The impact of non-ideality on reconstructing spatial and temporal variations of aerosol acidity with multiphase buffer theory

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Aerosol acidity is a key parameter in atmospheric aqueous chemistry and strongly influence the interactions of air pollutants and ecosystem. The recently proposed multiphase buffer theory provides a framework to reconstruct long-term trends and spatial variations of aerosol pH based on the effective acid dissociation constant of ammonia (Kₐ,NH₃⁺). However, non-ideality in aerosol droplets is a major challenge limiting its broad applications. Here, we introduced a non-ideality correction factor (cₙᵰ) and investigated its governing factors. We found that besides relative humidity (RH) and temperature, cₙᵰ is mainly determined by the molar fraction of NO₃⁻ in aqueous-phase anions, due to different NH₄⁺ activity coefficients between (NH₄)₂SO₄ and NH₄NO₃-dominated aerosols. A parameterization method is thus proposed to estimate cₙᵰ at given RH, temperature and NO₃⁻ fraction, and is validated against long-term observations and global simulations. In the ammonia-buffered regime, with cₙᵰ correction the buffer theory can well reproduce the Kₐ,NH₃⁺ predicted by comprehensive thermodynamic models, with root-mean-square deviation ~0.1 and correlation coefficient ~1. Note that, while cₙᵰ is needed to predict Kₐ,NH₃⁺ levels, it is usually not the dominant contributor to its variations, as ~90% of the temporal or spatial variations in Kₐ,NH₃⁺ is due to variations in aerosol water and temperature.