

# An Optimization Problem related to the Modeling of Atmospheric Inorganic Aerosols

## Un problème d'Optimisation lié à la Modélisation d'Aérosols Inorganiques

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### Abstract

A mathematical model for the computation of chemical equilibrium of atmospheric inorganic aerosols is proposed. The equilibrium is given by the minimum of the Gibbs free energy for a system involving an aqueous phase, a gas phase and solid salts. A primal-dual method solving the *Karush-Kuhn-Tucker* conditions is detailed. An active set/Newton method permits to compute the minimum and track solid salts at the equilibrium.

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### Résumé

Nous proposons un modèle pour l'étude de l'équilibre chimique d'un aérosol inorganique dilué dans l'air. L'état d'équilibre est caractérisé par le minimum d'énergie de Gibbs pour un système chimique faisant intervenir une phase liquide, une phase gazeuse et plusieurs phases solides. Nous présentons une méthode pour la résolution des conditions de *Karush-Kuhn-Tucker*. Nous utilisons un algorithme de type *active set*, couplé avec une méthode de Newton pour déterminer le minimum d'énergie ainsi que les phases solides apparaissant à l'équilibre.

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Over the last two decades, a series of thermodynamic modules, see for instance [1,5], has been developed to predict the phase transition of atmospheric inorganic aerosols. However, these modules either rely on *a priori* and incomplete knowledge of the presence of solid phases or are computationally intensive, implying that they often fail to accurately predict the existing solid phases at the equilibrium or are useless for three dimensional air quality models. In this note, a numerical method for the minimization of the Gibbs free energy in the framework of gas-liquid and solid-liquid equilibrium reactions [6] is presented. The Karush-Kuhn-Tucker (KKT) points are obtained with a primal-dual algorithm, where a Newton iteration is applied to the reduced KKT system of equations that is projected on an “active” set of solid phases to find the next primal-dual approximation of the solution. The active set strategy permits to add/delete constraints to/from a working set of active constraints until the equilibrium set of solid phases is obtained.

The chemical equilibrium problem for a closed inorganic aerosol system at constant temperature and pressure and for a specified feed vector  $\mathbf{b}$  is the solution of the minimization problem

$$\begin{aligned} \text{minimize} \quad & G(\mathbf{n}_l, \mathbf{n}_s, \mathbf{n}_g) = \mathbf{n}_l^T \boldsymbol{\mu}_l + \mathbf{n}_g^T \boldsymbol{\mu}_g + \mathbf{n}_s^T \boldsymbol{\mu}_s, \\ \text{subject to} \quad & \mathbf{n}_l > \mathbf{0}, \quad \mathbf{n}_g > \mathbf{0}, \quad \mathbf{n}_s \geq \mathbf{0}, \\ & \mathbf{A}_l \mathbf{n}_l + \mathbf{A}_g \mathbf{n}_g + \mathbf{A}_s \mathbf{n}_s = \mathbf{b}, \end{aligned} \tag{1}$$

where  $\mathbf{n}_\alpha \in \mathbb{R}^{m_\alpha}$ ,  $\boldsymbol{\mu}_\alpha \in \mathbb{R}^{m_\alpha}$  and  $\mathbf{A}_\alpha \in \mathbb{R}^{m_c \times m_\alpha}$  are the concentration vector, the chemical potential vector and the component-based formula matrix for species set  $\alpha$ , for  $\alpha = l, g, s$  respectively. The subscripts  $l, g, s$  denote the liquid, gas and solid phases respectively. Here  $m_c$  denotes the number of independent components in the system and  $m_\alpha$  denotes the number of species in species set  $\alpha$ .

