

## ***Interactive comment on “Soot-PCF: Pore condensation and freezing framework for soot aggregates” by Claudia Marcolli et al.***

**Anonymous Referee #3**

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The authors present an extensive theoretical framework to describe the heterogeneous ice nucleation ability of soot particles at cirrus conditions based on the pore condensation and freezing (PCF) mechanism. They provide a very careful analysis of the dependence of the individual steps of the PCF process, i.e., capillary condensation of water, homogeneous freezing of the “water pockets”, and ice growth out of the pores, on the geometry of the pore types that can typically occur in soot aggregates and on the soot-water contact angle. The pore geometries were modelled/calculated based on primary particle size and particle overlap. Overall, the analysis provides some very nice insights into the pathway of forming macroscopic ice crystals on an “active site” on the soot surface, which can be limited, depending on the pore size and geometry, either by capillary condensation or ice growth out of the pore (see analysis of Fig. 5).

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The approach is also useful to estimate the particles' susceptibility to pre-activation (see Sect. 7).

One point of criticism for me is the in some aspects somewhat limited discussion of the new parameterization introduced in Eq. (9). The authors present a rigorous mathematical treatment of the various steps in the PCF mechanism, but the motivation for choosing the specific formula to quantify the ice-active fraction in Eq. (9) is much less described. Also, the authors state that the parameterization can predict the ice activity of a soot sample (line 853) and that the active-site probability function can be derived from first principles (line 705), but in the end they just use in their current work some empirical formula to derive the active site probability function from fits to activated fractions measured for two soot types in a continuous flow diffusion chamber (Eq. E4 and E5). Furthermore, it is mentioned that the new approach has advantages over previously proposed parameterizations, but no comparison with other literature data is shown in Fig. 6. If these points are explained a little better, I will be very happy to accept the manuscript for publication in ACP.

Specific comments:

Line 75-77: Could you incorporate these literature data to Fig. 6 to compare them with the Mahrt et al. data?

Line 86: You specifically mention here “hydrophobic material” to suppress PCF. But wouldn't the same be true for water-soluble components like sulfates, because solutes would decrease the homogeneous freezing temperature compared to pure water?

Line 116: You state here that you “predict” the ice nucleation ability of soot particles which then “fits” experimental results – but in the end with Eq. E4 and E5 you use empirical formulas to derive the active site probability function from the experiments. So currently it is still more the development of a new framework, by which the experimental data should be fitted, than an a priori prediction of the ice nucleation ability of a soot sample.

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Line 120: Given the length of the manuscript and the numerous aspects of the discussion, you might add here a short paragraph describing the general structure of the article.

Line 209: The heading of Sect. 2.3 “promises” some information on “compaction”, but actually I couldn’t find much of it in this section. Given that compaction is indeed an important process which affects the number of pores in a soot aggregate (line 141) and also appears as a parameter (via the fractal dimension) in Eq. 9, I would like to see some more discussion of this, see also my later comment regarding Eq. 9.

Line 264: Isn’t it below that of bulk water?

Line 379: Can you briefly explain in the text what is the parameter “n”?

Line 590-593: You mention here the relatively large variability of the onset conditions in terms of  $S_{ice}$  with the chosen values for the contact angle, overlap factor, and primary particle size. It would be interesting, see comment above, to compare these onsets with existing literature data on ice nucleation by soot particles.

Line 703: Is there a “physical basis” behind the equation you used to represent the ice active fraction (Eq. 9), e.g. regarding the exponent defined as  $(N_p - n_m)^{D_f}$ ? Is there a quantitative relationship to describe the number of pores in a soot aggregate as a function of primary particle size and compaction which is reflected by this exponent or was this expression just found to be a suited formulation to represent that the AF increases with  $N_p$  and  $D_f$ ? Lines 1175/1176 state that  $N_p$  and  $D_f$  determine the probability that a soot aggregate contains a ring pore, but line 703 states that the factor  $P_n(RH)$  also is the probability of a primary particle to be part of ring pore with given ice nucleating potential. I am a bit confused by this interpretation, is  $P_n(RH)$  not more of a factor that describes a kind of “averaged” ice nucleation ability of the pores present in the soot aggregate and the exponent  $(N_p - n_m)^{D_f}$  a measure for the absolute number of pores in the aggregate? Maybe you could elaborate a bit more on the physical meaning of these parameters and clarify my potential misconception.

