Response to the Comment of Reviewer 1

We would like to thank Reviewer 1 for their comments and helpful suggestions. We reply to the individual points below.

General Comments

This manuscript describes the modification of the commercial instrument SPIN (SPectrometer for Ice Nuclei), which is a device for measuring ice nucleation activity of laboratory-prepared as well as natural ice-nucleating particles. In particular, by modification of the compressor system for cooling the measurement chamber of the instrument, the authors extended the temperature range of the SPIN device. The functionality in the entire (now extended) range of humidity and temperature is studied using model laboratory aerosols of ammonium sulfate and silver iodide. Overall, this is a valuable approach, although at the low temperature there seems to be an offset from the theoretical homogeneous ice nucleation curve. The authors speculate that this may be due to the fact that the aerosol particles do not reach equilibrium before freezing, see comment (6) below. I find this somewhat unsatisfactory and suggest that the authors spend more thought on this (and maybe, if possible, supply some additional sensitivity measurements). Moreover, because the paper's goal is allowing other scientists to make the same modifications to their SPIN instrument, I suggest a more detailed description/listing of the individual steps in order to become unambiguous.
Formally, the paper text, length, and figures are appropriate. However, I have a request regarding wording: apparently, the authors mix up vapor pressure and partial pressure and I request a correct and consistent usage of these terms, see comments (1) and (3) below.
In summary, the manuscript provides a useful approach and technical modification of an existing instruments, which I consider to be publishable in Atmospheric Measurement Techniques after the comments below have been considered in a revised version.

Scientific Comments

(1) *Page 2, Line 17; and caption to Fig.1: "Under steady state conditions a linear temperature and vapour pressure gradient establishes between the plates." I think the term vapor pressure is not used correctly and consistently. Vapor pressure is a property of a liquid or solid, and partial pressure is a property of a gas (mixture). The term vapor pressure is used here with its meaning of partial pressure. The IUPAC definition is: "For a mixture of gases the contribution by each constituent is called the partial pressure." In the caption of Fig.1 the term saturation pressure is used, which actually is the (saturation) vapor pressure.*

Following the reviewers recommendation, we replaced "vapour pressure" with "water vapour partial pressure" throughout the text when referring to the gas phase.

(2) *P.4, Figure 2: I would prefer that the figure directly indicated the modifications in the setup, either by colors or by shading etc. As it is now, the modifications are not evident to me. Given that these modifications are the essential novel part of this study, I also strongly recommend a more-detailed point-by-point listing of all modifications, so that any other SPIN user can follow and repeat it with their setup immediately. The latter may be provided in an appendix or supplement.*

To make the needed changes more evident, we added references to Fig. 2 and list the steps in the text as follows:
To reach lower temperatures, the SPIN cooling system has been modified by reconnecting the cold wall, cascade compressor system to deliver R116 refrigerant to both wall plates. The configuration of the modified setup is shown in Fig. 2. In practice, three modifications to the cooling system are needed:

1. At the upper part of the chamber, a junction is added to the high pressure liquid R116 line (lower stage, yellow line in Fig. 2) to connect it to the warm wall plate in parallel to the cold wall.
2. The refrigerant outlet lines of cold and warm wall, where the refrigerant exits the wall plates in the form of low pressure gas (lower stage, blue line in Fig. 2) are joint together to return to the cold 2 compressor.

3. Accounting for the increased volume of R116 needed to cool both wall plates, an additional expansion volume (14ℓ steel tank) is added to the return line (lower stage, blue line in Fig. 2), to give room to the gaseous refrigerant and prevent overpressure when the system is not running.

(3) *P.4, L.6/7: "decreasing absolute vapour pressure". What is an ABSOLUTE vapor pressure? I guess you mean total partial pressure, do you? See comment (1) above.*

As can be seen in Fig. 1, second row, the water vapour partial pressure at a certain relative humidity decreases with decreasing temperature, causing slower ice crystal growth. We changed the sentence accordingly.

(4) *P.5, Figure 3b and abstract and P.8, L.11: According to Fig.3b, the total experimental range to measure ice nucleation (indicated by the hatched area) is extended by 14 K at maximum when compared to the original SPIN range, but certainly less than the 20 K given in the abstract as well as in the conclusion (P.8, L.11). Please correct accordingly.*

The stated "more than 20K increase in measurement range" is based on experience and depends on ambient factors as well as operator's decisions. We consider it a good estimate, to give a SPIN owners an idea of what to expect if they decide to do the modification. Shown as hatched area in Fig. 3(a) and Fig. 1 below, in theory (neglecting heat transfer from the ambient), the temperature range achievable at the lamina position increases between 30K at RH_{ice} = 100% and 14K at RH_{ice}=190%. There are two practical factors to consider: First, operating SPIN in a laboratory or field station at around 293K ambient temperature limits the lowest achievable wall plate temperatures to 5-10K above the boiling point of the refrigerant due to imperfect insulation of the wall plates. Exemplary measurements conditions are shown in Fig. 1 below. Decreasing the cooling rate and ambient temperature can reduce this offset, but are often impractical. Secondly, not all refrigerant changes phase when the chamber is operated at a temperatures too close to the boiling point of the refrigerant. This causes incompressible liquid refrigerant to flow back to the compressor, causing what is known as "liquid slugging" that destroys the compressor. The "safe" temperature range of operating the SPIN chamber is therefore offset, both in the original and the modified configuration, by 5-10K from the maximum. Taking the two factors into account, shifts the calculated ranges (hatched in Fig. 1, below), 5-10K towards higher temperatures and larger ice crystals.

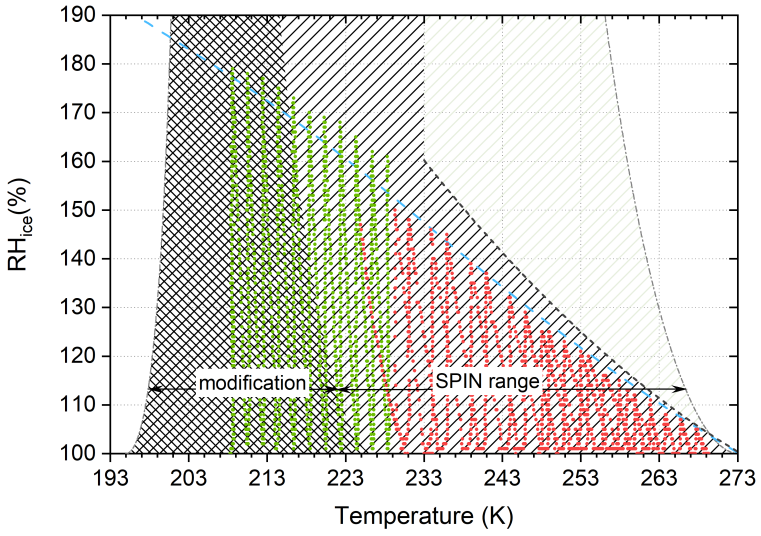

Figure 1. Comparison of the typical range of experimental conditions probable with the original SPIN (red points) to conditions after the modification (green points, lower 20 K of data shown in Fig. 4(a)).

