Review of "The Role of Contact Angle and Pore Width on Pore Condensation and Freezing," by R.O. David et al. 2019

In their submitted manuscript David et al. describe their attempts to utilize synthesized silica particles that have controlled surface pore widths, and alterations to those particles vis-á-vis functionalization, to test the utility of pore condensation freezing as a physical parameterization for ice nucleation under certain atmospheric conditions. I am impressed by the detail and depth of the described studies and the submitted manuscript. However, I do feel that there remains room for improvement and clarity in an updated manuscript before acceptance for full publication in ACP.

In particular, I suggest the authors strive to more clearly delineate where and when they think they can interpret their results purely on the basis of physical changes and where/when their understanding might be limited by the changes to the physical chemistry of the systems they are probing. In its current form the manuscript seeks to explain results primarily using physical parameters (i.e., size, geometry, bulk contact angle, etc.), but given the system (pore) sizes of exploration it might be that molecular-scale effects begin to play a role that cannot be dismissed.

Below I present an itemized list of thoughts and comments as I came to them in the text, which I hope put things into context. Following these comments I will return to some general items.

Itemized Scientific and Editorial Comments:

Specific Suggestions by Page and Line Number (page, line):

• (1,29) remove parentheses around (T)

• (1,30) I think it advisable to keep a more general definition of heterogeneous nucleation, like that of Vali et al.[1]. There he just says "nucleation aided by the presence of a foreign substance". "ice active site" could mean many things and does not necessarily give as general an impression.

• (2,7) The explanation of PCF that is when water "which can exist below water saturation in narrow pores" is confusing to me. Is it not that the local saturation condition is altered? In fact the pore water is at saturation, and this is why it condenses, it is simply not at *bulk* water saturation.

• (2, 12) I think that either "concave" should be curved, or the sign convention defined. I believe the equation is general up to the choice of sign convention for the radius of curvature.

• (2, Eq. 2) To me Eq. 2 represents an amalgamation of the critical cluster size of an ice germ in the vapor and liquid phases. Given the discussion I understand the critical radius for an ice germ in the liquid phase should be presented, and this is what is indicated by σ_{iw} I believe. Typically S_i would represent a pressure ratio p_v/p_i, that is the actual vapor pressure divided by the equilibrium vapor pressure over ice. In the presented case should the pressure ratio not refer to the pressure across the interface of the ice germ in liquid, i.e., p_w/p_i? See Marcolli[2] Eq. 11.

• (3,3) The assumption of $t = 0.38$ nm from Schrieber et al., 2001 might warrant an additional comment. It is important to note that this value will certainly be temperature dependent, and that given the changes in surface functional group it might vary between tested samples. Given that as is it represents a sizable fraction of the pore diameter such potential changes might be important. Fig.7 from Bartels-Rausch et al.[3] is a good summary of the variation over a range of temperatures that such a surface layer can take on – at the free surface, with respect to theory, measurements, and modeling. That said the pore surface is something different, beginning as a liquid/solid(pore material) interface, and when ice forms any 'quasi-liquid' layer would be a function of the specific intermolecular interactions of that system. It might be more simple to state that the expected thickness of such a layer at such temperatures would likely be of order 1 molecular layer (≈ 2.5Å for water).

As an additional comment related to this and Eq. (3), is that any 'quasi-liquid' layer thickness *t* would be an equilibrium phenomenon, and it is not self-evident that it should be considered as a limit to the volume available for nucleation, which is fundamentally non-equilibrium. In fact the heterogeneity at the pore surface might help to initiate nucleation even if the relaxed, low-energy state of the system would prefer disorder.

Remember taken from the point of view of pore ice the layer closest to the pore wall may be disordered or 'quasi-liquid' but taken from the viewpoint of pore water the surface layer may exhibit enhanced order. That might stimulate nucleation in analogy to what is noted (22, 25-27) in the 9.0M2 particles which the authors say contain ice nucleation sites even at higher temperatures.

• (3, 5-10) I find the discussion of water saturation in and out of the pore confusing, also see my comment on Eq. 2 above. My basic understanding is that within the pore everything is occurring in condensed liquid?

• (4,17) For the uninitiated a "Teflon bomb" is unfamiliar terminology.

• (4,25) Here and throughout the manuscript the authors should be careful with how they refer to contact angle. "these were observed to change contact angle with ageing in air" (Note aging misspelled). I believe they intend to say that the water contact angle with these was observed to change after aging in air? In any case the authors should review all uses of contact angle, or use a defined 'water contact angle' throughout, to make sure the use of contact angle is correct and consistent throughout the text.

As a follow-up question, was the changing water contact angle with calcinated particles systematic with aging as a function of any monitored variable, like RH? If so these types of particles might offer another useful experimental system.

• (5,2) "filtered off" What is meant here?

• (5,12) I think either BET should not appear as an acronym at first use, or perhaps it is enough to make it slightly more descriptive, for example: applying BET adsorption theory

• (6,14) p/p_0 could be better explained. It appears related to a comment below (13, 6), but the connection could be made more clear.