In (1), the chemical potential vector  $\boldsymbol{\mu}_l$ , is defined as the gradient of the Gibbs free energy of the aqueous phase  $G_l : \mathbb{R}_+^{m_l} \rightarrow \mathbb{R}_+$ , so that,  $\forall \mathbf{n}_l > \mathbf{0}$ ,  $\boldsymbol{\mu}_l = \nabla G_l(\mathbf{n}_l)$ . The Gibbs free energy  $G_l$  is assumed to be at least twice continuously differentiable in the interior of  $\mathbb{R}_+^{m_l}$ . The first-order homogeneity of  $G_l$  is the basis for the relation  $G_l(\mathbf{n}_l) = \mathbf{n}_l^T \boldsymbol{\mu}_l$ , and the *Gibbs-Duhem relations*  $\nabla^2 G_l(\mathbf{n}_l) \mathbf{n}_l = \mathbf{0}$ . The chemical potentials  $\boldsymbol{\mu}_s$  are constant. The hessian matrices for the liquid and gas species are respectively  $\mathbf{H}_l = \nabla^2 G_l(\mathbf{n}_l)$  and  $\mathbf{H}_g = \text{diag}(1/\mathbf{n}_g)$ . The aqueous and gas phases are assumed to be present at the equilibrium. The difficulty in solving (1) is to identify the solid phases existing at the equilibrium.

Taking into account the Gibbs-Duhem relations, the solution of (1) is characterized by the Karush-Kuhn-Tucker (KKT) system of the first order necessary optimality conditions:

$$\begin{aligned} \boldsymbol{\mu}_l + \mathbf{A}_l^T \boldsymbol{\lambda} &= \mathbf{0}, \\ \boldsymbol{\mu}_g + \mathbf{A}_g^T \boldsymbol{\lambda} &= \mathbf{0}, \\ \mathbf{n}_s \geq \mathbf{0}, \quad \boldsymbol{\mu}_s + \mathbf{A}_s^T \boldsymbol{\lambda} &\geq \mathbf{0}, \quad \mathbf{n}_s^T (\boldsymbol{\mu}_s + \mathbf{A}_s^T \boldsymbol{\lambda}) = 0, \\ \mathbf{A}_l \mathbf{n}_l + \mathbf{A}_g \mathbf{n}_g + \mathbf{A}_s \mathbf{n}_s &= \mathbf{b}. \end{aligned} \tag{2}$$

A primal-dual solution of the KKT system (2), generally non unique, is called a KKT point. One needs to perform phase stability analysis to determine whether a postulated KKT point is thermodynamically stable with respect to any perturbation in  $\mathbf{n}_l$ ,  $\mathbf{n}_g$  and  $\mathbf{n}_s$ . Let  $(\mathbf{n}_l^\dagger, \mathbf{n}_g^\dagger, \mathbf{n}_s^\dagger, \boldsymbol{\lambda}^\dagger)$  denotes a stable KKT point of (2) and let  $\bar{\mathcal{I}}_s^\dagger := \{i \in \{1, \dots, n_s\} : \mathbf{n}_{s,i}^\dagger > 0\}$  denotes the corresponding active set of solid phases, which is the set of the solid species actually formed in the system at equilibrium. The cardinal of  $\bar{\mathcal{I}}_s^\dagger$  is denoted by  $\bar{m}_s$ . Let  $\bar{\mathbf{A}}_s$  be the matrix composed by the columns of  $\mathbf{A}_s$  that are in  $\bar{\mathcal{I}}_s^\dagger$  and  $\bar{\mathbf{A}} = [\mathbf{A}_l, \mathbf{A}_g, \bar{\mathbf{A}}_s]$ . The matrix  $\bar{\mathbf{A}}$  is assumed to be of full row rank. The stability analysis is then based on the *second order sufficient condition*, which states that,

$$\mathbf{p}^T \mathbf{H} \mathbf{p} \text{ is positive definite for all nonzero vector } \mathbf{p} \text{ such that } \bar{\mathbf{A}} \mathbf{p} = \mathbf{0}, \quad (3)$$

where  $\mathbf{H} = \nabla_{\mathbf{n}_l, \mathbf{n}_g, \mathbf{n}_s}^2 G(\mathbf{n}_l^\dagger, \mathbf{n}_g^\dagger, \mathbf{n}_s^\dagger)$  is the Hessian matrix of the Gibbs free energy of the system.

Recall that the inertia of a symmetric matrix is an ordered triple  $(i_+, i_-, i_0)$ , where  $i_+$  is the number of positive eigenvalues,  $i_-$  the number of negative eigenvalues, and  $i_0$  the number of zero eigenvalues.

