varphi(r_i^n) (\mathbf{c}_0^{n+1} - \Gamma \exp(-\lambda_i^{n+1})), \\ \mathbf{c}_i^{n+1} - \mathbf{c}_i^n &= \tau \varphi(r_i^n) (\mathbf{c}_0^{n+1} - \Gamma \exp(-\lambda_i^{n+1})), \quad i = 1, \dots, N, \\ (y_\alpha^i)^{n+1} (\nabla g_i((\mathbf{x}_\alpha^i)^{n+1}) + \lambda_i^{n+1}) + (\zeta_\alpha^i)^{n+1} \mathbf{e} &= \mathbf{0}, \quad g_i((\mathbf{x}_\alpha^i)^{n+1}) + (\lambda_i^{n+1})^T (\mathbf{x}_\alpha^i)^{n+1} - \nu / (y_\alpha^i)^{n+1} = 0, \end{aligned} \quad (3)$$

$$\sum_{\alpha=1}^{P_i^{n+1}} (y_{\alpha}^i)^{n+1} (\mathbf{x}_{\alpha}^i)^{n+1} = \mathbf{c}_i^{n+1}, \quad \mathbf{e}^T (\mathbf{x}_{\alpha}^i)^{n+1} = 1, \\ (\mathbf{x}_{\alpha}^i)^{n+1}, (y_{\alpha}^i)^{n+1} > 0, \quad \alpha = 1, \dots, P_i^{n+1}, i = 1, \dots, N.$$

The radii of the particles are then updated with the algebraic relation  $\frac{4\pi}{3}(r_i^{n+1})^3 = \sum_{k=1}^{n_s} \frac{\mathbf{c}_{i,k}^{n+1} m_k}{\rho_k}$ .

At each time step  $t^{n+1}$ , a primal-dual interior-point algorithm [1,4] together with a Newton iteration, is used for the resolution of the coupled problem (3). The algorithm produces a converging sequence of solutions for decreasing values of  $\nu$  [4]. For given  $\nu$ , the system (3) is solved by a Newton iteration. The Newton system is solved with direct methods to compute increments for the particle concentrations and internal variables, and the corresponding variables are updated. Then  $\nu$  is decreased until the norm of the residuals is smaller than a given tolerance. The Newton system is sparse and block structured. If  $(b_1, \dots, b_N, b_0)^T$  and  $(p_1, \dots, p_N, p_0)^T$  denote the residuals and the increments respectively, the Newton system reads:

$$\begin{bmatrix} \mathcal{H}_1 & 0 & \dots & 0 & C_1 \\ 0 & \mathcal{H}_2 & \dots & 0 & C_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \dots & \mathcal{H}_N & C_N \\ D_1^T & D_2^T & \dots & D_N^T & \mathcal{H}_0 \end{bmatrix} \begin{bmatrix} p_1 \\ p_2 \\ \vdots \\ p_N \\ p_0 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_N \\ b_0 \end{bmatrix}, \quad \mathcal{H}_i = \begin{bmatrix} \tau^{-1} \mathbf{I} & 0 & B_i \\ 0 & O_i^{\nu} & A_i \\ E & A_i^T & 0 \end{bmatrix}, \quad C_i = \begin{bmatrix} -\text{diag } \varphi(r_i^n) \\ 0 \\ 0 \end{bmatrix}, \\ D_i = \begin{bmatrix} 0 \\ 0 \\ -B_i \end{bmatrix}, \quad \mathcal{H}_0 = \tau^{-1} \mathbf{I} + \sum_{i=1}^N \text{diag } \varphi(r_i^n), \quad E = \begin{bmatrix} I_n & 0 \\ \mathbf{e}^T & 1 \end{bmatrix}, \tag{4}$$

and  $B_i = \text{diag}(-\varphi(r_i^n) \Gamma e^{-\lambda_i}) E^T$ . The matrices  $O_i^{\nu}$ , resp.  $A_i$ , correspond to the projected Hessian of the objective function, resp. the projected constraints, in (1) [1]. The converged iterate of the Newton method is set to be the approximated solution at time  $t^{n+1}$ .

The block-structured linear system (4) is solved with direct decomposition techniques [5,6]. A Schur complement method decouples the blocks  $\mathcal{H}_i$  corresponding to each particle and solves a sequence of smaller linear systems related to a single particle. The Schur complement approach consists of building and solving the system  $\mathcal{S} p_0 = \mathcal{B}$ , where  $\mathcal{S} = \mathcal{H}_0 - \sum_{i=1}^N D_i^T \mathcal{H}_i^{-1} C_i$  and  $\mathcal{B} = b_0 - \sum_{i=1}^N D_i^T \mathcal{H}_i^{-1} b_i$ , followed by the resolution of a sequence of systems  $\mathcal{H}_i p_i = b_i - C_i p_0$ . Each individual matrix  $\mathcal{H}_i$  is decomposed with an LU decomposition in order to take advantage of the sparsity of the matrix and build on previously developed optimization techniques [1]. As the size of  $\mathcal{H}_0$  and  $\mathcal{S}$  is equal to  $n_s$  (and small compared to the number  $N$  of particles or blocks), the Schur complement approach is appropriate and known to be efficient [5,6].

