Response to review #2

We thank the anonymous referee #2 for his/her comments and suggestions for improvements. Below, the referee comments are in green, our response in black and the changed/added sections to the manuscript in *italics*.

1) As the first publication for this instrument from this group, this manuscript would benefit from more detailed descriptions of instrumental calibrations; most notably missing are an explicit description of the optical particle counter (OPC) calibration as well as a description of the instrument backgrounds. While the former omission, the OPC calibration, was partially described in the experimental section, more details are needed e.g., how many sizes of glass beads and what assumptions/analysis was conducted to get the full size distributions in the upper right panels of Figures 1 and 3. As for the latter, it seems qualitatively clear that signal is above the background in the upper right panels of Figures 1 and 3, but establishing background counts will be crucial to correctly quantifying frozen fractions and outline the frozen fraction limit of detection.

Most of the details of the instrumental calibrations were omitted because there is a technical paper on SPIN by Garimella et al. (2016) currently online. At the time of submission of the present study, the technical paper was not yet available online and we could not cite it. Although the instrument we have used in this study is the version previous to the one presented in Garimella et al. (2016), the descriptions of the optics calibration as well establishing the background counts are features that have not changed during the upgrade to the current version of SPIN.

Two sizes of polystyrene latex spheres (PSL), 0.9 and 2 µm, and glass beads of 5 and 8 µm were used to calibrate the optical detector of SPIN. A power law fit was applied to the calibration data in order to obtain the full size distribution. The detection efficiency of the OPC was investigated with different sizes of monodisperse PSL spheres in the range from 300 nm to 1.0 µm. Typical backgrounds during the experiments were of the order of 10-20 particles per litre.

We have included the following paragraphs to the text:

On page P35725, line 19:
“The final version and the performance of SPIN are described in more detail by Garimella et al. (2016). The main difference between the version of SPIN used in the present study and the final version is related to better temperature control of the final version.”

On page P35726, line 5 we have modified the sentence *“The size measurements of the SPIN OPC were calibrated using glass beads in the size range from 0.5 to 11.4 µm.”* to *“The size measurements of the SPIN OPC were calibrated using two sizes of polystyrene latex spheres (PSL), 0.9 and 2 µm, and glass beads of 5 and 8 µm.”* and added sentences *“A power law fit was applied to the calibration data and the full size distribution was extrapolated from the fit. The detection efficiency of the OPC was investigated with different sizes of monodisperse PSL spheres in the range from 300 nm to 1.0 µm.”* and *“Typical backgrounds during the experiments were of the order of 10-20 particles per litre.”*

2) Taking a closer look at Figure 1, it looks like the transition from regime A to regime B occurs at 97% RH, which corresponds to an ice saturation ratio (Sice) of 1.38. This is lower than the value reported for homogeneous freezing, likely because the authors have chosen a 10% activated fraction as their onset conditions for homogeneous freezing of ammonium sulfate. Given the onset conditions of the α-pinene SOA were at 1%, would not a 1% activated fraction for homogeneous freezing be a better comparison? This choice may have large implications for the results of the paper and should be addressed by the authors. For example, if 1% activated fraction for homogeneous freezing does indeed occur at an Sice of 1.38, then those homogeneous freezing points would overlap with the points that the authors consider to be heterogeneous freezing for their viscous α-pinene SOA. To add clarity to this discussion, the authors may also choose to show a frozen fraction vs. Sice plot as a supplemental figure; in doing so, the authors will increase the manuscript's transparency by allowing the reader to compare the maximum activated fractions from heterogeneous nucleation to those activated fractions seen in homogeneous freezing.

We have not used the transition from regime A to regime B to obtain our ice nucleation onset T and RH. Instead, the transition from regime B to regime C is used. This is because the operation mode of the instrument version used here was limited to only heating the SPIN chamber walls or keeping one wall at constant temperature and heating the other (warm) wall. The temperature control of the colder wall during active cooling was observed to be inadequate in most cases, resulting in "cold pockets" inside the chamber. Thus, the ice nucleation "onset" here is actually "offset": we do a temperature scan with a constant wall temperature difference in order to investigate the T and RH at which the ice disappears. These conditions correspond to the ice nucleation onset conditions.

