FREEZING OF SUPERCOOLED SULPHURIC ACID PARTICLES IN THE AEROSOL CHAMBER AIDA

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1. INTRODUCTION

Cirrus clouds in the upper troposphere can be formed by homogeneous freezing of supercooled liquid aerosol particles, by heterogeneous processes involving solid particles or by a combination of both. Homogeneous freezing is expected to occur in increasingly concentrated solution particles as temperature decreases. It can be parameterised by the approach of Koop et al. [2000] which assumes that the homogeneous freezing rate only depends on water activity and temperature of the solution. Thereby, the homogeneous nucleation of ice from an aqueous solution can be expressed as a function of temperature and relative humidity independently of the nature of the solute. Alternatively, the temperature in an expression for the homogeneous freezing of pure water [e.g. Jeffery and Austin, 1997] can be replaced by the effective freezing temperature T_{eff}. This approach was first proposed by Sassen and Dodd [1988]. T_{eff} can be calculated from the molality and a specific constant of the solution. Recent experiments in the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) cloud chamber of Forschungszentrum Karlsruhe have indicated that in particular at temperatures below 220 K both the water activity parameterisation and the effective temperature approach seem to overestimate homogeneous freezing rates of solution particles. In this contribution we compare the experimental findings with model output from our comprehensive process model MAID. We focus on onset relative humidity and ice number density. The different approaches to parameterise the homogeneous ice nucleation rate are assessed.

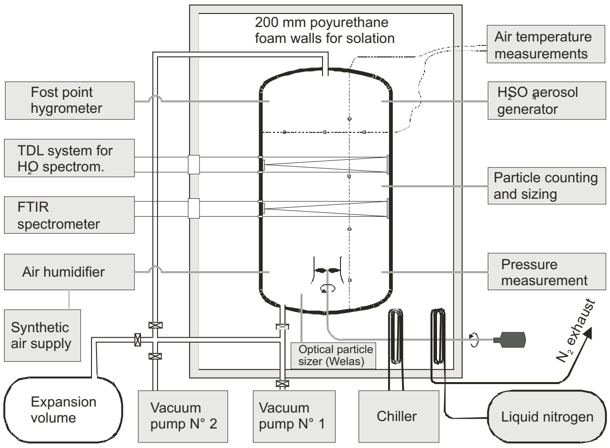

Figure 1: Schematic view of AIDA facility with key instrumentation

2. EXPERIMENTAL

The technical setup of the aerosol chamber and the experimental methods are described in our recent publications [Wagner et al., 2007, Möhler et al., 2006] and will be described here only briefly. Figure 1 depicts the AIDA setup including the key instrumentation. AIDA enables the investigation of ice clouds in the laboratory at realistic conditions with regard to temperature and cooling rate. It consists in substance of a large aerosol vessel (Volume 84 m^3) which is placed inside a coolable containment. At static conditions (with respect to temperature and ice saturation ratio) sulphuric acid particles were injected into the vessel at concentrations between 10^3 and 6×10^4 cm^{-3}. Ice supersaturated conditions in the aerosol vessel were achieved by expansion cooling with a mechanical pump at different pumping speeds corresponding to cooling rates between 1.7 and 0.5 K/min. In particular at the lowest temperatures we pumped very slowly to allow the aerosol taking up water from the gas phase. Thereby, a thermodynamic equilibrium between aerosol and gas phase is assured. Figure 2 depicts time series of AIDA experiment IN11-48 starting at –62 °C. The pressure was reduced from 1000 hPa to 750 hPa within 17 min. The water vapour concentration was measured in situ by a tunable diode laser absorption spectrometer (TDL). A frost point hygrometer measured ex situ total water concentration (gas + condensed phase). The ice saturation increased from a slightly subsaturated value to a maximum value $S_{ice}^{max} = 1.70$. After about 725 s (indicated by the blue vertical line) the threshold relative humidity for homogeneous freezing was exceeded. Due to water uptake of the growing ice particles the saturation ratio decreased shortly after onset of ice formation. An optical particle counter (WELAS) was used to monitor simultaneously the number concentration of ice and aerosol particles. Ice particles get visible in the WELAS record as they grow quickly to large sizes, clearly beyond the size range of the remaining aerosol particles. The light scattering device SIMONE was used to observe growth of solution particles by hygroscopic uptake of water as well as the onset of freezing. Onset of freezing is indicated by the sharp increase of depolarization ratio. Hygroscopic growth of aerosol particles causes the ratio of forward-to-backward scattered light to increase. By means of a FTIR-spectrometer the composition of the sulphuric acid/water particles was deduced (not shown here).

