



Micro-physical Consistent Modeling of the Deliquescence and Efflorescence Hysteresis (A13A-11)

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INTRODUCTION

A difference between **deliquescence** and **efflorescence** RH values is commonly observed for aqueous salt particles. Given the impacts of particle phase on atmospheric chemistry and the radiation balance, modeling the deliquescence and efflorescence behavior of mixed atmospheric particles is clearly essential to predict their roles in the atmosphere. A major weakness in current aerosol models lies in the way they treat the deliquescence and efflorescence hysteresis. By relying on **a priori** and often **incomplete knowledge** of the presence of solid phases at a certain relative humidity and overall composition, these models often fail to accurately predict the phase state, composition and the multistage growth phenomena of inorganic aerosols.

In this study, our goal is to develop a general multicomponent dynamics model that is capable of simulating the deliquescence and efflorescence behavior of atmospheric inorganic aerosols.

DESCRIPTION OF THE METHOD

Notations

Let x_{α} , a_{α} , k_{α} and A_{α} stand for the concentration vector, the activity vector, the canonical equilibrium constant vector, and the component-based formula matrix for the species set $\alpha = l$, s respectively. Let \mathcal{I}_s be the index set of salts in the system and define the saturation ratio vector S by

$$\ln S = A_s^T \ln a_c - \ln k_s.$$

Then \mathcal{I}_s has the **decomposition**

$$\mathcal{I}_s = \mathcal{W} + (\mathcal{M} + \mathcal{N})$$

where

$$\begin{aligned} \mathcal{W} &= \{i : x_{s,i} > 0, \ln S_i = 0\}, \\ \mathcal{M} &= \{i : x_{s,i} = 0, \ln S_i > 0\}, \\ \mathcal{N} &= \{i : x_{s,i} = 0, \ln S_i \leq 0\}, \end{aligned}$$

with \mathcal{W} , \mathcal{M} and \mathcal{N} denoting respectively the set of the **crystallized**, **supersaturated** and **subsatuated** salts.

Modeling Hysteresis Effects

For atmospheric aerosols, the particle phase behavior is accurately described by the thermodynamic phase diagrams during deliquescence. However, for efflorescence, a kinetic barrier must usually be overcome. Transformation from a metastable phase to a thermodynamically more favorable phase requires first the nucleation of a germ of the new phase and then the growth of that germ. Salt crystallization in atmospheric particles composed of supersaturated aqueous electrolytes is a sequential process in which crystal nucleation is followed by crystal growth. We assume, for our analysis on small particles, that the overall **crystallization time** is limited by the nucleation time for a single germ.

Classical Theory of Nucleation Kinetics

According to the classical nucleation theory, the **expectation time** τ_{nucl} after which a particle of volume V_{pm} forms a single nucleus is given by

$$\tau_{\text{nucl}} = 1 / (J_{\text{nucl}} V_{\text{pm}}),$$

where J_{nucl} ($\text{cm}^{-3} \text{sec}^{-1}$) is the volume **nucleation rate** describing the number of nuclei (i.e., a critical germ) formed per volume per time and is defined by

$$J_{\text{nucl}} = J_0 \exp(-\Delta G_{\text{crit}} / (kT)).$$

Here, J_0 ($\text{cm}^{-3} \text{sec}^{-1}$) is a pre-exponential factor of order 10^{24} - 10^{36} , k is the Boltzmann constant, and ΔG_{crit} is the **free energy barrier** that must be surmounted to form a germ of critical size and is defined by

$$\Delta G_{\text{crit}} = \frac{16\pi}{3} c_{\text{geom}} \sigma_{\text{germ}}^3 / \left(\rho_{\text{germ}}^0 RT \ln S \right)^2,$$

where ρ_{germ}^0 is the molecular density of the germ, σ_{germ} is the surface tension vector of the germ in the medium, c_{geom} is a geometrical parameter.

Surface Tension Model

In order to apply the classical nucleation theory (CNT) in our metastable computation, we need **surface tension** data for the supersaturated aqueous salts solutions, which is based on **Li & Lu's mixing rule** [5]

$$\sigma_{\text{liquid/air}} = \sigma_w - RT \sum_{i=1}^n \Gamma_i^{w0} \ln(1 + K_i a_i)$$

where σ_w is the pure water surface tension at the system temperature and a_i is the activity of the electrolyte i . The two sets of model parameters Γ_i^{w0} and K_i are obtained from correlating the surface tension σ_{germ} against the measurements.

Antonoff's rule is applied to obtain the surface tension of crystalline germs in aqueous electrolyte solutions, σ_{germ} (i.e., between the crystal and the liquid),

$$\sigma_{\text{germ}} = \sigma_{\text{crystal/liquid}} = |\sigma_{\text{crystal/air}} - \sigma_{\text{liquid/air}}|,$$

where $\sigma_{\text{crystal/air}}$ is a constant for a given crystal and can be determined as a parameter based on one value of σ_{germ} .