The "limiting conditions" from ice crystal grow in Fig. 3(b) assume spherical ice growth (equations are now added in appendix A) and are therefore a lower limit for ice growth within the residence time in SPIN. Time dependent ice nucleation on the other hand can introduce a spread in growth time of the forming ice crystals and thereby their size distribution. It is an operator's decision which sizes are counted as ice crystals. From practical experience, the modification increased the measurement range by > 20K at low RH_{ice} and > 15K at high RH_{ice}. The temperature range to conduct RH-scans at constant T is increased by > 20K. The statement of a gain in temperature range of over 20K is therefore kept as is in the conclusion. In the abstract we now state the lowest temperature (208 K) at which we performed experiments, instead.

(5) *P.6, L.10: "and 1% AF curve derived using the parametrization of Koop et al. (2000)" How was the Koop-line calculated for 1% activation? The line will depend upon the time interval for which the aerosol particles are exposed to the T and RH conditions. What time interval was used for the calculations?*

The equations to calculate the 1% AF using the parametrisation of Koop et al. (2000) have been added in appendix B. We use the total residence time of exposure to the respective conditions (residence times slightly change with operating conditions and are calculated individually at each point in the RH-T space) to obtain the droplet size. The line of homogeneous freezing in Fig. 4(b) gives an estimation for the lowest RH_{ice} at each temperature where homogeneous freezing can cause 1% of droplets to freeze.

(6) *P.6, L.15: "aqueous aerosol do not reach equilibrium before freezing in SPIN" This is indeed a possibility, and maybe at the lowest temperatures diffusional limitations within the liquid droplets may also become relevant. However, this non-equilibrium state before freezing hampers the accuracy and applicability of SPIN, in particular in the extended low temperature regime. I would hope for more investigations as this is the main additional range of the SPIN instrument introduced in this work.*

At this point we would like to consider the discrepancy an interesting observation and only speculate on the reason. From the scatter of literature data included in Fig. 4(b) it can be seen that deciding whether the experimental data or parametrization (partly based on this data) are more robust is difficult. If droplets were not in equilibrium, they would be smaller and more concentrated, resulting in the 1% AF line to shift towards higher RH. This would explain the observed offset at the lower temperatures. Alternatively, Cziczo and Abbatt (1999) argued against substantial excursion from equilibrium even at short timescales and low temperatures, leaving the interpretation that the Koop et al. (2000) parametrization has a small, eventually solute dependent (Swanson, 2009) offset. We disagree that the applicability of SPIN to investigate homogeneous freezing is affected. The SPIN setup can provide measurements to investigate and refine the current understanding, be it diffusion of water into particles or ice nucleation.

Minor and Technical Comments

(7) *P.1, L.15: "At intermediate temperatures (236K < T < 273K) heterogeneous ice nucleation above water saturation. . ." I believe this should be AT OR BELOW water saturation, rather than ABOVE it. Or do you mean to ". . . above ICE saturation"?*

We changed the wording to "... close to water saturation..."

(8) *P.1, L.24: Here and at many other places in the text "Often, the dependency of ice nucleation on T, RH by a specific mechanism" I do not like the notation T, RH within a sentence. I guess you mean ". . . on T and RH by a . . ."? Please reword and use consistently throughout text.*

"T, RH" was replaced by "T and RH" when used within a sentence.

(9) *P.2, L.29-30: I assume these are the boiling points at standard or ambient pressure, correct? Please refine wording.*

We added that boiling points are given at atmospheric pressure (1 atm).

(10) *P.3, Figure caption 1: Reference Murphy and Kopp (2005) is misspelled.*

Corrected.

(11) *P.4, L.7: "4 m in 10 s residence time" Replace "in" by "within".*

Corrected.

(12) *P.6, L.3: "are reports of $(NH_4)_2SO_4$ forming ice heterogeneously at cirrus temperatures" This is only correct for non-deliquesced (i.e. effloresced) particles. I suggest to add the deliquescence line of $(NH_4)_2SO_4$ to Fig 4b.*

We added the temperature dependent DRH line to Fig. 4(b).

(13) *P.8, L.11: "We describe a mechanically easy modification" Maybe "simple" is better than "easy"?*

We replaced "easy" with "simple".

(14) *P.8, L.18: Replace "AgI" by "AgI particles"*

Corrected.

(15) *P.8, L.23: There is no link provided to the repository.*

Unfortunately our data repository is not operational yet. The data are available upon request from the author.

References

Cziczo, D. J. and Abbatt, J. P. D.: Deliquescence, efflorescence, and supercooling of ammonium sulfate aerosols at low temperature: Implications for cirrus cloud formation and aerosol phase in the atmosphere, J. Geophys. Res., pp. 13 781 – 13 790, doi:10.1029/1999JD900112, 1999.

Koop, T., Luo, B. P., Tsias, A., and Peter, T.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611–614, 2000.

Swanson, B. D.: How Well Does Water Activity Determine Homogeneous Ice Nucleation Temperature in Aqueous Sulfuric Acid and Ammonium Sulfate Droplets?, J. Atmos. Sci., pp. 741 – 754, doi:https://doi.org/10.1175/2008JAS2542.1, 2009.

Response to the Comment of Reviewer 2

We would like to thank Reviewer 2 for their comments and helpful suggestions. We reply to the individual points below.

General Comments

The paper summarizes a design modification that will be of significant interest to other SPIN users and most likely other continuous flow diffusion chamber (CFDC) designs as well. Their technique has several demonstrable benefits. The authors note that the SPIN can now operate within the full set of conditions relevant to cirrus formation in the upper troposphere. One additional benefit not explicitly highlighted by the authors is the reduced number of compressors. Previous attempts to operate CFDCs at cold temperatures have resulted in the damage of compressors, and reducing the number of compressors used in the design will likely reduce instrument down-time due to repairs.
This paper is therefore well-suited for publication in AMT. Below, I provide a few questions and comments to strengthen the paper and clarify the interpretation of the SPIN results. The authors will note that most of these are minor points. I therefore recommend the paper be accepted for publications after the authors have adequately addressed or responded to them.

Major Comments

(1) *My only major comment concerns the interpretation of the apparent early-onset of homogeneous freezing of (NH4)2SO4). The authors note that the (NH4)2SO4) solution droplets appear to nucleate at a lamina RH lower than that expected for homogeneous freezing (Koop et al., 2000). The authors claim a discrepancy between their data and the Koop parameterization. However, I would venture a guess that their data actually presents no discrepancy if the uncertainty in lamina RH is taken into account.*

   a. *I believe Fig. 4 reports the average lamina conditions. However, at high RH and cold temperatures, CFDCs (and I would guess SPIN) generally show a few % uncertainty in the lamina RH. This uncertainty is caused by variability in the wall temperatures. Colder regions of the wall – for example, where refrigerant is injected – can cause certain areas of the lamina to experience a higher RH than the average. See e.g. Kulkarni and Kok, 2012, for a simple method and pre-written code to calculate the variability in lamina RH for a CFDC with SPIN's geometry.*

      The experimental variability in RH and T has been added to Fig. 4(b) and 5(b). The indicated range of variability represents the maximal deviation from the average conditions along the sample lamina, obtained from RH and T profiles calculated between 15 pairs of opposite temperature measurements along the cold and warm wall.

   b. *If this is lamina range is taken into account, does the onset of (NH4)2SO4) nucleation more closely align with the Koop homogeneous freezing parameterization?*

      Taking the RH and T variability into consideration does not change the observation that the measured slope of homogeneous freezing conditions is steeper than the Koop-line.

