Reviewer comments are reproduced in bold and the author responses are in regular typeface. All line numbers in the authors' response refer to the revised manuscript. New text added to the manuscript in italics.

Interactive comment on "The Role of Contact Angle and Pore Width on Pore Condensation and Freezing" by Robert O. David et al.

Anonymous Referee #1

David et al. present ice nucleation measurements with well-characterized porous silica particles to investigate the efficiency of the pore condensation and freezing (PCF) ice formation pathway as a function of the particles' pore diameter, contact angle, and surface functionalization. The reported ice nucleation behavior is generally in agreement with that predicted by the inverse Kelvin equation, which is the starting point to theoretically describe the PCF mechanism. In some cases, further considerations, like limited growth time of ice crystals in the ZINC CFDC and pressure-dependent homogeneous ice nucleation rates, were taken into account to fully explain the experimental observations. It therefore remains challenging to derive a general parameterization of the PCF mechanism for e.g. ambient dust particles, but the experiments presented in this manuscript with the synthesized particles are an important step to understand which factors control the ice nucleation behavior of porous particles. A particular strength of the study is the comprehensive characterization of the particles with a number of different techniques as presented in Sect. 3.1. The manuscript itself is well-structured and in most parts clearly written. Reading the discussion of the ice nucleation measurements, however, was sometimes a bit challenging due to the variety of explanations taken into account to reconcile the findings with theory. I suggest below a couple of points which would need further clarifications, but otherwise recommend the publication of this article in ACP.

We thank the reviewer for the positive recommendation and for raising several points that we now address individually below and in the revised manuscript to make the paper clearer.

Specific comments:

1) Page 13, line 7: How did you exactly infer the range of contact angles for a given MCM-41 sample as also listed in Table 1 – did you use the uncertainty of d_DFT listed in Table 1, thus using e.g. pore diameters between 3 and 3.6 nm for the 3.3M1 sample in the calculation?

Indeed, we used the mean d_{DFT} and its uncertainty to report the spread in measured contact angles reported in Table 1 based on the humidity where the steepest condensation step was observed in the water sorption measurements. This has now been clarified on page 14 lines 7-8 by changing the sentence to read: "*The water contact angles for the MCM-41 particles ranged between 41°- 45° and 75 °- 80°, for the hydroxylated and methylated samples, respectively, based on the observed value and uncertainty (listed in Table 1) in the measured* d_{DFT}."

2) Page 13, line 12: Concerning the difficulty in the assignment of the "correct pore diameter responsible for the *initial* pore condensation": This statement seems to me a bit in contradiction with the one on page 6, line 14/15, saying that you did not use the onset relative humidity in the water sorption isotherms to compute the contact angle but the value where the pore condensation step is the steepest. So, the average pore diameters listed in Table 1 should be a reasonable choice for the computation and not the lowest value of e.g. 7 nm for the SBA-15 samples.

Table 1 represent the bulk properties of the particles, which in this case would be representative of the majority of the pores within the particles. The narrow pore size distribution of the MCM-41 particles, allows for the steepest condensation step in the sorption measurements to be representative of the majority of the pores, especially when the uncertainty in d_{DFT} is considered. Indeed, the uncertainty in d_{DFT} accounted for in Table 1 and a range of possible contact angles is reported for all of the samples that underwent sorption measurements. However, as the SBA-15 particles have a wide distribution in pore diameters (7 – 16 nm, see Fig. 2), the uncertainty in d_{DFT} (9 ±1.1 nm) is no longer enough to account for the range of possible pore sizes and corresponding contact angles. Furthermore, as the narrowest pores in the SBA-15 samples, which fill at lower humidities than their wider counterparts, are likely responsible for the observed freezing, it is necessary to obtain a larger range in contact angles for these particles. We have now added: "*based on the uncertainty in d_{DFT} alone (±1.1 nm)*", to the sentence to clarify this point on page 15 lines 1-2.