Relationship (3) is equivalent to requiring the so-called KKT matrix  $\mathbf{K} = \begin{pmatrix} \mathbf{H} & \bar{\mathbf{A}}^T \\ \bar{\mathbf{A}} & \mathbf{0} \end{pmatrix}$ , to have a certain inertia.

**Lemma 1** *If the matrix  $\bar{\mathbf{A}}$  is of full rank, the condition (3) is equivalent to*

$$\text{inertia}(\mathbf{Z}_{\bar{\mathbf{A}}}^T \mathbf{H} \mathbf{Z}_{\bar{\mathbf{A}}}) = (m_l + m_g + \bar{m}_s, 0, 0), \quad (4)$$

where  $\mathbf{Z}_{\bar{\mathbf{A}}}$  is a null-space matrix for  $\bar{\mathbf{A}}$ .

Based on an inertia result of Gould [3], the inertia of  $\mathbf{K}$  is given by  $\text{inertia}(\mathbf{K}) = \text{inertia}(\mathbf{Z}_{\bar{\mathbf{A}}}^T \mathbf{H} \mathbf{Z}_{\bar{\mathbf{A}}}) + (m_c, m_c, 0)$ . Hence (3) implies that  $\mathbf{K}$  is invertible.

In the active set algorithm, a sequence of guesses of the active set of solid phases  $\bar{\mathcal{I}}_s^\dagger$  is constructed. This sequence of the so-called working sets, denoted by  $\bar{\mathcal{I}}_s$ , is defined in the *dual* sense by  $\bar{\mathcal{I}}_s := \{j \in \{1, \dots, m_s\} : (\boldsymbol{\mu}_s + \mathbf{A}_s^T \boldsymbol{\lambda})_j = 0\}$ . The dual variable  $\boldsymbol{\lambda}$ , together with the primal variable  $(\mathbf{n}_l, \mathbf{n}_g, \mathbf{n}_s)$  consists of a sequence of iterates that converges to the optimal primal-dual solution  $(\mathbf{n}_l^\dagger, \mathbf{n}_g^\dagger, \mathbf{n}_s^\dagger, \boldsymbol{\lambda}^\dagger)$ , as the set  $\bar{\mathcal{I}}_s$ , starting from an approximation of  $\bar{\mathcal{I}}_s^\dagger$ , is expected to converge to  $\bar{\mathcal{I}}_s^\dagger$  [4].

Along the process of applying the active-set strategy, the KKT system (2) is first projected onto the current working set  $\bar{\mathcal{I}}_s$  to form a reduced KKT system. The concentration vector  $\mathbf{n}_s$  is decomposed into  $\mathbf{n}_s = (\bar{\mathbf{n}}_s, \hat{\mathbf{n}}_s)$  where  $\hat{\mathbf{n}}_s = \mathbf{0}$  and  $\bar{\mathbf{n}}_s > \mathbf{0}$ . Let  $\bar{\mathbf{A}}_s$  be the matrix composed by the columns of  $\mathbf{A}_s$  with indices in  $\bar{\mathcal{I}}_s$  and  $\hat{\mathbf{A}}_s$  the matrix composed by the columns of  $\mathbf{A}_s$  which are not in  $\bar{\mathcal{I}}_s$ . Similarly, define  $\bar{\boldsymbol{\mu}}_s$  and  $\hat{\boldsymbol{\mu}}_s$  as the vector composed by the components of  $\boldsymbol{\mu}_s$  with indices that are in  $\bar{\mathcal{I}}_s$  and that are not in  $\bar{\mathcal{I}}_s$  respectively. Let  $\mathbf{Z}_{\bar{\mathbf{A}}_s}$  be a null-space matrix of  $\bar{\mathbf{A}}_s$ ,  $\mathbf{A}_{zl} = \mathbf{Z}_{\bar{\mathbf{A}}_s} \mathbf{A}_l$  and  $\mathbf{A}_{zg} = \mathbf{Z}_{\bar{\mathbf{A}}_s} \mathbf{A}_g$ . Let us also define  $\boldsymbol{\eta}$  by  $\boldsymbol{\lambda} = \boldsymbol{\lambda}^* + \mathbf{Z}_{\bar{\mathbf{A}}_s} \boldsymbol{\eta}$ , where  $\boldsymbol{\lambda}^*$  is a particular solution satisfying  $\bar{\boldsymbol{\mu}}_s + \bar{\mathbf{A}}_s \boldsymbol{\lambda}^* = \mathbf{0}$  and  $\hat{\boldsymbol{\mu}}_s + \hat{\mathbf{A}}_s \boldsymbol{\lambda}^* \geq \mathbf{0}$ . The system (2) projected on  $\bar{\mathcal{I}}_s$  consists of the equality constraints