Minor Comments
Abstract

(2) *Page 1 Lines 4-5: "The modification extends the measurement range of SPIN by more than 20 K to the temperature regime relevant for ice formation in cirrus clouds." Can the authors specify in the abstract the lower temperature range now achievable with their design modification?*

We now specify the lowest temperature (208 K) at which measurements were performed. Measurements at lower temperatures are possible, but generate detection issues of distinguishing the sample aerosol from ice crystals.

Introduction

(3) *Page 1 Lines 13-15: "Tropospheric ice nucleation at low temperatures (T < 236 K), typical for cirrus clouds, proceeds at water sub-saturated conditions by homogeneous nucleation of aqueous aerosol or heterogeneous nucleation from the vapour phase." The authors should briefly mention the possibility that heterogeneous nucleation below water supersaturation could be due to the pore-condensation freezing mechanism. E.g. (David et al., 2019; Marcolli, 2014)*

Pore condensation freezing is already mentioned explicitly further down in this paragraph (line 19) and a reference to the recent overview by Marcolli, 2020 is given in line 25.

Operating Principles

(4) *Page 2 Lines 17-18: "For an explicit derivation of the linear temperature and vapour pressure field in a CFDC we refer to Rogers (1988); Luond (2009)." I recommend also citing here Kulkarni and Kok, 2012 – it specifically discusses calcualtion of lamina conditions for the parallel plate (SPIN) design.*

We thank the reviewer for pointing to this useful publication. We added: "A ready to use code to determine the position of the sample lamina can be found in Kulkarni and Kok (2012)."

(5) *Page 2 Line 21: "...a lamellar sample, which is confined by a sheath flow to a narrow position between the ice covered wall plates..." The authors should briefly note here recent work that demonstrates aerosol samples are *not* constrained by sheath flows but rather spread outside the lamina. See e.g. DeMott et al., 2015; Garimella et al., 2017. This fact should not much change the author's results or interpretation, but it is important for the field of CFDC users to start to acknowledge.*

We agree that the fraction of particle leaving the lamina does not considerably change the results and interpretation. We added: "For a discussion on sampling bias due to particle displacement outside the lamina we refer to Garimella et al. (2017); Korhonen et al. (2020)."

Modified Cooling System

(6) *Page 3 Line 31: "To reach lower temperatures, the SPIN cooling system has been modified by reconnecting the cold wall, cascade compressor system to deliver R116 refrigerant to both wall plates." The authors may know that R116 is a HFC whose use is being phased out in the European Union as per the Kigali Amendment to the Montreal Protocol. At this time, do the authors have knowledge of any non-HFC refrigerant (e.g. hydrofluoroolefin, CO2) that might be an acceptable substitute in the future? The authors might note that if HFC refrigerants are banned, a new overall to the SPIN or other CFDC instruments' refrigeration loops may be needed anyways.*

The use of HFC as refrigerant is a concerning issue, even in small quantities for scientific purposes. R116 as low-temperature refrigerant has already been phased out in the EU. We have been searching for non-HFC refrigerants that have a boiling point near the one of R116, but at present there are few suitable substitutes available. The referee is right that, e.g. CO_2 (boiling point 195 K) might suit for retrofitting the SPIN, but it will need to be tested.

(7) *Page 3 Lines 4-6: "A consequence of using only one instead of two compressors to deliver the refrigerant for both walls, is a reduction in the achievable cooling rate from approximately 2 K min1 to 1 K min1 above 233 K and decreasing to < 0.5 Kmin1 towards the lowest temperatures." Please comment on the circumstances when both walls need to be cooled concurrently (i.e. during cooling down to start experiment).*

The reduced cooling rate refers to the situation when both walls are cooled simultaneously. We added: "Simultaneous cooling of both walls is needed during cooling of the chamber to start an experiment or measurements in which temperature is changed at a constant humidity (T-scan)."

(8) *Page 3 Lines 11-13: "The range of the original SPIN setup is calculated with the cold wall varying from 273.15 K-194.95 K and the warm wall between 273.15 K-226.65 K (boiling point of R404A)." The authors should note how this range compares to the coldest temperatures previously achieved for SPIN experiments. The coldest I can find published are -58 °C (Wolf et al., 2019) and -56 °C (Nichman et al., 2019).*

The only possibility to achieve these low temperatures in the original SPIN, is by applying an asymmetrical sheath flow, pushing the sample lamina towards the cold wall. As can be seen in Fig. 1 in the manuscript, this leads to a not well constrained RH within the lamina. The two mentioned articles did not reveal the method they used to achieve low temperatures, therefore we prefer not to speculate.

(9) *Page 4 Lines 7-8: "Conditions for ice crystals to grow to a diameter of 0.5 m, 1 m, 2 m and 4 m in 10 s residence time in the ice super-saturated section of SPIN are calculated according to Rogers and Yau (1989)..." Can the authors please include the ice crystal growth equation in the manuscript? This will help readers understand the important point they are raising about the kinetic-limitations of the new instrument setup.*

The equation to calculate the ice crystal size is now included in appendix A.

Homogeneous freezing of freezing of Ammonium sulfate solution

(10) *Should "Ammonium" be capitalized in this section title?*

Changed to "ammonium".

(11) *In this section title you say "ammonium sulfate solution," but you introduced dried particles into the SPIN. The (NH4)2SO4) particles obviously deliquesced; please briefly report the deliquescence RH in the text, or show it in Figure 4.*

The DRH-line has been added to Fig. 4(b).

(12) *Page 6 Lines 13-15: "Possible reasons for the discrepancy between the measurements in this study and the Koop-parametrisation are time dependent effects, i.e. aqueous aerosol do not reach equilibrium before freezing in SPIN." See my Major Comment (1) above. Could the apparent early onset of homogeneous freezing be due to heterogeneities in wall temperature, leading some sections of the aerosol lamina to experience homogeneous freezing conditions while the mean conditions are below homogeneous freezing? Tt would help to report the standard deviation of lamina supersaturation here or show it in Figure 4.*

The variability in experimental conditions is now shown in Fig. 4(b) and Fig. 5(b). The standard deviation when repeating the experiment several times is much smaller.

