Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 9, 9491-9522, 2009
www.atmos-chem-phys.net/9/9491/2009/

Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations

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Abstract. Interactions with water are crucial for the properties, transformation and climate effects of atmospheric aerosols. Here we present a conceptual framework for the interaction of amorphous aerosol particles with water vapor, outlining characteristic features and differences in comparison to crystalline particles. We used a hygroscopicity tandem differential mobility analyzer (H-TDMA) to characterize the hydration and dehydration of crystalline ammonium sulfate, amorphous oxalic acid and amorphous levoglucosan particles (diameter ~100 nm, relative humidity 5–95% at 298 K). The experimental data and accompanying Köhler model calculations provide new insights into particle microstructure, surface adsorption, bulk absorption, phase transitions and hygroscopic growth. The results of these and related investigations lead to the following conclusions:

(1) Many organic substances, including carboxylic acids, carbohydrates and proteins, tend to form amorphous rather than crystalline phases upon drying of aqueous solution droplets. Depending on viscosity and microstructure, the amorphous phases can be classified as glasses, rubbers, gels or viscous liquids.

(2) Amorphous organic substances tend to absorb water vapor and undergo gradual deliquescence and hygroscopic growth at lower relative humidity than their crystalline counterparts.

(3) In the course of hydration and dehydration, certain organic substances can form rubber- or gel-like structures (supramolecular networks) and undergo transitions between swollen and collapsed network structures.

(4) Organic gels or (semi-)solid amorphous shells (glassy, rubbery, ultra-viscous) with low molecular diffusivity can kinetically limit the uptake and release of water and may influence the hygroscopic growth and activation of aerosol particles as cloud condensation nuclei (CCN) and ice nuclei (IN). Moreover, (semi-)solid amorphous phases may influence the uptake of

gaseous photo-oxidants and the chemical transformation and aging of atmospheric aerosols.

(5) The shape and porosity of amorphous and crystalline particles formed upon dehydration of aqueous solution droplets depend on chemical composition and drying conditions. The apparent volume void fractions of particles with highly porous structures can range up to ~50% or more (xerogels, aerogels).

(6) For efficient description of water uptake and phase transitions of aerosol particles, we propose not to limit the terms deliquescence and efflorescence to equilibrium phase transitions of crystalline substances. Instead we propose generalized definitions according to which amorphous and crystalline components can undergo gradual or prompt, partial or full deliquescence or efflorescence.

We suggest that (semi-)solid amorphous phases may be important not only in the upper atmosphere as suggested in recent studies of glass formation at low temperatures. Depending on relative humidity, (semi-) solid phases and moisture-induced glass transitions may also play a role in gas-particle interactions at ambient temperatures in the lower atmosphere.

Final Revised Paper (PDF, 1242 KB) Discussion Paper (ACPD)

Citation: Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Pöschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmos. Chem. Phys., 9, 9491-9522, 2009. Bibtex EndNote Reference Manager