3) Page 14: I have a couple of questions regarding the DSC measurements: Is there an influence of external ice on the initiation of freezing in the pores (in the caption of Fig. 4 you use the expression "ice growth into pores"? Did you also record the DSC thermograms during heating, are the peak positions different from the cooling runs? How do your results compare with previous DSC measurements for MCM-41 and SBA-15 as e.g. summarized in Marcolli (2014)?

Indeed, ice grows into the pores from the frozen bulk water in the slurry. Thus, the freezing of pore water in DSC experiments is not determined by nucleation rates but by the melting point depression within pores, as is explained on page 15 lines 6-13. Unfortunately, the heat uptake during the warming cycle was undetectable for the smaller diameter pores and is therefore not shown. For the larger diameter pores, the heat release during freezing corresponds approximately with the heat uptake during melting considering the difference in enthalpy between freezing and melting. The observed freezing temperatures are in accordance with values reported in Fig. 1 of Marcolli (2014).

4) Page 16, line 22/23 & page 26, line 27: The reference to Skrotzki et al. (2013) does not agree with the choice of an accommodation coefficient as low as 0.1 to compute the ice growth. As far as I can see, Skrotzki et al. (2013) reported accommodation coefficients > 0.2 for all conducted experiments with an overall average value of 0.7. So, I am not fully convinced that the limited ice growth is the best explanation for the absence of immediate ice growth as soon as ice saturation is reached in ZINC.

The reviewer is correct in that the accommodation coefficient proposed by Skrotzki et al, (2013) are above 0.2. However, Skrotzki et al, (2013) also report values from previous studies that are as low as 0.004, therefore an accommodation coefficient of 0.1 is also realistic. We have now updated the citations to cover the complete range in values reported in the literature. The following citations have been added to the main text and in the appendix: Earle et al., (2010), Isono and Iwai, (1969) and Magee et al., (2006). Therefore, we still believe that a low accommodation coefficient is a valid explanation for the delayed onset and keep the lines for 0.2 and 0.1 as accommodation coefficients in Figure 6 and Figure 6, 7, and 8, respectively.

The authors discuss on page 17 that a non-negligible fraction of the aerosol might experience a lower supersaturation than computed for the center of the aerosol lamina in the CFDC - this might also explain in part the higher onset values for ice growth on the 2.8C2 and 2.8H2 particles.

Yet, we agree with the reviewer that a low accommodation coefficient is not the only possible explanation for the absence of immediate ice growth. The increase in humidity above 100% for first ice crystal detection could also be due to the initial ice growth out of the pores being stacking disordered. As has been shown in molecular dynamic simulations, initial ice nucleation and ice in confinement is typically stacking disordered (e.g. Lupi et al., 2017; Moore et al., 2010). Stacking disordered ice requires a higher humidity to be stable than bulk ice. As such, a higher humidity would be required for the ice to initially grow. However, once the first few monolayers of ice covers the particle surface, ice growth likely transitions to hexagonal ice. If this transition takes longer than some seconds, ice growth within ZINC would require supersaturation with respect to bulk ice, since the growth is occurring on stacking disordered ice. Additionally, it is possible that some of the particles are exposed to lower humidities than expected, if they are traveling outside of the lamina (Garimella et al., 2017). However, this effect is more relevant at higher humidities when the gradient in temperature between the cold and warm wall is higher. Therefore, we do not expect this to be a major issue at these low humidities.

Also, the onset RHi values are given for an already quite high ice-active fraction of 5%. In the full ZINC scans for 2.8H2 in Fig. A1 a and b one can see that the ice growth initiates clearly below 110% RHi – so not too far from the expected value of 100% RHi if also considering the RHi uncertainty in ZINC.