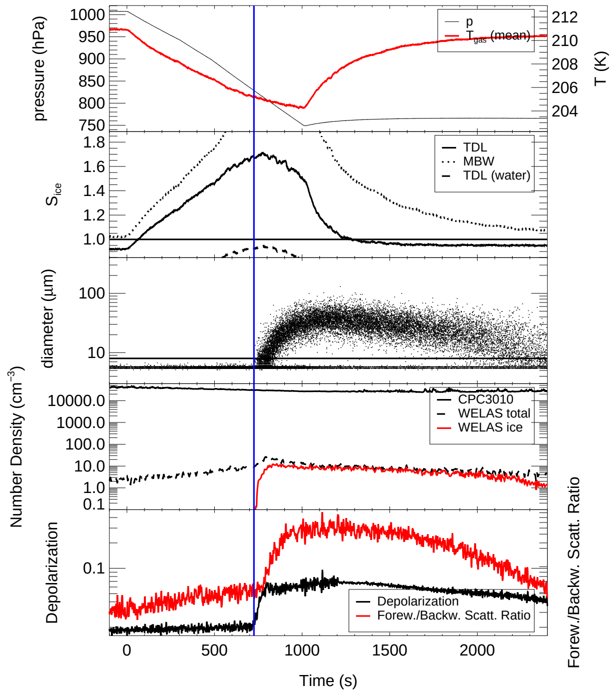

Figure 2: AIDA Experiment IN11-48: Experimental course of pressure and temperature (*Panel 1*); ice and water saturation ratio (gas-phase water, TDL) and ice saturation ratio (gas-phase + condensed phase, MBW) (*Panel 2*); optical particle counter WELAS (each dots represents an individual particle as function of experimental time and size based on Mie-calculations for spherical particles with refractive index 1.33, horizontal line separates aerosol particles from ice particles) (*Panel 3*); aerosol number concentration (CPC 3010), WELAS ice and total number concentration (*Panel 4*); backscattering depolarization ratio and ratio of forward to backward scattered laser light intensity (SIMONE) (*Panel 5*). Vertical blue line denotes onset time of freezing.

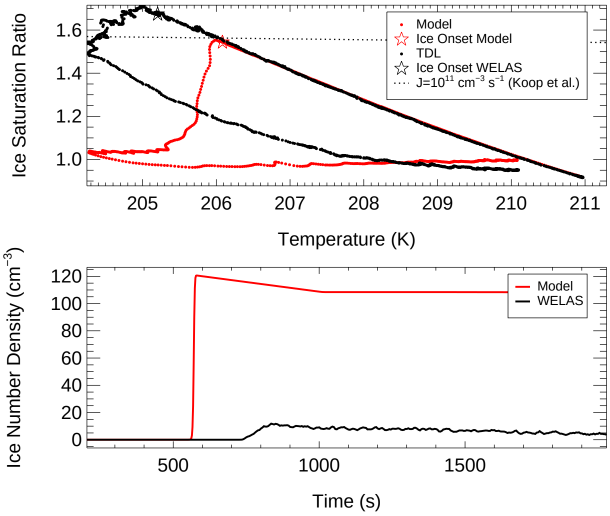

Figure 3: *Upper Panel:* Evolution of the ice saturation ratio (modelled and measured) as function of temperature. Dashed line indicates constant homogeneous ice nucleation rate $J = 10^{11}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ according to Koop et al. [2000]. Open asterisk indicate onset of freezing. *Lower Panel:* Development of calculated and measured ice number density

3. MODELLING

The detailed process model MAID (**M**odel for **A**erosol and **I**ce **D**ynamics, Bunz et al. [2008]) was applied to analyze the experimental findings. It simulates the growth and freezing of the solution droplets by taking into consideration the thermodynamic conditions in the aerosol vessel. The aerosol ensemble is simulated by a log-normal density function. The size distribution keeps its shape with distribution parameters varying as function of time. The temporal courses of pressure and temperature were prescribed to the model. The course of ice saturation ratio is calculated by the model taking into account the fluxes of water vapour from the ice covered chamber wall into the volume and the partitioning of water vapour to the condensed and gas phase. By model calculations we could show that 98 % of the aerosol volume exhibited a composition which did not deviate more than 1 % from the equilibrium composition given by the temperature and humidity during the expansion cycle. We tested both approaches to parameterise the homogeneous ice nucleation rate by comparing model and experimental results.

4. RESULTS

At the lowest temperature investigated we observed the freezing onset of the aerosol at a considerably higher ice saturation ratio than expected from literature data: At $T = 204\,\mathrm{K}$ we measured a freezing onset threshold of 1.73 ($\pm\,0.06$) while according to the activity based parameterisation for homogeneous ice nucleation [Koop et al., 2000] an ice saturation ratio of 1.57 is expected to freeze the solution particles during the AIDA experiment. Furthermore, the process model significantly overestimated the measured ice particle number concentration. The effective-temperature approach [Sassen and Dodd, 1988] revealed somewhat smaller deviations between modelled and measured values. At higher temperature a much better accordance was found by using the parameterisation of Koop et al. [2000]: at $T = -42.5$ we found experimentally an onset value of $S_{ice} = 1.41$ ($\pm\,0.05$) while the model run revealed $S_{ice} = 1.46$ at $T = -42.8\,^{\circ}$. The approach of Sassen and Dodd [1988] revealed a similar ice saturation ratio while the number density of ice particles formed was notably larger than observed.

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