Responses to Anonymous Referee #2

We thank the reviewer for his/her constructive comments that we address below point by point (responses are in italic).

In this study, authors describe the ice formation dynamics within the soot aggregates. They describe and parameterize the relationship between various thermodynamic variables that control the nucleation of ice and soot morphology. The paper is well written, the analysis is original in such that they extend the previously PCF based theory to soot aggregates, and the development of a parameterization to predict AF is unique. I have few minor comments, and after addressing them I recommend the paper for publication.

1) Abstract: This section is bit long. To improve the readability, I would suggest reduce the length of the abstract. Some of the sentences can be moved to the main text.

We have shortened the abstract.

2) Section 8: Soot particles in the atmosphere undergo aging, and the morphology of soot aggregates changes rapidly. The co-emitted gases (in biomass burning kind of event) condense and modify the physical and chemical properties. Can the theoretical framework (equation 9) be applied in such case? The related question is how one can model if some pores are partially filled with the sulfates and organics. This will change or at least alter the ice formation mechanism. Any thoughts on applying this framework in a transient environment where the soot properties are evolving in time?

This is a highly relevant question that cannot be fully answered within this study based on the currently available experimental data. We have addressed the different roles of aging occurring on soot particles acquiring coatings in Sect. 9, and extended the specific discussion in the revised manuscript to include the following points:

"In general, coatings of soot aggregates with semi-volatile material are expected to inhibit PCF. Yet, thin coatings with hydrophilic material should only have a minor effect. In general, they will (i) shift condensation of pore water to lower RH, (ii) lead to a freezing point depression, and (iii) may facilitate ice growth if diluted aqueous coatings wet the soot surface. Thus, the inhibiting effect of thin coatings should be most pronounced in the temperature range around 230 K where homogeneous ice nucleation rates are critical."

Thicker, more hydrophobic or viscous and glassy coatings will block water uptake by pores and inhibit PCF, while thick hydrophilic coatings will shift the freezing mode to immersion freezing or homogeneous freezing of solution drops depending on the ice activity of the specific soot in immersion mode. This is now addressed in the revised manuscript. Specifically, we have added the following:

"When sulfuric acid condensation leads to thick coatings, the freezing mode will shift to immersion or homogeneous freezing of solution droplets, depending on the ice activity of the specific soot in immersion mode. Whether a coating inhibits PCF depends on the amount of condensed material and on its distribution on the soot aggregate. Semi-volatile species may preferentially condense within the pores and block them for water condensation. Hydrophilic coatings do not spread on soot particles as an even coating but will form patches or droplets on soot aggregates, depending on the contact angle. A reasonable value to discriminate thin from thick coatings might be 20 % of the soot mass as chosen by Ullrich et al. (2017)."

Lastly, we acknowledge that the currently available experimental data on the impact of coating on the ice nucleation activity of soot particles is insufficient to make reliable and quantitative estimates about the amount of coating required to inhibit soot-PCF, which is addressed in a short outlook. Please see our answer to comment 17 of reviewer 3.

3) There is vast literature on soot ice nucleation onset and AF at temperature less than -38 degC. How this previous data compares with the Fig 6? I wonder if it is possible to plot the

Fig 6 data in RH-T space (RH on y-axis and Temperature on x-axis) to compare against literature data. AF can be colored with the marker size or colorbar.

Ice nucleation studies often only report ice formation onsets in terms of relative humidity and temperature, for AF thresholds typically lying between 0.1 to 1 %. Based on these studies, many soot samples have been found to activate along the homogeneous freezing line of solution droplets (Koop et al., 2000)*, while some form ice well below these conditions, as can be seen e.g. in Fig. 1-7 of Kanji et al.* (2017)*.We have added a table to Appendix F, that reports ice nucleation data together with physicochemical characterization reported in literature. Moreover, we discuss these data and set them into perspective with the soot-PCF framework presented here. To further acknowledge the available literature data on soot ice nucleation at cirrus conditions, we have added a new figure to our introduction that summarizes previous work.*

Unfortunately, hardly any of the literature data is sufficiently detailed to develop an empirical soot-PCF parameterization, since most of them just report ice onset RH and T for one mobility diameter and/or do not report the physicochemical properties of the soot particles investigated. What is lacking in most cases is the whole AF curve up to homogeneous ice nucleation to obtain the fraction of particles that exhibits pores suited for soot-PCF and in many cases the primary particle size. We have specified this in the revised manuscript, as written in our answer to comment 17 of reviewer 3.

4) Can this parameterization (equation 9) be modified to take into account the vertical velocity (the information typically needed to model the cirrus clouds)?

Indeed, the vertical velocity is relevant for homogeneous ice nucleation, which is a stochastic process and should be parameterized as a temperature dependent rate. For soot-PCF, pore condensation and ice growth are deterministically determined by the critical ice activation RH. Therefore parameterizations should provide time-independent, ice active fractions similar to Eq. (9) instead of nucleation rates. Vertical velocity therefore does not need to be taken into account. We have clarified this by adding the following statement to Appendix E:

"For soot-PCF as described in Eq. (E1), macroscopic ice formation is determined by the processes of pore filling or ice growth out of the pore, which both occur deterministically at a critical RH. Only at temperatures around 230 K, where the homogeneous ice nucleation rates may be critical, the stochastic nature of ice nucleation can be relevant. Therefore, vertical velocity, which is a determining factor for the number of homogeneously nucleated ice crystals (Kärcher and Lohmann, 2002; Hoyle et al., 2005; Sullivan et al., 2016), does not influence the number of ice crystals nucleated through soot-PCF and can be neglected in the soot-PCF framework."

5) Line 749: Discussion on aerosol-lamina is not clear. Is this means some particles were outside the lamina and did not had a chance to induce nucleation of ice? Does this artifact also affect all other measurements?