• (7,13) Were any other sized particles bigger or smaller than 400 nm tested? Why or why not? It would be nice to rule out any effect of particle size when considering the results.

• (7,27) Contact angle again. Here it is not the pores contact angle, but I think water's contact angle with or within the pores.

• (13,6) See also comment above with regard to how the RH of the first sorption cycle is used. As a general comment, I would expect the hysteresis between adsorption and desorption should offer an additional verification of the pore size that is presented earlier in §3.1. It seems that the magnitude of the hysteresis, if the RH ramping is done is a quasi-steady state manner, should be directly related to the stability of the liquid in the pores. Was an effort made to use the information in this manner, or do I miss a complicating factor? Finally, have the author's considered how to propagate the uncertainty to bound the uncertainty in contact angle as derived from use with Eq. 7?

• (Figure 4) The upper axes are missing a unit label. I am impressed by the agreement between the observed heat flow and the predicted critical pore diameter from the bulk physical model.

• (16,6) Why is AF 0.05 chosen? Is this simply an experimental choice of the minimum AF at which nucleation can be observed? A clear explanation would be useful, especially given that in many nucleation studies of controlled materials different AF may be chosen for plotting.

• (16, 23) Although the Skrotzki paper is directed to cirrus clouds, many such uptake measurements have been undertaken over the years and are notoriously difficult to parse. Furthermore the values in the literature vary over orders of magnitude. Direct studies of molecular uptake are presented in Kong et al.[4] as well as a review and comparison with measurement and simulation studies (including the Skrotzki paper). However, perhaps for these studies it must also be considered that the changes in functional groups that are utilized also likely lead to changes in uptake coefficient. This is clear from the adosorption/desorption isotherms in Fig. 3. It has also been previously documented that even thin surface coatings can significantly affect uptake.[5,6] I would recommend some reference to this body of work be included.

• (Fig. 7 caption) As in Fig. 6 caption it should be stated that points correspond to AF 0.05 condition.

• (Fig. 8) This figure seems a bit out of place and is of limited use in the explanation here. Perhaps it could be introduced earlier in the particle characterization section and returned to here?

• (25, 26) It might be a bit strong to say that parameterizations should be based on PCF. Perhaps, should include?

• (25, 26) The final sentence links this work to understanding anthropogenic emissions, but this is really the first mention of such emissions up to this point. Are these particles particularly analogous to any known anthropogenic emission? If the link is not strong I think this point can be left out, there are of course many reasons to better understand the effects of porosity and geometry on freezing.

Summary:

I have enjoyed reading the submitted manuscript. I reiterate that I think it could benefit from an improved clarity with regard to the concrete conclusions the authors would like to posit. My understanding is that basic edifice of PCF which rests on the inverse Kelvin equation does a good job of predicting the experimental observations if some of the asserted assumptions are valid. It appears that as with many systems a complete understanding of the data would involve a much more comprehensive picture of the intermolecular interactions specific to each system. The measurements rely both on ice nucleation and crystal growth to a detectible size, thus many details related to both the ice initiation and macroscopic state are convoluted. Such complexities are intrinsic in many experiments, yet I still feel this study brings the community a step forward. However, it appears the open question remains as to how this might be utilized and tested in a *messier* real atmospheric aerosol scenario.

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[1] Vali, G., DeMott, P. J., Möhler, O., and Whale, T. F. (2015). Technical note: A proposal for ice nucleation terminology. *Atmospheric Chemistry and Physics*, 15(18):10263–10270.

[2] Marcolli, C. (2014). Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities. *Atmospheric Chemistry and Physics*, 14(4):2071–2104.

[3] Bartels-Rausch, T., Jacobi, H.-W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P. D., Ammann, M., Blackford, J. R., Bluhm, H., Boxe, C., Domine, F., Frey, M. M., Gladich, I., Guzmán, M. I., Heger, D., Huthwelker, T., Klán, P., Kuhs, W. F., Kuo, M. H., Maus, S., Moussa, S. G., McNeill, V. F., Newberg, J. T., Pettersson, J. B. C., Roeselová, M., and Sodeau, J. R. (2014). A review of air–ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow. *Atmospheric Chemistry and Physics*, 14(3):1587–1633.

[4] Kong, X., Papagiannakopoulos, P., Thomson, E. S., Marković, N., and Pettersson, J. B. C. (2014a). Water accommodation and desorption kinetics on ice. *The Journal of Physical Chemistry A*, 118(22):3973–3979.

[5] Kong, X., Thomson, E. S., Papagiannakopoulos, P., Johansson, S. M., and Pettersson, J. B. C. (2014b). Water accommodation on ice and organic surfaces: Insights from environmental molecular beam experiments. *The Journal of Physical Chemistry B*, 118(47):13378–13386.

[6] Thomson, E. S., Kong, X., Marković, N., Papagiannakopoulos, P., and Pettersson, J. B. C. (2013). Collision dynamics and uptake of water on alcohol-covered ice. *Atmospheric Chemistry and Physics*, 13(4):2223–2233.