The 10% activated fraction was chosen because of better counting statistics in the case of homogeneous freezing of ammonium sulphate droplets. We have now plotted the 10% activated fractions for the α-pinene SOA as well, for better comparison and consistency, and included the ice nucleation onset conditions of viscous α-pinene SOA for 1, 5 and 10 % activated fractions in the supplementary Table S1.

We have added a paragraph to section 2.3 for clarification (P35728, line 15):

"The way ice nucleation onsets in these homogeneous freezing experiments are obtained is the following. In Fig. 1, we use the transition from regime B to regime C, not from regime A to regime B, to obtain the ice nucleation onset temperature and ice saturation ratio. Due to the risk of cold pockets forming during active wall cooling, we scan the aerosol sample temperature upwards until the observed ice crystal mode vanishes and only liquid droplets remain. This temperature, at which a certain fraction (e.g. 10 %) of ice remains, is considered the ice nucleation onset. Although the ice nucleation onset here is actually ice offset, the conditions correspond to the ice nucleation onset conditions."

We have also added another clarifying paragraph to section 2.3 (P35729, line 2):

"It would be expected that > 10% of the droplets formed inside SPIN are exposed to temperatures > 0.3 °C below the reported average aerosol sample temperatures, which can

explain most of the gap between the reported average aerosol temperatures and the theoretical homogeneous freezing temperature."

3) The authors mention that they first show "size distributions in order to distinguish depositional nucleation from homogeneous freezing;" however, no explicit description of how the size distributions facilitate this was explained. To the reviewer, the size distribution B in both Figure 1 and 3 do look qualitatively different, but I am not sure how that correlates to depositional vs. homogeneous freezing. In the reviewer's opinion, an explicit explanation of this differentiation and all underlying assumptions would greatly increase the clarity provide further transparency to the results section.

The referee is correct: the size distributions themselves do not give exact information about the freezing mode. We have rephrased the sentence *"First, we show size distributions in order to distinguish deposition nucleation from homogeneous freezing"* on page P35729, line 26 to *"First, we show size distributions in order to demonstrate how we distinguish between inactivated seed aerosol particles, ice crystals and liquid droplets".*

Also, we have modified a sentence in the Conclusions (P35736, line 16): the sentence *"We conducted reproducible measurements and applied a size distribution method"* has been changed to *"We conducted reproducible measurements and performed uncertainty estimation and modelling of the temperatures and ice saturation ratios inside the INP counter".*

4) The authors also mentioned in this section testing for "droplet breakthrough," or that RH where a fraction of the formed liquid droplets survive the evaporation region; from size distribution C in Figure 1 it looks like droplet breakthrough may happen at relatively low supersaturations. Do the authors have any quantitative numbers for droplet breakthrough RH at the temperatures explored? Additionally, it appears from the upper right panel of Figure 3 that, when droplet breakthrough occurs (regime C), the authors also seen a large suppression of homogeneous freezing despite being at -36.8 °C and above water saturation. The reviewer suggests the authors address this behavior to increase the utility of the paper.

The droplet breakthrough for SPIN is systematically investigated and reported in Garimella et al. (2016). Following this issue raised by the referee, we have reconsidered our interpretation of what we previously considered as liquid droplets in Figure 3. It is more likely that at the temperatures investigated, the large size mode in Fig. 3 panel C consists of frozen droplets that have not grown very much due to potential activation close to the evaporation section of SPIN. This would also explain the slightly higher *S/P* ratios compared to Fig. 1 panel C.