$$\boldsymbol{\mu}_l + \mathbf{A}_{zl}^T \boldsymbol{\eta} = \mathbf{0}, \quad \boldsymbol{\mu}_g + \mathbf{A}_{zg}^T \boldsymbol{\eta} = \mathbf{0}, \quad \mathbf{A}_{zl} \mathbf{n}_l + \mathbf{A}_{zg} \mathbf{n}_g = \mathbf{Z}_{\bar{\mathbf{A}}_s} \mathbf{b}, \quad (5)$$

together with inequality constraints

$$\hat{\boldsymbol{\mu}}_s + \hat{\mathbf{A}}_s^T \boldsymbol{\lambda} \geq \mathbf{0}. \quad (6)$$

Let us ignore for the moment the fact that  $\bar{\mathbf{n}}_s$  must remain non-negative and apply one *Newton iteration* to the reduced system (5) to find the next *primal-dual* approximation  $(\mathbf{n}_l, \mathbf{n}_g, \boldsymbol{\eta})$  of the solution. The resulting Newton system for the displacements  $\mathbf{p}_l$ ,  $\mathbf{p}_g$ , and  $\mathbf{p}_\eta$  is

$$\begin{pmatrix} \mathbf{H}_l & \mathbf{0} & \mathbf{A}_{zl}^T \\ \mathbf{0} & \mathbf{H}_g & \mathbf{A}_{zg}^T \\ \mathbf{A}_{zl} & \mathbf{A}_{zg} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{p}_l \\ \mathbf{p}_g \\ \mathbf{p}_\eta \end{pmatrix} = \begin{pmatrix} \mathbf{b}_l \\ \mathbf{b}_g \\ \mathbf{b}_\eta \end{pmatrix}, \quad (7)$$

where  $\mathbf{b}_l = -(\boldsymbol{\mu}_l + \mathbf{A}_{zl}^T \boldsymbol{\eta})$ ,  $\mathbf{b}_g = -(\boldsymbol{\mu}_g + \mathbf{A}_{zg}^T \boldsymbol{\eta})$  and  $\mathbf{b}_\eta = \mathbf{Z}_{\bar{\mathbf{A}}_s} \mathbf{b} - \mathbf{A}_{zl} \mathbf{n}_l - \mathbf{A}_{zg} \mathbf{n}_g$ . The displacement in  $\boldsymbol{\lambda}$  is obtained as a displacement in the null-space, defined by  $\mathbf{p}_\lambda = \mathbf{Z}_{\bar{\mathbf{A}}_s} \mathbf{p}_\eta$ . The displacement  $\mathbf{p}_\lambda$  is restricted to a certain length so that the next  $\boldsymbol{\lambda}^+$  stays feasible with respect to (6). Finally, the next working set  $\bar{\mathcal{I}}_s^+$  is obtained by adding constraints that are encountered by the new  $\boldsymbol{\lambda}^+$ , *i.e.*  $\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \cup \bar{\mathcal{I}}_s^a$ , with  $\bar{\mathcal{I}}_s^a = \{j \notin \bar{\mathcal{I}}_s : (\hat{\boldsymbol{\mu}}_s + \hat{\mathbf{A}}_s^T \boldsymbol{\lambda}^+)_j = 0\}$ . Constraints are added in the working set until the sequence