Active-Set Method

Our **unsymmetrical active-set method** for modeling the deliquescence and efflorescence hysteresis is based on the **classical nucleation theory**.

At t_n , assume that the partition $(\mathcal{W}(t_n), \mathcal{M}(t_n), \mathcal{N}(t_n))$ and the crystallization time $t_{\text{cryst}}(t_n)$ for $\mathcal{M}(t_n)$ are known. For a new feed vector and RH at t_{n+1} , compute $(\mathcal{W}(t_{n+1}), \mathcal{M}(t_{n+1}), \mathcal{N}(t_{n+1}))$ and $t_{\text{cryst}}(t_{n+1})$ as follows:

1. **Update the crystallization set** $\mathcal{W}(t_{n+1})$ Activate the supersaturated salts $\delta\mathcal{M}(t_{n+1})$ that are expected to crystallize in the time interval (t_n, t_{n+1})

$$\begin{aligned} \mathcal{M}(t_{n+1}) &= \mathcal{M}(t_n) - \delta\mathcal{M}(t_{n+1}), \\ \mathcal{W}(t_{n+1}) &= \mathcal{W}(t_n) + \delta\mathcal{M}(t_{n+1}), \end{aligned}$$

with $\delta\mathcal{M}(t_{n+1}) = \{i \in \mathcal{M}(t_n) : t_{\text{cryst},i}(t_n) \in (t_n, t_{n+1})\}$.

2. **Newton Iteration** Compute x_l by Newton iterations on the reduced KKT system.

3. **Optimality Test** If x_l is a stationary point, then proceed as follows:
 - a) If $\mathcal{W}(t_{n+1}) = \emptyset$, i.e., no constraints are active, then the current point is a local (unconstrained) stationary point and go to 4.
 - b) If $\mathcal{W}(t_{n+1}) \neq \emptyset$, then compute the concentrations of the crystallized salts in the active set, \bar{x}_s . If $\bar{x}_s \geq 0$, then a local stationary point has been reached and go to 4; otherwise, drop constraints corresponding to the crystalline salts having **negative** concentration from the active set

$$\begin{aligned} \mathcal{W}(t_{n+1}) &= \mathcal{W}(t_{n+1}) - \delta\mathcal{W}(t_{n+1}), \\ \mathcal{N}(t_{n+1}) &= \mathcal{N}(t_{n+1}) + \delta\mathcal{W}(t_{n+1}), \end{aligned}$$

with

$$\delta\mathcal{W}(t_{n+1}) = \{i \in \mathcal{W}(t_{n+1}), x_{s,i} < 0\},$$

and go to 2.

4. **Update the metastable set** Compute the saturation ratio vector S and update the metastable set:

$$\begin{aligned} \mathcal{N}(t_{n+1}) &= \mathcal{N}(t_{n+1}) - \delta\mathcal{N}(t_{n+1}), \\ \mathcal{M}(t_{n+1}) &= \mathcal{M}(t_{n+1}) + \delta\mathcal{N}(t_{n+1}), \\ \mathcal{M}(t_{n+1}) &= \mathcal{M}(t_{n+1}) - \delta\mathcal{M}(t_{n+1}), \\ \mathcal{N}(t_{n+1}) &= \mathcal{N}(t_{n+1}) + \delta\mathcal{M}(t_{n+1}), \end{aligned}$$

with

$$\begin{aligned} \delta\mathcal{N}(t_{n+1}) &= \{i \in \mathcal{N}(t_{n+1}), \ln S_i > 0\}, \\ \delta\mathcal{M}(t_{n+1}) &= \{i \in \mathcal{M}(t_{n+1}), \ln S_i \leq 0\}. \end{aligned}$$

Compute $\tau_{\text{nucl},i}$ for $i \in \mathcal{M}(t_{n+1})$ according to the classical nucleation theory $\tau_{\text{nucl},i} = 1 / (J_{\text{nucl},i} V_{\text{pm}}(t_{n+1}))$, update the expected crystallization time $t_{\text{cryst},i}(t_{n+1})$ for the meta-stable phases $\mathcal{M}(t_{n+1})$

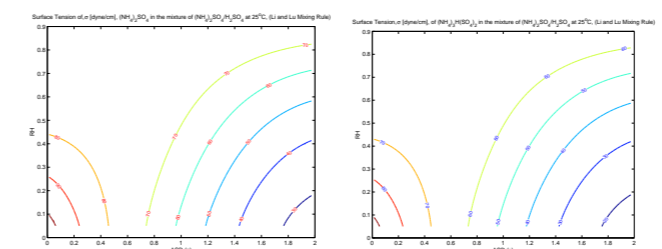
$$t_{\text{cryst},i}(t_{n+1}) = \min(t_{\text{cryst},i}(t_n), t_{n+1} + \tau_{\text{nucl},i})$$

and go to 1.