We have removed the sentence on page P35730 lines 9-11 "*The latter experiment was performed in order to investigate droplet breakthrough, i.e. at which RH a fraction of the formed liquid droplets remain as droplets after the SPIN evaporation section."* since droplet formation, not droplet breakthrough, was investigated in the experiment. We have also removed the last sentence of the paragraph (P35730, lines 15-17) and replaced it with "*The droplet mode in panel (c) likely consists of frozen droplets that have not grown very much due to potential activation close to the evaporation section of SPIN. This could also explain the slightly higher S/P ratios (0.3) compared to the S/P ratios of 0.1–0.2 for the liquid droplets in Fig. 1 (c)."*

It is not clear which freezing mechanism is responsible for the freezing we observe in Fig. 3 regime C. It does take place at conditions where we have observed homogeneous freezing of highly diluted ammonium sulphate droplets, but we cannot distinguish whether it is caused by homogeneous freezing of liquefied SOA, immersion freezing of partly deliquesced SOA with a highly viscous core, or immersion freezing of droplets containing suspensions of organic ice nucleating macromolecules such as reported by Pummer et al. (2012). Therefore, we refrain from using the term "homogeneous freezing" in this context. The possible different freezing mechanisms are discussed in a new added section 3.4 (P35732). For details, please see below.

5) The error bars here are represented by the statistical standard deviation (1.96σ) between measured points. While the reviewer appreciates the authors providing this metric as it indicates that the ice nucleation onsets are reproducible between experiments and/or the aerosol is physio-chemically similar between experiments, the reviewer would argue that this does not necessarily conclude that these points are statistically different from homogeneous nucleation. The authors are comparing experimentally derived ice nucleation points to water saturation derived from a parameterization. This analysis ignores the instrumental uncertainties associated with the SPIN. The authors mention throughout the text the temperature uncertainty (± 0.4 K); however an associated RH/Sice error has not been explicitly addressed for the heterogeneous nucleation points. Interestingly, the authors did provide a maximum Sice error for the α-pinene SOA homogeneous freezing point and it was +0.13/-0.11. Similar-sized instrumental uncertainties for the heterogeneous freezing regime would clearly put at least 1% of the aerosol into homogeneous freezing conditions. The authors should explain, in detail, how their instrumental uncertainties factor into how they differentiate homogeneous and heterogeneous freezing.

We thank the referee for useful suggestions for improving the uncertainty estimation of our results. Consequently, we have re-evaluated our data and applied a more suitable way of representing the instrumental uncertainties of the observed ice nucleation onset temperature and S_{ice}.

The temperatures of the SPIN chamber walls were monitored with 4 pairs of thermocouples on each side, and the aerosol lamina temperature and S_{ice} are corrected for the buoyancy effect following Rogers (1988) at each of the 4 locations. The deviation in the temperatures vertically along the walls needs to be taken into account when estimating the uncertainties in the ice saturation ratio S_{ice}.

We have used the random instrumental error in average aerosol sample temperature from our measurements of homogeneous freezing with ammonium sulphate also in the case of SOA particles. This instrumental error is the standard deviation of 0.50°C from the reproducible temperature measurements of homogeneous freezing. The mentioned ± 0.4 °C range is related to the modelled temperature range to which the aerosol sample was exposed to during the homogeneous freezing experiments where the temperature difference between the walls was pronounced.

In order to obtain meaningful estimates for uncertainties in S_{ice}, we take the modelled equilibrium maximum range the aerosol sample is possibly exposed to, based on the pairwise temperature readings of the chamber walls. The modelled maximum range in sample temperature and saturation ratio is illustrated in supplementary Fig. S1. If the maximum saturation ratio with respect to water the sample is exposed to is under the homogeneous freezing line (Koop et al., 2000) or the water saturation line, freezing is considered heterogeneous. This is the basis for our differentiation between homogeneous and heterogeneous freezing.

We have now plotted the 10 % activated fractions of the SOA particles in Fig. 5 in order to allow for better comparison with homogeneous freezing of ammonium sulphate droplets. 10 % frozen fraction was not reached in every experiment; thus, the number of data points in Fig. 5 has decreased. Also, re-evaluation of the data has revealed such large uncertainties in S_{ice} for some data points that they may be susceptible to large systematic errors, and it is no longer possible to determine at which conditions the freezing was initiated. Such data points have also been omitted.

We have added the following paragraph to the manuscript:

P35729, line 23:

"The standard deviation of the experimentally determined homogeneous freezing temperatures for 10 % frozen fractions is 0.50 °C. This variation can be considered to reflect the experimental random errors on the average aerosol sample temperature for the instrument for these operation conditions."