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You mention in line 771-774 the very interesting finding from Mahrt et al. that the ice nucleation ability of compacted soot particles was found to be significantly higher compared to unprocessed, more fractal soot. Have you tried to model or even predict this behavior with your new parameterization? This would be in my opinion clear evidence of the advantages of your approach compared to previous parameterizations. Would compaction only affect the parameter  $D_f$  so that one could use the same active-site probability function of a given soot type both before and after compaction? Or would compaction also alter  $P_n(RH)$  (a question which is somehow related to my comment above regarding the physical meaning of the parameters)? Also, is it immediately intuitive that compaction, i.e., a higher  $D_f$ , leads to an increase in the AF? Would compaction not also lead to the situation that some potentially ice-active pores are no longer in the vicinity of the particle surface but somehow “shielded” in the inner part of the particle and can thus no longer contribute to macroscopic ice growth? This also relates to my question above how one can determine the number of pores that are actually accessible to the PCF depending on agglomerate size and compaction.

Line 705: You mention that  $P_n(RH)$  can be computed from first principles for a given soot type. But how would that look in practice – you would have to deal with a large parameter range with respect to primary particle size, overlap factor, and contact angle even for a single soot type, as reviewed in the first chapters of your manuscript, which then also depend on fuel type and operation conditions of the engine?

Line 751-753: You mention here the previously proposed parameterizations. Which are these exactly and can you provide some quantitative comparison with your new parameterization? I assume that in some of the previous parameterizations the activated fraction was normalized to the surface area of the aerosol (soot) particles to yield the so-called ice nucleation active surface site (INAS), whereas your approach specifically considers the number of active sites, i.e., pores in the soot aggregates, which in principle, no doubt, is the better physically-constrained approach. But how big would be the difference? I think it would be an important information for the mod-

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elling community to quantify the difference of your new theoretical framework to the widespread INAS approach, and to investigate with your size-resolved ice nucleation measurements and modelling simulations in Fig. 6 whether such an approach that only relies on the overall particle surface area is in accordance with the data or not. With a more quantitative comparison to previous parameterizations, you could really underline the advantages of your approach.

Line 855: I would rather say your parameterization increases the complexity of the parameters. You emphasize that you need different fit values for each soot type, and instead of just using the overall aerosol surface area as a parameter, you need additional values for the primary particles size and the degree of compaction. Depending on the soot type, you also discriminate between parameterizations with respect to either RH<sub>i</sub> or RH<sub>w</sub> (Eq. E4 and E5). This is by no means meant as a criticism of your approach – but my understanding of your study is rather that you need more parameters to characterize the actual ice active sites in the soot agglomerates using a physically-constrained approach so that you can properly describe their ice nucleation ability.

Line 871: “may vastly improve” – is a rather strong statement which also requires a more quantitative comparison to previous parameterizations.

Line 882: “have used available literature data” – yes, but there are many more previous measurements which you could include in Fig. 6, as suggested above.

Line 1004/1005: What is meant here with “example of a pore of 8 nm diameter”? Don't you calculate the saturation ratios for the whole range of filling levels?

Some technical corrections:

Line 38: Delete “of” before “ice formation”.

Line 54: “major gaps exist”.

Line 70: add “freezing”, i.e. condensation/immersion freezing mode.

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Line 187: Maybe add comma after “Overall”.

Line 267: Delete comma after “graphite”.

Line 324: Delete comma after “cell”.

Line 403: “in the immersion freezing mode”.

Line 546: please add: “growing ice phase out of a three-membered ring pore”

Line 568/569: You may briefly add here that the point for a filling level of 1.25 nm is indicated by “A” in Fig. 5.

Line 1077: “randomly” fluctuating

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