Discussion

Page 8 Lines 3-5: "While the data are generally consistent, the measurements of this study show systematic discrepancies in T-RH dependance both from the predicted heterogeneous ice nucleation of CNT (Fletcher, 1962) and from the widely used parametrisation of homogeneous ice nucleation of solution droplets by Koop et al. (2000). Apart from differences in the method of particle generation, size segregation and detection, it is unclear why partly systematically deviating T-RH dependencies were observed in similar experiments." Again, see my comments above about whether uncertainty/variability in the average lamina RH could be responsible for discrepancies in the onset of homogeneous freezing.

We added the variability in the lamina RH and T to Fig. 4(b). While the Koop-line is within the variability of conditions during an experiment, the slope of the conditions clearly deviate from theory. Additional investigations are needed to elucidate this observation.

Figure 1

Caption: The citation here is Murphy and "Koop," not "Kopp." Koop's name is also misspelled in the references (Page 11 Line 15).

Corrected.

Figure 4-5

The coverage of T and RH space for these experiments is impressive!

References

Garimella, S., Rothenberg, D. A., Wolf, M. J., David, R. O., Kanji, Z. A., Wang, C., Rösch, M., and Cziczo, D. J.: Uncertainty in counting ice nucleating particles with continuous flow diffusion chambers, Atmos. Chem. Phys., pp. 10 855 – 10 864, doi:https://doi.org/10.5194/acp-17-10855-2017, 2017.

Korhonen, K., Kristensen, T. B., Falk, J., Lindgren, R., Andersen, C., Carvalho, R. L., Malmborg, V., Eriksson, A., Boman, C., Pagels, J., Svenningsson, B., Komppula, M., Lehtinen, K. E. J., and Virtanen, A.: Ice-nucleating ability of particulate emissions from solid-biomass-fired cookstoves: an experimental study, Atmos. Chem. Phys., pp. 4951 – 4968, doi:https://doi.org/10.5194/acp-20-4951-2020, 2020.

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SPIN modification for low temperature experiments

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Abstract. The SPectrometer for Ice Nuclei (SPIN) has been modified to access ice nucleation at low temperatures. The modification consists of a reconfiguration of components from SPIN's cooling system to provide refrigerant with a low boiling point to the chamber. We describe the setup modification and determine the temperature and humidity range accessible to experiments. The modification extends the measurement range of SPIN ~~by more than 20~~to 208 K~~to~~, which enables measurements in the temperature regime relevant for ice formation in cirrus clouds. This addition of low temperature capability allows for far more comprehensive measurements of the temperature- and humidity- dependent ice nucleation of test substances, to investigate fundamentals of ice nucleation mechanisms. We present exemplary data of heterogeneous ice nucleation on silver iodide and homogeneous ice nucleation in solution droplets to demonstrate the usefulness of the modified SPIN setup for precision measurements to detect discrepancies between experiments and widely used theories.

1 Introduction

The fundamental understanding of atmospheric ice formation is a complex problem that has been under investigation for almost a century (Findeisen, 1938). Part of the complexity of studying ice nucleation experimentally arises from different mechanisms that initiate ice formation at different temperatures and humidities. Tropospheric ice nucleation at low temperatures ($T < 236\,\mathrm{K}$), typical for cirrus clouds, proceeds at water sub-saturated conditions by homogeneous nucleation of aqueous aerosol or heterogeneous nucleation from the vapour phase. At intermediate temperatures ($236\,\mathrm{K} < T < 273\,\mathrm{K}$) heterogeneous ice nucleation above water saturation leads to glaciation of mixed-phase clouds (Pruppacher and Klett, 1997). Experimental work on heterogeneous ice nucleation mechanisms include the study of a variety of substances and their ice nucleation potential (e.g. Hoose and Möhler, 2012), both at water saturated (immersion freezing, contact freezing) and sub-saturated conditions (deposition ice nucleation, (pore-) condensation freezing). Experimental techniques to study each ice nucleation mechanism have been developed over the years (e.g. DeMott et al., 2011). The continuous flow diffusion chamber (CFDC) type of experiment has proven to be a versatile method to isolate and observe different mechanisms, especially ice nucleation from the vapour phase. As Rogers (1988) pointed out, the advantage of CFDCs is the separate control over temperature and humidity in contrast to expansion or mixing chambers for which T and relative humidity (RH) are interdependent. Often, the dependency of ice nucleation on T ~~,~~and RH by a specific mechanism, can be predicted from theoretical considerations (e.g. Fletcher, 1962; Koop et al., 2000; Marcolli, 2020). Experimental characterization of T-, RH-dependent ice formation is a tool to validate and

refine the theories on ice nucleation mechanisms.

We describe a mechanically uncomplicated way to modify the cooling system of the SPIN instrument to expand its ~~T-, RH-range~~ T and RH range in which experiments can be performed. The modification is beneficial for laboratory studies investigating ice nucleation in a broad ~~T-, RH-range~~T and RH range.

2 The SPectrometer for Ice Nuclei (SPIN)

SPIN ~~,~~is a parallel plate CFDC manufactured by Droplet Measurement Technologies (DMT). It follows the working principle discussed in Rogers (1988) with the parallel plate design from Stetzer et al. (2008). For a description of the original SPIN instrument and reference experiments we refer to Garimella et al. (2016). Here, the focus is on the compressor cooling system of SPIN, which is the component that was modified for low temperature operation. The cooling system generates high pressure, liquid coolant used to cool and maintain temperature of the chamber wall plates by dosed evaporation of the coolant. In the following, we describe how experimental conditions (T, RH) are generated by controlling the wall plate temperatures, and how much the limits of achievable experimental conditions are extended by modifying the cooling system.

2.1 Operating principles

Experimental conditions (T, RH) in SPIN are created by coating the parallel (10 mm apart) wall plates of the chamber with a thin (1 mm) ice layer acting as water reservoir, and individually controlling the temperatures of the front (warm) and back (cold) plate. The ice coated walls keep the vapour pressure boundary conditions at ice saturation with respect to the set wall temperature. Under steady state conditions a linear temperature and ~~vapour~~ water vapour partial pressure gradient establishes between the plates. For an explicit derivation of the linear temperature and ~~vapour~~ water vapour partial pressure field in a CFDC we refer to Rogers (1988); Lüönd (2009). Because of the non-linear temperature dependance of saturation on ~~vapour~~ water vapour partial pressure (Clausius-Clapeyron), super-saturated conditions can be generated in the 8 mm gap between the ice covered walls by setting different wall temperatures. For experiments, a lamellar sample, which is confined by a sheath flow to a narrow position between the ice covered wall plates, is passed through the chamber. T and RH at the lamina position are controlled by the linear temperature and ~~vapour~~ water vapour partial pressure gradient between the cold and warm plate. Fig. 1 shows exemplary temperature and ~~vapour~~ water vapour partial pressure gradients in SPIN, at water saturation ($RH_w = 100\%$) and T=203 K, 213 K and 223 K at the position of the sample lamina. A ready to use code to determine the position of the sample lamina can be found in Kulkarni and Kok (2012). For a discussion on sampling bias due to particle displacement outside the lamina we refer to Garimella et al. (2017), and Korhonen et al. (2020).