The measurement of the ice nucleation activity of different soot types shown in Fig. 6 were performed with a continuous flow diffusion chamber (CFDC). The general working principle of a CFDC is detailed elsewhere (Rogers, 1988) *and a more detailed characterization of the CFDC used to sample the data shown in Fig. 6, called the horizontal ice nucleation chamber (HINC), has been published in previous studies* (Kanji and Abbatt, 2009; Lacher et al., 2017; Mahrt et al., 2018). *In brief, in a CFDC a linear temperature gradient is established between two ice-coated walls, resulting in a parabolic water vapor supersaturation profile, due to the non-linear relationship between temperature and saturation vapor pressure, as described by the Clausius-Clapeyron relation. In an attempt to expose the aerosol particles in the CFDC to distinct temperature and relative humidity conditions, the aerosol flow in a CFDC is sandwiched by a particle free sheath flow. This sheath flow constrains the particles to a small region within the CFDC, called the aerosol-lamina (that largely coincides with the peak of the supersaturation profile), where the variation of RH and T is smallest. The ratio of the aerosol-to-sheath flow determines the width of the aerosol-lamina and hence the variation in RH and T that the aerosol particles are exposed to while travelling through the CFDC. A detailed discussion of the resulting uncertainties for the instrument used to sample the data in Fig. 6 can be found in Appendix D of Mahrt et al.* (2018)*. The RH and*

T conditions in this aerosol-lamina correspond to the ice nucleation conditions that are reported in most studies. While even across the aerosol lamina some variation in RH and T exists, the assumption of ideal instrument behavior, i.e. all particles remaining in the aerosol-lamina, is incorrect and to some extent also impacted by the difference in wall temperature, as demonstrated by previous studies (DeMott et al., 2015; Garimella et al., 2017). *Specifically the comprehensive study by Garimella et al.* (2017) *performed experiments using two different CFDCs and demonstrated that some fraction of the injected aerosol particles leave the lamina, ultimately resulting in correction factors to the measured AF between 1.5 to 9.5. Both CFDCs tested by Garimella et al.* (2017) *had a vertical orientation. In this design, a buoyant flow of relatively warmer air close to the warmer CFDC wall causes a replacement of the aerosol-lamina (as a function of the wall temperature difference). Such a buoyant airflow is absent in CFDCs with horizontal orientation, where the warmer wall is above the colder wall. As a result, the AF correction factors for horizontally oriented CFDCs, such as the one used to measure the data shown in Fig. 6, should be different and likely lower. However, we are not aware of any systematic quantification of such a correction factor for horizontally oriented chambers, and to the data shown in Fig. 6 no correction factor has been applied.*

In conclusion, particles leaving the aerosol-lamina are likely an inherent issue in all types of CFDCs. We have modified the relevant lines to direct the reader to the appropriate studies that focus on discussing this issue in more detail. Specifically, our revised paper reads:

"This suggests that the levelling off observed for the experimental data points at AF ≈0.2 results from instrumental limitations. Specifically, for the data depicted in Fig. 6, that were sampled with a continuous flow diffusion chamber (CFDC), it could result from divergence of particles out of the region of highest RH conditions within the CFDC, the so-called aerosol-lamina, as has been demonstrated in previous studies (e.g. DeMott et al., 2015; Garimella et al., 2017)."

6) Line 752: what are other examples of previous parameterizations?

We have specified this by making the following additions to the revised manuscript in Sects. 8 and 9:

"The way current parameterizations in global climate models predict the ice nucleation activity of soot particles are hampered by a number of factors. Most importantly, they often do not include a size dependence, but simplistically assume a fixed percentage of ice active soot particles ranging from 0.1 to 100 % with ice activation occurring at one distinct RH_i level (Gettelman et al., 2012; Gettelman and Chen, 2013; e.g. Hendricks et al., 2005; Penner et al., 2009; Wang and Penner, 2010; Zhou and Penner, 2014). Detailed cirrus models with spectral aerosol representations are capable of accommodating size- and supersaturation-dependent INP activity (Jensen et al., 2013, 2018; Kärcher, 2020; Kienast-Sjögren et al., 2015), leading to more realistic simulations of indirect aerosol effects on cirrus. While accounting for soot aggregate size is indispensable to correctly estimate the number of primary particles and pores present that ultimately determine the ice nucleation activity, explicitly measuring the size- and relative humidity dependent ice nucleation activity has only been the focus of a limited number of studies to date. Recently, Lohmann et al. (2020) used a more sophisticated parameterization derived from the ice nucleation activity of 400 nm miniCAST black soot aggregates, measured at 233 K and 218 K, with AF being a function of RH_i but still independent of aggregate size. Moreover, Zhou and Penner (2014) and Lohmann et al. (2020) assumed that soot aggregates are rendered inactive over time upon acquiring a coating of three or one monolayer, respectively. Compared to these parameterizations the soot-PCF parameterization denotes a key step forward as it comprehensively reflects the strong size dependence of ice nucleation on soot aggregates and can easily be adapted to specific soot properties."

As another example, Ullrich et al. (2017) present an empirical active site parameterization relying on AIDA campaigns carried out with different types of soot. As this parameterization assumes an active site density per surface area, it includes a size-dependence, but it does not differentiate between more hydrophilic and hydrophobic soots. Moreover, its temperature dependence does not reflect the data well as it shows a continuous decrease with increasing temperature even

above the homogeneous nucleation threshold. Nevertheless, the parameterization by Ullrich et al. (2017) requires five fitting parameters and just describes the isolines of the ice nucleation activity, but does not have a deeper physical background. We further discuss this point in our answer to comment 14 of reviewer 3.

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