Indeed, as mentioned by the reviewer, at these humdities, the uncertainty due to the temperature reported by the thermocouples and thus the calculated relative humidity that the particles are exposed to (~ ± 5% RH_i) presents an additional uncertainty in our reported onsets. As such it is possible that the observed onsets (Fig. A1) could be occurring closer to ice saturation than we show considering the 5% uncertainty in RH_i. We revised the manuscript to discuss all these potential explanations in the text by stating the following:

"Moreover, the reported AF of 0.05 do not correspond with the ice onset. Considering Fig. A1, the initial ice is observed at RH_i 110 % and 108% for 223 and 228 K, respectively. Lupi et al., (2017) and Moore et al., (2010) have shown in MD studies that stacking disordered ice is formed in confinement and during nucleation, requiring a humidity higher than 100% to grow ice. Additionally, the calculated humidity that particles are exposed to in ZINC depends on the temperatures of the warm and cold walls, which are measured by thermocouples that have an uncertainty of ±0.1 K (Stetzer et al., 2008)*. This uncertainty (±5 %) can lead to a higher reported humidity than required to observe ice nucleation and is included in the vertical error bars in Figure 6, 7 and 8."* on page 18 lines 22-29.

Did the particles enter ZINC in a dry air flow (without pre-condensed water in the pores) – could this also influence the ice nucleation measurements?

Additionally, we have now mentioned in the text that the particles were aerosolized and transported to ZINC using evaporated liquid nitrogen on page 8 lines 5-6.

5) Page 16, line 25 and page 26, line 24: The reference to Järvinen et al. (2016) also does not seem appropriate for me to justify a spherical shape of ice particles in the computations. They observed "quasi-spherical" ice crystals from the freezing of water droplets during strong convection, which is a clearly different process from growth of ice crystals on near-spherical solid silica particles as in the present study.

We agree with the reviewer's opinion that the freezing and subsequent growth of supercooled droplets is likely a different process than the growth of ice on spherical aerosol particles. We have therefore changed the citation to Harrington et al., (2019), where it is assumed that at such small ice crystal sizes (~1 µm), the ice is spherical. We have now updated the sentence to read: *"The ice crystal shape in the growth calculation was assumed to be spherical due to the small final size (~1 µm) and its growth on spherical particles (Harrington et al., 2019)."* on page 18 lines 19-20.

6) Page 18, line 22ff, discussion related to the increase in the AF to 0.02 for the 2.8H2 sample up to RHi = 120%. I am a bit confused by this paragraph: In the preceding paper by David et al. (2019) in PNAS, the authors show in Fig. 2 the ZINC scans for porous MCM-41 particles with 3.8 nm pore diameter. This pore diameter should be large enough to host a critical ice germ at 233 K. But in the ZINC scan at -40◦C, ice formation did not occur below water saturation, and was explained by the fact that the homogeneous ice nucleation rates are not large enough to observe ice within the residence time of ZINC. If you applied the same argumentation with the pressure dependent parameterization of CNT as presented in the current manuscript, why didn't you detect any freezing signal for the 3.8 nm pore diameter particles at low RH? Could the small freezing signal for the 2.8H2 sample at lower RH not simply be due to immersion freezing within the pores? If I understood correctly, you used this explanation for the freezing signal observed for the 9.0M2 particles at 233 K (Fig. A2c and page 22, lines 24-27). The ZINC scan at 238 K with the 2.8H2 particles shows that at least the external particle surface contains active sites for condensation or immersion freezing (page 19, line 4/5). In contrast, the 3.8 nm pore diameter particles did not reveal a distinct immersion freezing signal at -35◦C (Fig. 2 in David et al., 2019).

The width of the pore size distribution and the dependence of nucleation rates and critical embryo size on CNT parameterization hamper the precise analysis of how freezing of pore water and growth out of pores depends on pore width and pore water volume. Because of these uncertainties, it is difficult to come to exact conclusions whether nucleation rates or pore diameter limit freezing within pores at 233 K. Applying a pressure dependent nucleation rate, ice in the 3.8 nm pores is expected to freeze at 233 K at negative pressures and within the residence time of ZINC, as the pores should be wide enough to host ice. However, since we did not observe freezing, the increase in the nucleation rate due to negative pressure is likely not the reason or counteracted by some other effect. We explain this in the following.