We have re-written section 3.3 in the following way (P35731):

"The ice nucleation onset conditions were systematically investigated for frozen fractions of 1, 5 and 10 %. These data are listed in Table S1. In general, the conditions for the observations of 1, 5 and 10 % frozen fractions were very similar. In Fig. 5 the conditions for 10% frozen fractions are depicted. The random instrumental error on the average aerosol sample temperature is expected to be similar to the variations observed above for homogeneous freezing with a standard deviation of 0.5 °C. The depicted range of the saturation ratio with respect to ice (S_{ice}) is the modelled equilibrium maximum range the aerosol sample possibly is exposed to - in the vertical and horizontal dimensions - based on the pairwise temperature readings of the chamber walls at 4 locations. This is illustrated in Fig. S1. The modelling is done by taking the warm and cold wall temperature pairs at the 4 thermocouple locations where they are monitored and then calculating the aerosol lamina temperatures and saturation ratios with respect water and ice at those locations according to Rogers (1988). The reported ice nucleation onset temperatures in Fig. 5 are the mean values of the 4 aerosol lamina temperatures, and the reported Sice values are the mean values of the 4 calculated lamina Sice values. All the maximum saturation ratios for the observed 10% frozen fractions are below the depicted lines in Fig. 5 indicating where homogeneous freezing occurs. In terms of the saturation ratio with respect to water, the maximum modelled values are found in the range 0.90-0.98 and in the range 0.92-0.98 for frozen fractions of 1 and 10%, respectively. For the water saturation to reach 1 for all of these freezing conditions, a systematic wall temperature deviation in between thermocouples of >2 °C would be required. Such a systematic wall temperature deviation is highly unlikely considering the reasonable and reproducible homogeneous freezing results presented above. Hence, it is highly unlikely

that the observed freezing occurring at subsaturated conditions with respect to water is homogeneous freezing.

From our measurements, we have a strong indication that the studied α-pinene SOA induced ice nucleation heterogeneously. Despite instrumental limitations, the results were reproducible and the uncertainty for the ice nucleation onset temperatures and supersaturations could be inferred."

Page 35721, line 18: Delete "(IN)," this abbreviation is unnecessary here
Done.

Page 35722, line 2: Delete "e.g.," this is unnecessary here
Done.

Page 35722, line 5: Change "and contributes" to "and can contribute"
Done.

Page 35722, line 7: Given the references, did the authors mean "cold-cloud" instead of "mixed-phase cloud?"

Yes. This change has been made to the text on lines 6-8 on page P35722: *"Heterogeneous ice nucleation is considered to be an important pathway for ice formation in the troposphere, especially in mixed-phase clouds (Hoose and Möhler, 2012; Murray et al., 2012), but also in cirrus clouds (Krämer et al., 2009; Cziczo et al., 2013)."*

Page 35724, line 26: Please give a brief description of why aspherical here means viscous as this does not make sense out of context of (Järvinen et al., 2015)

The assumption of asphericity being indicative of high viscosity for SOA particles is the result of investigations of the optical properties of SOA formed and exposed to different temperatures and humidities. During the experiments, the near-backscattering depolarisation ratio measured by the SIMONE-Junior instrument was used to detect the phase of the particles. Liquid particles have a spherical shape and do not change the polarisation state of the incident light. Viscous phase state can change the particle morphology so that a non-zero depolarisation ratio is observed. Here, a non-zero depolarisation ratio was measured throughout the growth of the SOA particles at low RH, which indicated a viscous phase state. (Järvinen et al., 2016)

The lines 24-26 on page P35724 *"The depolarisation ratio was measured, and based on the determined depolarisation of the incident light, it was determined that the particles were aspherical and thus viscous."* have been modified to: *"The depolarisation ratio was measured, and based on the determined depolarisation ratio of the backscattered light, it was determined whether the particles were aspherical and thus viscous (detectable depolarisation)."* Also, for clarity and consistency, line 29 on page P35724 has been modified to *"the phase transition of the particles from higher to lower viscosity or liquid phase, i.e. the point where the depolarisation ratio decreased significantly to a level of spherical particles."*

Page 35725, line 3: If 80% RH is the transition RHw for this α-pinene SOA, the authors may consider to re-define their freezing mode as immersion-mode freezing as per (Berkemeier et al., 2014)

The referee is correct: the freezing mode is not necessarily pure deposition nucleation, but immersion freezing of the liquid/low –viscosity outer layer of the SOA particles, following the suggested 'core-shell-morphologies' in Berkemeier et al. (2014) and more recently in Price et al. (2015).