2.2 Modified cooling system

To control the chamber wall temperatures in the original SPIN setup, two independent refrigeration compressor cycles are used. The warm wall is cooled by a single stage compressor cycle using refrigerant R404A, while the cold wall is cooled by a two stage (cascade) compressor system with refrigerant R404A in the first, higher stage and refrigerant R116 for the second, lower

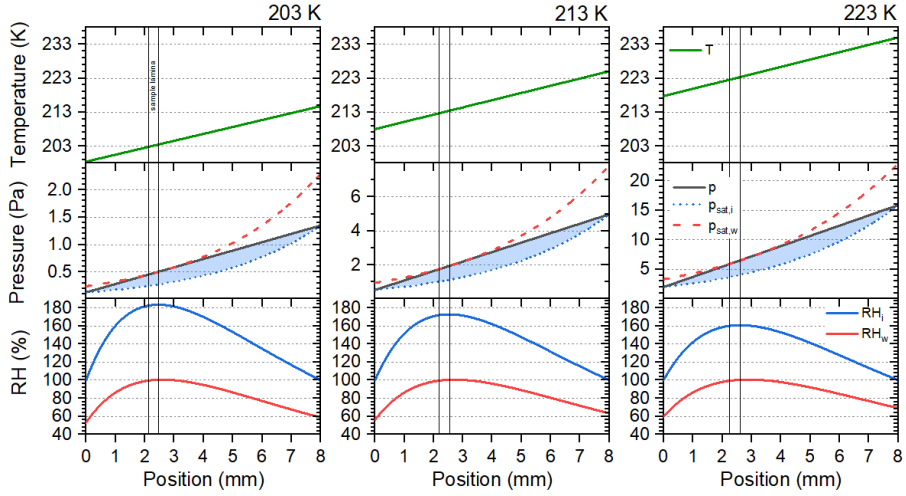

Figure 1. Linear temperature (top row) and water vapour partial pressure (second row) gradients between the wall plates of SPIN at 203 K, 213 K, 223 K lamina temperature and $RH_w = 100\%$. ~~Vapour~~ Water vapour partial pressure (p) is compared to the saturation vapour pressure over water ($p_{sat,w}$) and ice ($p_{sat,i}$), calculated according to Murphy and Koop (2005). Ice super-saturated conditions are indicated as shaded areas. The resulting profiles of relative humidity with respect to ice (RH_i) and with respect to water (RH_w) are given in the third row. Sample position is indicated by vertical lines.

stage (see Fig. 2 for a cascade compressor diagram). Refrigerant R116 has a boiling point of 194.95 K (at 1 atm pressure), refrigerant R404A has a boiling point of 226.65 K (at 1 atm pressure). The single stage compressor cycle using R404A to cool the warm wall plate in the original setup limits the range of T ~~,~~ and RH achievable at the sample lamina position. To reach lower temperatures, the SPIN cooling system has been modified by reconnecting the cold wall, cascade compressor system to deliver R116 refrigerant to both wall plates. The configuration of the modified setup is shown in Fig. 2. In practice, three modifications to the cooling system are needed:

1. At the upper part of the chamber, a junction is added to the high pressure liquid R116 line (lower stage, yellow line in Fig. 2) to connect it to the warm wall plate in parallel to the cold wall.

2. The refrigerant outlet lines of cold and warm wall, where the refrigerant exits the wall plates in the form of low pressure gas (lower stage, blue line in Fig. 2) are joint together to return to the cold 2 compressor.

3. Accounting for the increased volume of R116 needed to cool both wall plates, an additional expansion volume (~~9~~14 ℓ steel tank) is added to the ~~system,~~ return line (lower stage, blue line in Fig. 2), to give room to the gaseous refrigerant and prevent overpressure when the system is not running. ~~The configuration of the modified setup is shown in Fig. 2.~~

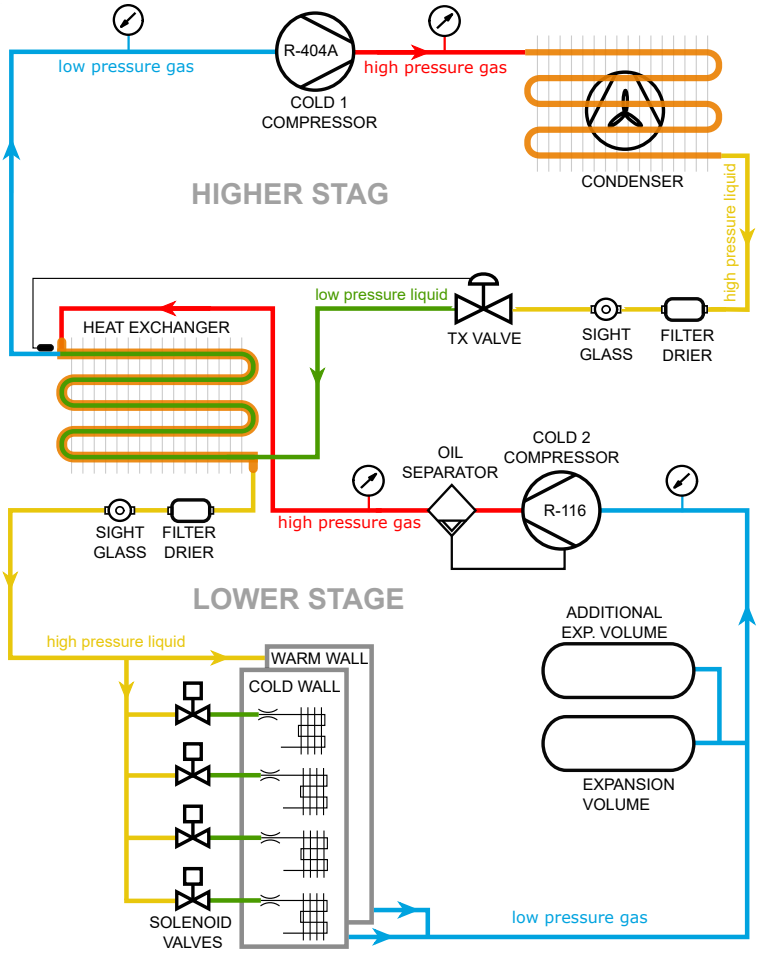

Figure 2. Diagram of two stage cascade compressor setup. Direction of refrigerant circulation is indicated by arrows. Pressure and phase state of the refrigerant is indicated by line colors. For the low temperature SPIN modification, R116 from the lower stage is used to cool both wall plates, and an additional expansion volume is added.

A consequence of using only one instead of two compressors to deliver the refrigerant for both walls, is a reduction in the achievable cooling rate from approximately $2\,\mathrm{K min^{-1}}$ to $1\,\mathrm{K min^{-1}}$ above 233 K and decreasing to $< 0.5\,\mathrm{K min^{-1}}$ towards the lowest temperatures. ~~For measurements varying humidity~~ Simultaneous cooling of both walls is needed during cooling of the chamber to start an experiment or measurements in which temperature is changed at a constant humidity (T scan). For measurements in which humidity is varied at a constant lamina temperature (~~RH scan~~RH scan) only one wall plate is cooled while the other is heated. During such experiments, where most of the refrigerant is used to cool one wall, the cooling rate of original and modified setup are identical.