First, we consider immersion freezing as an alternative explanation for the weak freezing signal below water saturation for the sample 2.8H2 (see Fig. A1c). Yet even if there were nucleation sites within the pores, the DSC measurements indicate that the pores should be too narrow to host ice at 233 K (see Fig 5b) and the immersion sites are therefore, ineffective for ice nucleation. However, we cannot rule out that there are some pores large enough to accommodate the critical ice germ in the 2.5-2.8 nm samples where the freezing is not detectable in the DSC measurements. Indeed, the pore size distributions shown in Figure 2 indicate that these samples do have some pores larger than 3 nm in diameter, which is close to the critical ice germ size at 233 K depending on the parametrization used (for example with the Murray et al, (2010) parametrization for hexagonal ice, the critical ice germ should be 2.9 nm at 233 K assuming a quasi-liquid layer of 0.38 nm). As such, it is possible that some pores in a small fraction of the particles are capable of supporting ice that freezes either homogeneously due to negative pressure or heterogeneously due to ice active sites within some of the pores. As to why we do not observe this freezing in the 3.8 nm samples used in David et al. (2019) we cannot fully isolate one reason. It may be because the particles in David et al. (2019) were not hydroxylated like the ones in this work (i.e. they were calcined), the water contact angle with the pore wall is expected to be higher. If this is the case, the pore fills at a higher relative humidity when the curvature of the pore water is less and the water would therefore experience a lower negative pressure in these wider pores, thus decreasing the homogeneous nucleation rate due to negative pressure in these pores.

As the reviewer states, since the 3.8 nm samples did not exhibit any heterogeneous freezing ability (at T = 238 K) in David et al. (2019), then it is likely that no active sites exist in the pores even at 233 K. The combination of no active sites and a low nucleation rate from the lower negative pressure may be the reason no freezing was observed in the 3.8 nm samples in David et al. (2019).

7) Page 21, lines 5-13: See above, would a pressure dependent parameterization of CNT not also predict a strong increase in AF for the 3.8 nm pore diameter particles at 233 K and low RH? If you also plotted the active fraction curve for the 3.8 nm pore diameter particles at 233 K from David et al. (2019) into Fig. A1c (hydroxylated and calcined samples seem to behave rather similar, see Fig. 5), the 3.8 nm sample would not show an "intermediate" ice nucleation behavior between that of the 9 nm pore diameter and that of the 2.5 – 3.3 nm pore diameter particles, but just reveal a very low ice-active fraction until reaching water saturation. How would you interpret this difference?

Here again, the width of the pore size distribution and the dependence of nucleation rates and critical embryo size on CNT parameterization hamper a precise analysis. Comparing the pore size distribution of the 3.8 nm sample investigated in David et al. (2019, Fig.S5) and of 3.3H1 (Fig. 1b), there is a large overlap in pore diameters and especially the tail to large pores reaches for both samples up to 4.5 nm. If the pore width is limiting the stability of ice within pores, these pores indeed should behave similarly. However, as mentioned in the previous response, the negative pressure in the 3.8 nm pores in the samples from David et al, (2019) may differ even from the calcined samples (2.8C2) examined in this study due to the unstable nature of calcined samples depending on their age and exposure to water vapour (Muster et al., 2001). Therefore, it is not straightforward to extrapolate the results from the current study to those of David et al. (2019).

Minor comments and technical corrections:

1) Page 1, line 11: Maybe explicitly state "due to the inverse Kelvin effect"

We have now rephrased the sentence to state "*due to the inverse Kelvin effect*." (see page 1 line 13)

2) Page 1, line 14 + 17: Avoid the repetitive statements "play an important role in determining the relative humidity" and "play an important role in predicting the humidity" in the abstract. Instead, you could also mention what type of chemical functionalization was employed and its effect on the ice nucleation behavior.

We remove the sentence referenced by the reviewer and shorten the sentence to read (see page 1 lines 16-18):

"*We find that for the pore diameters (2.2 – 9.2 nm) and water contact angles (15 – 78˚) covered in this study, our results reveal that the water contact angle plays an important role in predicting the humidity required for pore filling while the pore diameter determines the ability of pore water to freeze*."

