Competition of homogeneous and heterogeneous ice nucleation on secondary organic aerosol particles: The role of particle phase state

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Recently, secondary organic aerosol (SOA) particles have been found to exhibit a highly viscous, amorphous state under atmospherically relevant conditions (Virtanen *et al.*, 2010). Besides retardation of chemical reactions (Shiraiwa *et al.*, 2011) and incomplete gas-to-particle partitioning of semi-volatile constituents (Vaden *et al.*, 2011), these particles were found to suppress homogeneous ice nucleation (Murray *et al.*, 2008), which normally takes place when a liquid particle reaches its respective homogeneous nucleation limit (Koop *et al.*, 2000). In turn, glassy SOA particles may act themselves as heterogeneous ice nuclei as recent studies suggest (e.g. Murray *et al.*, 2010, Wang *et al.*, 2012). The predominant nucleation pathway for SOA particles is thus controlled by particle phase state.

The phase state of SOA particles depends on several factors such as composition, temperature and relative humidity. In atmospheric updrafts, inducing a change in temperature and relative humidity, moisture- and temperature-induced phase transitions can occur (e.g. Shiraiwa *et al.*, 2011). In fast updrafts, these particles may also deviate from humidification equilibrium, i.e. the agreement between ambient relative humidity and water activity inside the particle may not be established at any point in time. The extent of this temporal delay is governed by the updraft velocity, the particle size and the diffusivity of water inside the glassy organic particle matrix.

Here we show how the delayed deliquescence of SOA particles can be quantified for SOA from a variety of precursors. A kinetic flux model (Shiraiwa *et al.*, 2012) is applied and the predominant ice nucleation pathway is inferred from particle phase state at the respective homogeneous and heterogeneous nucleation limits. To estimate diffusivities inside the organic particle matrix for the relevant range of temperature and humidity, we developed a novel method that relies on glass transition and hygroscopic growth data that are more easily available. The model simulations suggest upper temperature boundaries, below which heterogeneous ice nucleation of glassy aerosols may occur, depending on updraft velocities and particle size. We also show that the predominant ice nucleation pathway depends on precursor material and oxidation state.

References

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