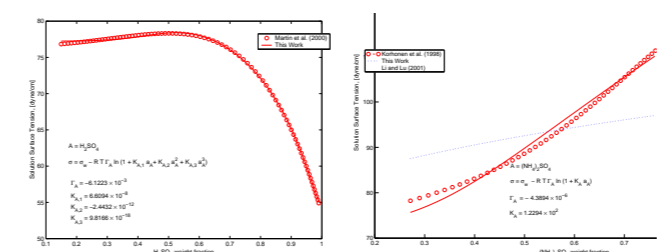
NUMERICAL EXPERIMENTS ON SULFATE AEROSOLS

Surface Tension

We depict here the surface tension of the **crystalline germs** $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ in $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ aqueous electrolyte solutions, as function of the ammonium-sulfate-ratio (ASR) and relative humidity (RH).



We choose $n = 2$, $i \in \{1, 2\} = \{(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4\}$ when applying Li & Lu's mixing rule [5] for the binary system $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$. The corresponding model parameters Γ_i^{w0} and K_i are obtained from **correlating** the surface tension σ against the **measurements** of [6] and [4].

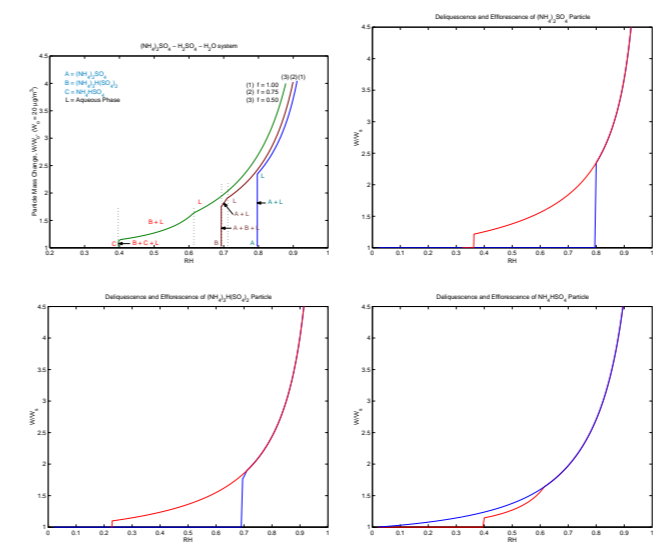


The activity calculation is based on the **ExUNIQUAC** activity coefficient model [9].

Hysteresis Curves

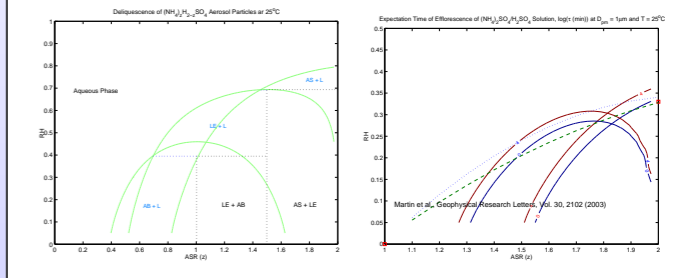
We depict the **deliquescence/efflorescence hysteresis curves** as a function of RH for $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ aqueous electrolyte solutions.

$$\begin{aligned} \text{DRH}_{(\text{NH}_4)_2\text{SO}_4} &= 79\% & \text{CRH}_{(\text{NH}_4)_2\text{SO}_4} &= 36\% \\ \text{DRH}_{(\text{NH}_4)_3\text{H}(\text{SO}_4)_2} &= 68\% & \text{CRH}_{(\text{NH}_4)_3\text{H}(\text{SO}_4)_2} &= 22\% \\ \text{DRH}_{\text{NH}_4\text{HSO}_4} &= 39\% & \text{CRH}_{\text{NH}_4\text{HSO}_4} &= \text{NONE} \end{aligned}$$



Phase Diagram

We depict the **deliquescence/efflorescence RH** for $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ aqueous electrolyte solutions.



CONCLUSION and FUTURE WORK

In this work [1, 2, 3, 10], we present a modeling framework based on classical theory of nucleation kinetics to simulate the transformation from a metastable phase into a thermodynamically more favorable phase. We apply classical nucleation theory in the active set algorithm in order to predict explicitly the physical state of the aerosol particles and the deliquescence and efflorescence hysteresis. Our micro-physical consistent model is incorporated in **UHAERO** as module 3, a general dynamic module that predicts efficiently the aerosol deliquescence and efflorescence, solid to solid phase transitions, and acidity transitions. We present computational results on sulfate aerosols to illustrate the model performance to simulate aerosol deliquescence and efflorescence.

To further assess the performance of **UHAERO** module 3 in modeling the deliquescence and efflorescence behavior of mixed atmospheric particles, we will rely mostly on **model-data comparisons** based on extensive laboratory data obtained by Prof. Martin's group [7, 8]. We will use one subset of data for parameter tuning, and another independent subset of data for demonstration of key features (e.g., induced crystallizations and other hysteric hygroscopic responses of atmospheric particles containing water-insoluble components such as mineral dusts).

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For additional information, please see

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