The range of experimental conditions achievable with the original and the modified cooling system of SPIN are shown in Fig. 3. Fig. 3(a) shows the theoretical limits of ~~RH-, T-conditions,~~ T and RH conditions, determined according to the examples shown in Fig. 1 by varying the cold and warm wall temperatures from 273.15 K-194.95 K (ice melting temperature to boiling point of R116). The range of the original SPIN setup is calculated with the cold wall varying from 273.15 K-194.95 K and the warm wall between 273.15 K-226.65 K (boiling point of R404A). Note that ambient heat loss is not considered for the shown range. In practice, the achievable wall temperatures lie 5-10 K above the boiling point of the refrigerant (at 293 K ambient temperature). In addition to instrumental limitations, the conditions under which experiments can be conducted are limited by the optical detection method used to distinguish ice crystals from test aerosol and droplets by size. The SPIN chamber comprises an isothermal section at the end in which conditions are maintained at ice saturation to evaporate droplets (Garimella et al., 2016). Fig. 3(a) shows the experimentally determined droplet breakthrough conditions where droplets growing above water saturation do not shrink below the size range where particles are classified as ice crystals. Droplet breakthrough limits the explorable humidity range of ice nucleation down to temperatures at which droplets freeze homogeneously. A second limit to detect ice nucleation is caused by the ice crystal growth velocity, which slows down considerably towards lower temperatures due to the ~~decreasing absolute vapour~~ lower water vapour partial pressure (cf. second row of Fig. 1) at a certain relative humidity. Conditions for ice crystals to grow to a diameter of 0.5 µm, 1 µm, 2 µm and 4 µm ~~in~~ within $\sim$ 10 s residence time in the ice super-saturated section of SPIN are calculated according to Rogers and Yau (1989) and shown in Fig. 3(b). Details on the calculation of the ice crystal size are included in Appendix A. Ice nucleation experiments often use test aerosol with diameter up to 1 µm, thus limiting experiments to conditions where the test aerosol can be distinguished from ice crystals to above the 1 µm ice crystal growth conditions shown in Fig. 3(b). Note that droplet breakthrough line and ice crystal growth, limit the experimental conditions to the same T ~~,~~ and RH in any CFDC with dimensions and flows similar to SPIN.

3 Laboratory performance

The modified SPIN setup is used to measure the ice nucleation activity of two reference materials in a ~~T,RH-range~~ T and RH range covering all tropospheric ice nucleation conditions. Experiments with ammonium sulfate ($(NH_4)_2SO_4$) are conducted to measure homogeneous ice nucleation and to determine the droplet breakthrough RH of the setup. Experiments with silver iodide (AgI) are conducted as an example for the setups utility to investigate heterogeneous ice nucleation.

Aqueous $(NH_4)_2SO_4$ aerosol is generated with an atomizer (Aerosol Generator Model 3076, TSI) and subsequently dried below the efflorescence point, while AgI particles are dry generated by agitation of powder with a magnetic stirrer. For both test substances, experiments are performed using dry 200 nm aerosol particles, size selected with a differential mobility ~~analyser~~ analyzer (DMA; TSI Model 3081).

3.1 Homogeneous freezing of ~~Ammonium~~ ammonium sulfate solution

$(NH_4)_2SO_4$ is a prevalent aerosol throughout the troposphere and commonly used for instrument calibration. Although there are reports of $(NH_4)_2SO_4$ forming ice heterogeneously at cirrus temperatures (Abbatt et al., 2006), it is often applied as a

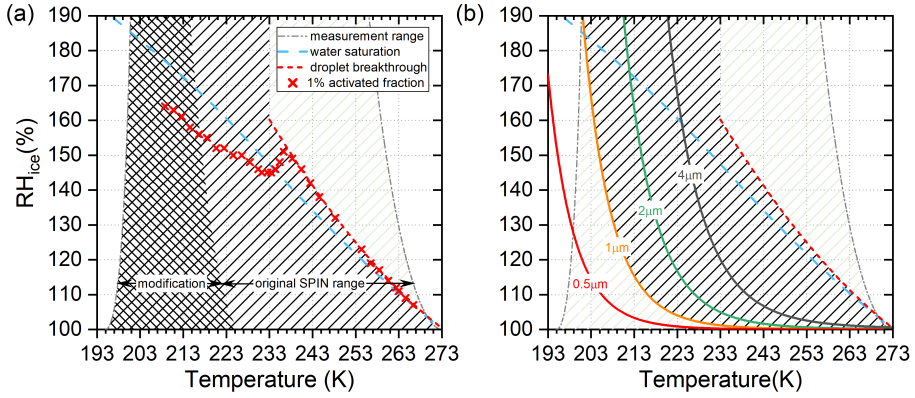

Figure 3. Calculated range of T-,RH_i-conditions. (a) Extended limit of experimental capacity with the modified SPIN cooling system (cross-hatched area) compared to the original setup (hatched area). Water saturation is indicated as blue dashed line. Red crosses show 1% activated fractions, measured with 200 nm ammonium sulfate particles (see Fig. 4). Above 235 K the data indicate onset of water breakthrough conditions, below 235 K homogeneous freezing of solution droplets. (b) Limiting conditions to distinguish 0.5 µm, 1 µm, 2 µm and 4 µm (diameter) test particles from growth limited ice crystals. Conditions excluded from ice detection by droplet breakthrough and ice crystal growth are lightly hatched. Total experimental range to measure ice nucleation with the modified SPIN setup is shown as dark hatched area.

hygroscopic test substance for forming aqueous aerosol to investigate homogeneous ice nucleation of solutes (e.g. Koop et al., 2000).

Fig. 4(a) shows the measured activated fraction (AF) of particles, calculated as the concentration ratio of detected ice crystals exiting SPIN to injected dry particles. Within the limits of detection of the SPIN experiment (approximately $AF \geq 1E-4$), no heterogeneous ice nucleation on solid $(NH_4)_2SO_4$ particles was observed. The very steep onset of ice formation in dependance of relative humidity below 235 K indicates homogeneous ice nucleation. A comparison of 1% AF conditions to literature data and 1% AF curve derived using the parametrization of Koop et al. (2000) are shown in Fig. 4(b). Details on the calculation of the homogeneous freezing line are given in Appendix B. While the data are in general agreement to previous observations, there is a clear offset between the slope of the Koop-line for 1% AF and the SPIN data. Homogeneous freezing is observed to set in at lower relative humidities just below 235 K and the temperature dependent increase in ice super-saturation necessary for constant activity is steeper (almost parallel to the water saturation line). Possible reasons for the discrepancy between the measurements in this study and the Koop-parametrisation are time dependent effects, i.e. aqueous aerosol do not reach equilibrium before freezing in SPIN.