In order to avoid very small time steps, multi-scale methods, as well as numerical methods for the detection of discontinuities in the evolution of the particles (see e.g. [3]) will be added in the future.

We consider the three-component system ( $n_s = 3$ ) with 1-hexacosanol ( $C_{26}H_{54}O$ ), pinic acid ( $C_9H_{14}O_4$ ) and water ( $H_2O$ ) at temperature 298.15 K and pressure 1 atm. A maximum of three phases occurs at equilibrium for suitable compositions.

The evolution of three particles of radii ranging from 6.5  $\mu\text{m}$  to 27  $\mu\text{m}$  is considered, when the global system reaches its equilibrium. Each particle undergoes phase separations. A time step of  $\tau = 0.5d_0$  is chosen. Initial concentrations are given by  $\mathbf{c}_{1,0} = (1.79 \times 10^0, 4.21 \times 10^0, 15.63 \times 10^0)$ ,  $\mathbf{c}_{2,0} = (2.00 \times 10^{-1}, 1.00 \times 10^{-1}, 7.00 \times 10^{-1})$ ,  $\mathbf{c}_{3,0} = (10.50 \times 10^0, 15.90 \times 10^0, 2.00 \times 10^0)$  and  $\mathbf{c}_{0,0} = (2.00 \times 10^0, 0.11 \times 10^{-2}, 1.27 \times 10^0)$ .

Fig. 1 (left) shows the evolution of the normalized particle feed  $\mathbf{c}_i(t)/\mathbf{e}^T \mathbf{c}_i(t)$ ,  $i = 1, 2, 3$ , in the two-dimensional 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 specific 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 occur when the particle feed changes region, that is crosses the solid black lines. Fig. 1 (middle) shows the total number of moles  $\mathbf{e}^T \mathbf{c}_i(t)$  in each particle, and Fig. 1 (right) illustrates the evolution of  $r_i(t)$ ,  $i = 1, 2, 3$ .

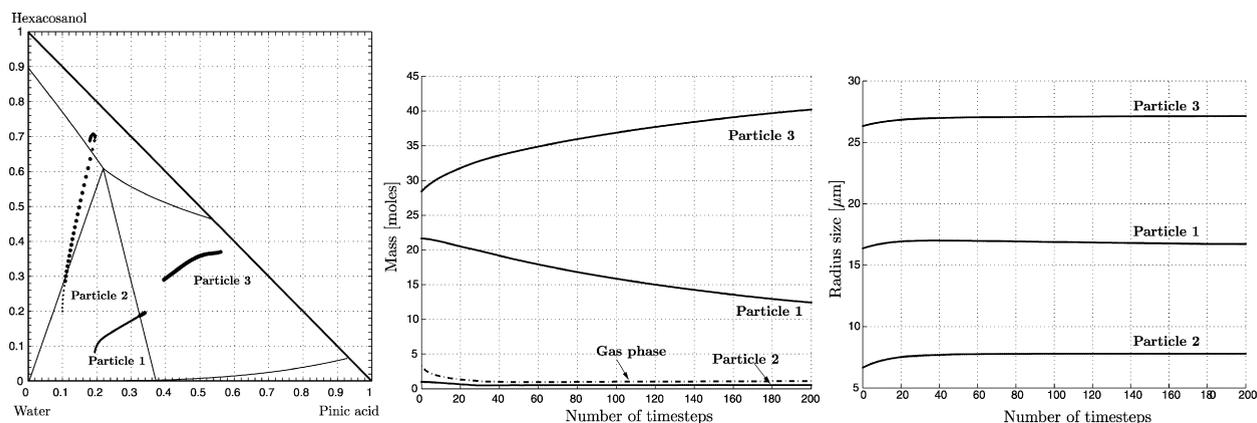


Fig. 1. Dynamics for three particles and three components (water, pinic acid, 1-hexacosanol). Left: evolution of the normalized concentration vector  $\mathbf{c}_i(t)/e^T \mathbf{c}_i(t)$ ,  $i = 1, 2, 3$ , in the phase diagram; middle: evolution of the total number of moles  $e^T \mathbf{c}_i(t)$ ,  $i = 1, 2, 3$ , in the particles; right: aerosol growth and evolution of the radii  $r_i(t)$ ,  $i = 1, 2, 3$ , of the particles.

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