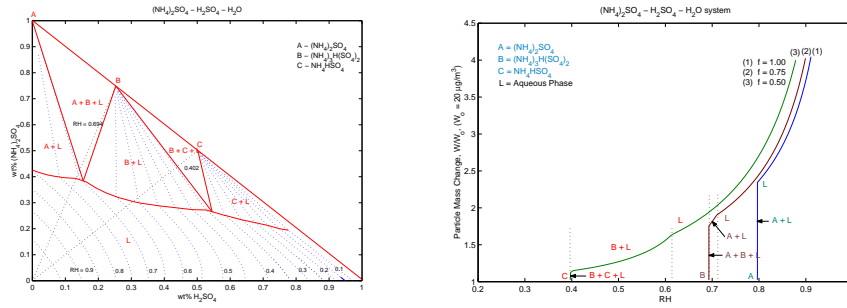


Figure 1. Modeling of a sulfate aerosol. Left: reconstruction of the phase diagram at  $25^\circ\text{C}$  with tracking of the presence of solid phases. Right: evolution of the particle mass in function of the *relative humidity* RH for three different feed vectors  $\mathbf{b}$ .

of  $(\mathbf{n}_l, \mathbf{n}_g, \boldsymbol{\lambda})$  converges to a solution of the reduced KKT system (5). The concentrations  $\bar{\mathbf{n}}_s$  in the working set  $\bar{\mathcal{I}}_s$  are then computed based on the last equality of (2) via  $\bar{\mathbf{n}}_s = (\mathbf{A}_s^T)^{-1}(\mathbf{b} - \mathbf{A}_l \mathbf{n}_l - \mathbf{A}_g \mathbf{n}_g)$  where  $(\mathbf{A}_s^T)^{-1}$  is the left pseudo-inverse of  $\mathbf{A}_s^T$ . The non-negativeness of  $\bar{\mathbf{n}}_s$  is enforced by *removing a saturated salt* from the working set  $\bar{\mathcal{I}}_s$  when its concentration becomes negative, that is  $\bar{\mathcal{I}}_s^+ = \bar{\mathcal{I}}_s \setminus \bar{\mathcal{I}}_s^d$ , with  $\bar{\mathcal{I}}_s^d = \{j \in \bar{\mathcal{I}}_s : \mathbf{n}_{s,j} < 0\}$ . If  $\bar{\mathcal{I}}_s^d \neq \emptyset$ , a new loop of Newton iterations is restarted; otherwise, the algorithm stops at a stable KKT point and the active set of solid phases  $\bar{\mathcal{I}}_s^+$  at the equilibrium is obtained. It is assumed that  $\mathbf{A}_s$  remains of full rank by addition or deletion of constraints in the working set, see also [2]. The solvability of the linear system (7) and the condition (3) are ensured by the following lemma.

**Lemma 2** *The condition (3) is equivalent to*

$$\mathbf{Z}_l^T (\mathbf{H}_l + \mathbf{S}_l) \mathbf{Z}_l > 0, \quad (8)$$

where  $\mathbf{S}_l = \mathbf{A}_{z_l}^T \mathbf{Q}_g \mathbf{R}_g^{-T} \mathbf{H}_g \mathbf{R}_g^{-1} \mathbf{Q}_g^T \mathbf{A}_{z_l}$  and  $\mathbf{Z}_l = (\tilde{\mathbf{Q}}_l, \mathbf{Q}_l \mathbf{R}_l^{-T} \mathbf{Q}_g)$  with  $(\mathbf{Q}_\alpha, \tilde{\mathbf{Q}}_\alpha)$  and  $\mathbf{R}_\alpha$  being the QR factorization of  $\mathbf{A}_{z_\alpha}$ ,  $\alpha = l, g$ . Under condition (8), the system (7) is solvable.

To ensure that the primal-dual algorithm converges to a *minimum or stable equilibrium*, the condition (3) is enforced via (8), by replacing  $\mathbf{H}_l$  with a modified matrix  $\tilde{\mathbf{H}}_l$  so that  $\mathbf{Z}_l^T (\tilde{\mathbf{H}}_l + \mathbf{S}_l) \mathbf{Z}_l > 0$ .

To illustrate the efficiency of the algorithm, a numerical example of atmospheric sulfate aerosol  $(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  is considered here. An aqueous phase is present and three solid phases may appear at equilibrium. Figure 1 shows, on the left side, the reconstructed sulfate aerosol phase diagram, and, on the right side, the evolution of the particle mass in function of the *relative humidity* RH for three different feed vectors  $\mathbf{b}$ . It illustrates that the method allows to track phase changes very accurately.

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