3.2 Heterogenous ice nucleation on silver iodide

Silver iodide (AgI) is an exceptionally active ice nucleating substance (Vonnegut, 1947). AgI is widely used for cloud seeding operations to induce glaciation in supercooled liquid clouds, and also for seeding of cloud free, ice super-saturated parts of the

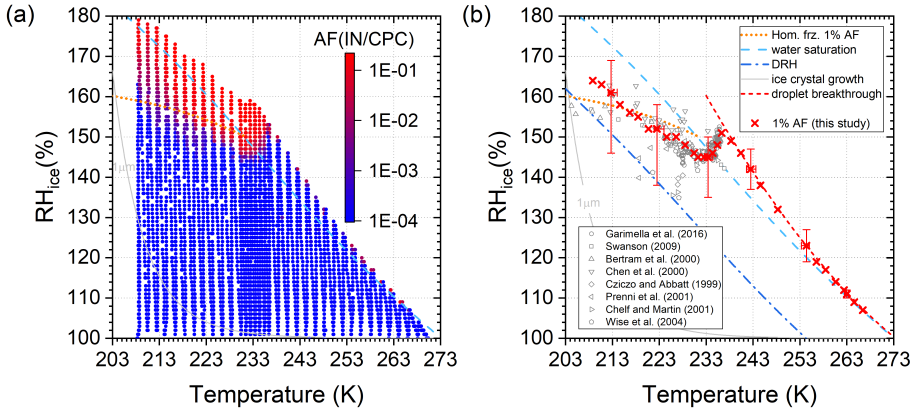

Figure 4. (a) Activated fraction of 200 nm $(NH_4)_2SO_4$ particles, (b) 1% AF in comparison to literature data (references indicated in the figure legend) and the parametrization given in Koop et al. (2000). ~~The~~ Lines indicate the Koop-line for homogeneous ice formation, water saturation, deliquescence relative humidity (DRH, Seinfeld and Pandis, 2006), droplet breakthrough and 1 µm ice crystal growth conditions~~are indicated as lines~~. The range of experimental variability in RH_{ice} and T is shown at 10 K intervals.

atmosphere to generate cirrus clouds (Vonnegut and Maynard, 1952). AgI has also served as a model substance to investigate the size and time dependance of ice nucleation and to develop the classical nucleation theory (CNT) of heterogeneous ice formation (Fletcher, 1959).

Measurements in the entire T-RH space are shown in Fig. 5(a). Fig. 5(b) shows a comparison of 1% AF conditions to literature data. Most previous laboratory experiments were limited to T>233 K by the measurement devices. The data collected here show good agreement to the large amount of data in this temperature range. Below 233 K only Bailey and Hallett (2002) and Detwiler and Vonnegut (1981) previously reported data. The two studies used static diffusion chambers and reported ice nucleation onset conditions without specifying the activated fraction and conditions for 1% AF, respectively. While the two previous studies observed an inflection in the slope of ice super-saturation needed for a constant amount of ice formation with decreasing temperature, the current study shows a more monotonic increase in ice super-saturation to activate 1% of the monodisperse AgI particles. A monotonic but less steep increase in ice super-saturation with decreasing temperature for a constant AF is predicted by CNT (Detwiler and Vonnegut, 1981).

4 Discussion

The modification of the cooling system of SPIN increases the experimentally accessible conditions to the entire ~~T-RH~~ T and RH range of ice and mixed-phase cloud formation in the troposphere. Overall, the modification maximizes the measurement range of a CFDC type instrument with the dimensions of SPIN, since the growth of ice crystals limits the lowest temperature at which ice crystals can be detected and distinguished from dry aerosol (shown in Fig. 3(b)). In comparison to the original

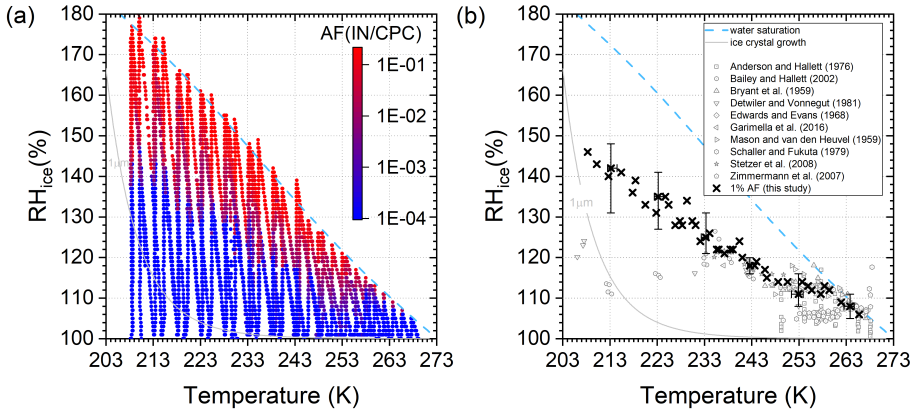

Figure 5. (a) Activated fraction of 200 nm AgI particles, (b) 1% AF in comparison to literature data (references indicated in the figure legend). Water saturation and 1 µm ice crystal growth conditions are indicated as lines. The range of experimental variability in RH_{ice} and T is shown at 10 K intervals.

SPIN setup, it allows a broader study of ice nucleation at lower temperature conditions, where ice super-saturation extensively occurs in the atmosphere and ice crystals form before humidities approach water saturation (Detwiler and Vonnegut, 1981).

To evaluate the performance of the modified SPIN for measuring homogeneous and heterogeneous ice nucleation, experiments using size selected, 200 nm $(NH_4)_2SO_4$ and AgI particles are compared to extensive literature data (see Fig. 4 and Fig. 5). While the data are generally consistent, the measurements of this study show systematic discrepancies in ~~T-RH-dependance~~ T-, RH-dependance both from the predicted heterogeneous ice nucleation of CNT (Fletcher, 1962) and from the widely used parametrisation of homogeneous ice nucleation of solution droplets by Koop et al. (2000). Apart from differences in the method of particle generation, size segregation and detection, it is ~~not clear why in similar experiments~~ unclear why partly systematically deviating ~~T-RH-dependencies were observed~~ T-, RH-dependencies were observed in similar experiments. It highlights the need for comprehensive ice nucleation data sets, measured for a wide range of substances, to improve the understanding of natural and artificial ice nucleation. The automation of the SPIN setup in combination with the extended measurement capability through the modification described here can be a tool to lay the experimental groundwork.

5 Conclusions

We describe a mechanically ~~easy~~ simple modification of the cooling system of the commercial SPIN instrument. Compared to the cooling system of the original SPIN setup, the modified system has a reduced cooling rate during initial cooling of the chamber in preparation for an experiment, however cooling rates during experiments are identical. In practice, the modification extends the experimental possibilities by more than 20 K to the full ~~T-RH~~ T and RH range of ice nucleation under tropospheric cirrus cloud conditions. This additional temperature range is particularly useful for experiments investigating the temperature-

and humidity- dependence of ice nucleation, since a number of aerosol species only efficiently trigger ice nucleation at such low temperatures. The usefulness of the modified SPIN instrument for laboratory studies, is exemplified by characterising the ~~T-RH- dependence~~ T-, RH-dependence of heterogeneous ice nucleation on AgI particles and homogeneous ice nucleation in $(NH_4)_2SO_4$ solution droplets. From both new data sets a systematic discrepancy between experimentally measured and theoretical predicted ice nucleation is discovered. With the modified SPIN instrument, specific ice nucleation mechanisms can be studied in a broader ~~T-RH-~~ T and RH range. The instrument is useful to validate theoretical aspects of ice nucleation and it can be used to investigate ice nucleation on natural and artificial aerosols.