3) Page 2, line 28: "is the interfacial energy"

Added, thanks.

4) Sect. 2.1.2: You should already indicate here the larger pore sizes of the SBA-15 particles compared to MCM-41.

We have now mentioned that larger pores were achieved using SBA-15 stating: "*To obtain larger pore diameters (~9 nm), SBA-15 particles (see Fig. 1c and d.) were synthesized similarly to Linton et al., (2009b) where…*" on page 4 line 18.

5) Page 5, line 4: Missing parenthesis ")" after "60◦C".

Added, thanks

6) Page 6, line 13/14: Could be phrased more clearly, you could also indicate the respective values for bulk water as a comparison.

We have rephrased the sentence to read "*For water in confinement at 25 ˚C, the values of* $\gamma(T)$ *and* $v_l(T)$ *are 71.69 mN/m and 20.5* m^3*/mol, respectively (Kocherbitov and Alfredsson, 2007)."* on page 7 lines 9-10. We do not discuss the values for bulk water as it is beyond the scope of the current study.

7) Sect. 2.4: What was the relative humidity of the air before entering ZINC? Please indicate.

The humidity of the air entering ZINC is close to zero (< 1 %) as evaporated liquid nitrogen was used to aerosolize and transport the particles to ZINC. We have now clarified this in the text by stating: "…*supplied with evaporated liquid nitrogen (purity 6.0) to eliminate any residual humidity (RH < 1 % at 223 K)…*" on page 8 lines 5-6.

8) Fig. 1b & 2b: It is hard to discriminate the various bluish colors.

We thank the reviewer for pointing this out. We have now increased the resolution of the figure, which makes the color scheme more distinguishable (now Fig. 2b and 3b).

9) Page 12, line 4: You could also mention here in the text that you did a series of two adsorption/desorption cycles with the samples.

We have updated the text to read: "*Two water vapour sorption cycles were obtained for the samples 2.4M1, 2.5H1, 3.3M1, 3.3H1, 9.1H2 and 9.0M2 and the resultant isotherms are shown in Fig. 4*" on page 13 line 4-5.

10) Page 12, line 19: "The relative mass . . . does not return"

Corrected, thanks

11) Page 14, line 18: Maybe: "By contrast, the freezing temperature . . ."

We have updated the text to read: "*In contrast*,…" on page 15 line 20

12) Page 16, line 22: "peach" lines vs. "salmon" lines used in the caption of Fig. 5.

Thank you, we have updated to read "salmon" throughout the text**.**

13) Page 17, line 3 (second line in figure caption): Could you please briefly include the factors contributing to the RHi uncertainty in ZINC?

Thank you, we have now reworded the sentence to read: "*The error bars represent the maximum uncertainty in the calculated* RH_i *(±5 %) in ZINC arising from the uncertainty in the reported thermocouple temperature (±0.1 K; Stetzer et al., 2008) and encompass the standard deviation from averaging the experiments.*" in the figure caption

14) Page 17, line 9: "an AF_0.05"

Updated, thanks.

15) Page 21, line 25/26: Please check sentence structure.

We have updated the sentence to read: "*At 223 and 228 K, the samples with 2.4 nm pore diameter had the lowest $AF_{0.05}$ RH_i and the 3.3 nm particles the highest. The 2.6, 2.7, and 9.0 nm samples are in-between and overlap (Fig. 8)*." on page 23 lines 31-33.

16) Page 25, line 18 – 20: Please check sentence structure (avoid to use twice subclauses with "while").

Thank you for pointing this out. We have now split the sentence to read as follows: "*Therefore, ice nucleation parameterizations should be based on PCF below the HFT. Above the HFT, active sites present on the particle surface determine the ice nucleation activity at water saturation, while below water saturation active sites within pores are required to nucleate ice*." on page 27 lines 5-7.

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