Another possibility could be immersion freezing of large, suspended organic macromolecules formed through oligomerisation during the ageing process in the CLOUD chamber. Organic macromolecules have been suggested to be the ice nucleation active entity causing the observed immersion freezing of e.g. birch pollen washing water (Pummer et al., 2012). That could explain why we do not observe any clear particle size effect on the ice nucleation behaviour.

We have added a new section 3.4 to the text (below). Due to partly overlapping content between sections 3.4 and 3.5, we have also shortened section 3.5 considerably.

"The results presented in the section above clearly indicate heterogeneous freezing of SOA particles below saturation with respect to water vapour. Various freezing mechanisms could potentially be in play. It can be speculated that we observe (i) deposition nucleation occurring directly onto highly viscous SOA particles; (ii) immersion freezing of partly deliquesced SOA particles, where the core of the particle is still (highly) viscous; (iii) hygroscopic growth of the particles leading to freezing of droplets due to suspensions of large organic molecules. The relevance of the first two potential freezing processes are related to the relative timescales of the viscosity transition vs the freezing of the SOA particles for increasing humidities as discussed e.g. by Berkemeier et al. (2014), Lienhard et al. (2015) and Price et al. (2015). Lienhard et al. (2015) conclude that heterogeneous freezing of biogenic SOA particles would be highly unlikely at temperatures higher than 220 K in the atmosphere since according to their modelling, the timescales of equilibration would be very short. On the other hand, the modelling results presented by Price et al. (2015) indicate that α-pinene SOA particles are likely to exhibit viscous core-liquified shell morphologies on timescales long enough to facilitate ice nucleation via the suggested mechanism (ii) in our study.

In this context, it is worth mentioning that the maximum ice nucleation time in SPIN is of the order of 10 s. However, nucleation taking place on much shorter timescales can be observed if the nucleation rates are high enough to yield detectable numbers of ice crystals. In other words, the observed number of ice crystals corresponds to the time integral over the nucleation rate distribution. This implies that from our measurements, no further conclusions concerning nucleation times and rates can be drawn.

The (iii) potential freezing mechanism has been reported for ice nucleating macromolecules (INM) originating from pollen (Pummer et al., 2012). It is not likely that the molecules formed in the current study grow to masses comparable to the several kDa reported for the pollen macromolecules (Pummer et al., 2012), but it does not necessarily rule out that large enough molecules or agglomerates to facilitate freezing may have been produced during the conducted experiments, even though it did not seem to be the case in *previous comparable studies (Möhler et al., 2008; Ladino et al., 2014). Based on the current study, it is not possible to conclude which heterogeneous freezing mechanism(s) may be dominating."*

Page 35726, line 29: If the absolute concentration is always under 1000 cm-3, what is the frozen fraction limit of detection?

The lower limit of the frozen fraction to be determined depends on the investigated particle number concentration and the observed background – which both varied between different experiments. However, typically the lower limit for most experiments would be at the order of $1\text{x}10^{-4}$. We have added a sentence to page P35726, line 29: *"The frozen fraction lower limit of detection was typically of the order of* $1\text{x}10^{-4}$*."*

Page 35729, line 9: While interesting, I am not sure why the authors report the freezing depression for 200 nm particles as 500 nm particles were used in this study

Also 200 nm particles were used in the measurements, as mentioned in the text on page 35727, line 10. The example in Fig. 1 is from an experiment with 500 nm particles.

Page 35730, line 6: Change "Analogously" to "Analogous" – Done.

References

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