Data availability. Data sets are available from the authors upon request.

Author contributions. AW, KK and PM modified the chamber. AW conducted the experiments with contributions from KK and AAP. AW prepared the manuscript with contributions from KK, AAP and AL. All authors commented the manuscript. YV, AV and AL acquired funding and supervised the project.

Competing interests. The authors declare that they have no conflict of interest.

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Appendix A: Ice crystal growth

The growth of ice crystals is estimated from the mass growth rate, $\frac{dm}{dt}$ (Rogers and Yau, 1989; Lohmann et al., 2016):

$$\frac{dm}{dt} = \alpha \cdot 4 \cdot \pi \cdot C \cdot \left(\frac{S_i - 1}{F_k + F_d} \right), \tag{A1}$$

where α is the accommodation coefficient for water molecules (Skrotzki et al., 2013), S_i the saturation ratio with respect to ice, and C the particle capacitance which incorporates the size and shape of the ice crystal (Lohmann et al., 2016). Assuming a spherical shape of the ice crystal for simplicity, C equals its radius, $C = r$ (see Lamb and Verlinde, 2011, for C for different shapes). F_k and F_d in the denominator of Eq. A1 are

$$F_k = \left(\frac{L_s}{R_v \cdot T} - 1 \right) \cdot \frac{L_s}{K \cdot T}, \tag{A2}$$

$$F_d = \frac{R_v \cdot T}{D_v \cdot p_{sat,i}}, \tag{A3}$$

where L_s is the latent heat of sublimation (Murphy and Koop, 2005), R_v is the individual gas constant for water vapour (Rogers and Yau, 1989), T is temperature, K is the thermal conductivity of air (Tsilingiris, 2008), D_v the water vapour diffusion coefficient in air (Hall and Pruppacher, 1976), and $p_{sat,i}$ is the saturation vapour pressure over ice (Murphy and Koop, 2005).

Substituting $\frac{dm}{dt}$ with $\rho_i \cdot 4\pi r^2 \frac{dr}{dt}$ in Eq. A1 and rearranging leads to the growth equation in terms of the ice crystal radius:

$$r\frac{dr}{dt} = \alpha \cdot \left(\frac{S_i - 1}{\rho_i \cdot (F_k + F_d)} \right), \tag{A4}$$

where r is the ice crystal radius, and ρ_i is the mass density of ice.

Integration yields the time dependent radius of an ice crystal:

$$r = \sqrt{r_0^2 + 2 \cdot \alpha \cdot \left(\frac{S_i - 1}{\rho_i \cdot (F_k + F_d)} \right) \cdot t}, \tag{A5}$$

where r_0 is the seed particle radius, and t is time.

Appendix B: Homogeneous freezing of $(NH_4)_2SO_4$ solution droplets

The fraction of $(NH_4)_2SO_4$ solution droplets expected to freeze according to the water activity (a_w) dependent, homogeneous nucleation rate parametrization by Koop et al. (2000) is given by

$$FF = 1 - exp(-J_{hom}(a_w) \cdot V_d \cdot t), \tag{B1}$$

where FF is the frozen fraction, $J_{hom}(a_w)$ the nucleation rate, V_d the volume of the solution drop, and t is time. The volume V_d of $(NH_4)_2SO_4$ solution droplets can be calculated based on the a_w dependent growth factor (GF) reported in Wise et al. (2003):

$$GF = 1.49 + 2.81 \cdot (a_w)^{24.6}, \tag{B2}$$

leading to

$$V_d = \frac{4}{3} \cdot \pi \cdot (r \cdot GF)^3, \tag{B3}$$

with r the radius of the dry $(NH_4)_2SO_4$ particle.

The parametrization of $J_{hom}(a_w)$ is reproduced from Tab. 1 in Koop et al. (2000):

$$\log_{10}(J_{hom}) = -906.7 + 8502 \cdot \Delta a_w - 26924 \cdot (\Delta a_w)^2 + 29180 \cdot (\Delta a_w)^3, \tag{B4}$$

with

$$\Delta a_w = a_w \cdot \exp\left(\frac{\int (v_w - v^i) dp}{R \cdot T}\right) - a_w^i, \tag{B5}$$

where R is the ideal gas constant. The integral can be approximated by

$$\int (v_w - v^i) dp \approx v_w^0 \cdot (p - \frac{1}{2} \cdot \kappa^0 \cdot p^2 - \frac{1}{6} \cdot \frac{\partial \kappa^0}{\partial p} \cdot p^3) - v_i^0 \cdot (p - \frac{1}{2} \cdot \kappa^i \cdot p^2 - \frac{1}{6} \cdot \frac{\partial \kappa^i}{\partial p} \cdot p^3), \tag{B6}$$

with $v_w^0 = -230.76 - 0.1478 \cdot T + \frac{4099.2}{T} + 48.8341 \cdot \ln(T)$, $v_i^0 = 19.43 - 2.2 \times 10^{-3} \cdot T + 1.08 \times 10^{-5} \cdot T^2$, $\kappa^0 = 1.6 GPa^{-1}$, $\frac{\partial \kappa^0}{\partial p} = -8.8 GPa^{-2}$, $\kappa^i = 0.22 GPa^{-1}$, and $\frac{\partial \kappa^i}{\partial p} = -0.17 GPa^{-2}$, where κ^0, κ^i are the isothermal compressibility of water and ice at ambient pressure. v_w^0 and v_i^0 are the molar volume of liquid water and hexagonal ice at ambient pressure.

The internal droplet pressure $p[GPa]$ in Eq. B6 can be calculated using the GF from Eq. B2 and the surface tension of the solution droplet (σ_{sol}):

$$p = \left(\frac{2 \cdot \sigma_{sol}}{r \cdot GF} + p_{sat,w}\right) \times 10^{-9}, \tag{B7}$$

where $p_{sat,w}$ is the saturation vapour pressure over water (Murphy and Koop, 2005). σ_{sol} is given in (Seinfeld and Pandis, 2006) :

$$\sigma_{sol} = 0.0761 - 1.55 \times 10^{-4} \cdot (T - 273) + 2.17 \times 10^{-3} \cdot M, \tag{B8}$$

where M is the molarity of $(NH_4)_2SO_4$ in the droplet which can be determined from the GF.
a_w^i in Eq. B5 is given by

$$a_w^i = \exp\left(\frac{210368 + 131.438 \cdot T - \frac{3.32373 \times 10^6}{T} - 41729.1 \cdot \ln(T)}{R \cdot T}\right). \tag{B9}$$

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