

Referee Comments: Deposition nucleation viewed as
homogeneous or immersion freezing in pores and cavities, by
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1 General Comments:

This paper puts forth an interesting hypothetical mechanism (PCF) for the phenomenon of droplet freezing at low relative humidities. The phenomenon is important in the atmosphere (although it is not clear that elucidation of this mechanism will have practical consequences there) and the idea is intriguing. However, the author's meticulous review of available measurements relevant to melting and freezing in confined spaces (a herculean task) makes the paper at the same time too focussed on technical details and too little focussed on assessment of the strength of evidence for the new hypothesis.

The paper should be accepted; it provides a basis for new understanding of a basic atmospheric phenomenon. My major comments have to do with suggestions for substantial editing. The major hypothesis and strongest evidence for it should be put forth in focussed paragraphs; secondary observations, details and comments (in particular, in sections 2.4, 2.5 and 3.1) should be relegated to another (review) paper or to tables and appendices. Criteria for disregarding the old ("deposition nucleation") hypothesis in favor of the new ("PCF") hypothesis should be stated and evoked for each case study investigated.

2 Specific Comments

1. Abstract:

Instead of immediately providing the detailed observations of freezing on certain classes of particles, it would be better to clearly identify (quantitatively) the signatures of "deposition" freezing, homogeneous freezing in pores and Immersion freezing in pores. Preactivation should be discussed in another paper.

2. Figures 2 and 3 compile observations made with a wide range of techniques. The scatter in the data is thus both due to the scatter in the freezing itself and due to

differences among techniques. The melting observations (shown in Figure 2) seem to correspond to a single mechanism but freezing observations (Figure 3) show a great deal of scatter. This scatter should be discussed in light of the range of observational techniques, the range in characteristics of confined water, the possible distribution of pore sizes in the various samples, and possible solute effects. With what uncertainty can we identify (for each data set) one freezing mechanism? The overall message of this figure as it now stands is not clear.

3. Section 2.6:

Melting and freezing are different phenomena, but are discussed together here, which is a bit confusing. The relevance of classical, macroscopic thermodynamics to the first stages in freezing even in unconfined samples is always suspect. In Sections 2.3 - 2.5 the author has emphasized the anomalous character of water and ice in confined spaces, including suggestions that the freezing might not be first order, the ice formed has intermediate density, and the water surrounding ice embryos is 'bound'. This discussion renders surprising the return to classical thermodynamics and standard parameter values such as the so-called ice-water surface energy. There should be some link between these two discussions.

Having chosen to refer to the classical theory it would be helpful to include a reminder primer on phase transitions involving the gas phase; i. e., the chemical potentials of water in all three phases should be written down so that we can understand statements about where and when (under what relative humidities and temperatures) phase transitions are expected. Conceivably, a schematic "phase diagram" for confined water might help in the presentation.

Line 20: The argument that the surface properties do not impact freezing and melting temperatures in pores because the pore walls are covered by water is a bit surprising; one would expect a layer of bound water 0.6 nm thick at temperatures well below 0 deg C to be very different from bulk water and to reflect the pore wall characteristics.

4. Figures 5 and 6:

The broad distributions of data points show that many different factors in technique as well as in physical processes affect the results. It is almost impossible to extract a coherent message here. As suggested above, it would be helpful to have a checklist showing the PCF hypothesis is consistent with the stated criteria for this mechanism and inconsistent with other freezing hypotheses, in those cases for which the argument is strongest. The large number of subsidiary caveats and speculations necessary to support the PCF hypothesis in weaker cases should be organized as part of the discussion of future work.

5. There should be a more ample discussion of the impact on freezing of the distribution of pore and inter-particle gap sizes. Presumably, freezing occurs first in the tail of

the distributions, and the average pore size is of less importance.

6. The active site parameterization (Marcolli, 2007) was derived from observations on entire single particles, not cracks within or between particles. Is it obvious that the same parameterization should be relevant within the individual surface features?
7. Soluble and insoluble impurities in the cracks must be important. They are yet another source of possible scatter in the observations but receive little mention.
8. Section 3.2: Preactivation is very interesting, as is the speculation about "ink-bottle" shaped pores, but these topics should be relegated to a second paper or to an appendix.
9. Section 4: In this paper the data are assembled, but their quantitative analysis is preliminary. Future work should include analysis of results of each laboratory technique separately, with particular focus on the scatter of results within a given technique, which would provide estimates of the amount of scatter expected from "deposition" nucleation and from PCF (and, possibly, other mechanisms). When these are included, what is the degree of certainty with which "deposition" nucleation can be excluded?

Molecular dynamics calculations would also be interesting.

Incorporation of pore size parameters into atmospheric models seems fruitless; these already are overloaded with unknowable parameters. That is not the goal of this paper, which is instead to extend our understanding of freezing.

3 Technical Corrections/ Suggestions

1. line 23, Abstract: Liquid does not 'attract' vapor. The rest of the sentence is unclear.
2. Eq (1) Relative humidities are used in the rest of the paper; add " $\equiv RH_w$ ". D, V_m are not used further on.
3. Section 2.6 The notation needs a bit of editing; (p in eq (1) is now p_l and μ in eq (2) is not the same (doesn't have the same dimensions) as μ in eq (6); r_{ps}, r_{pl} in eq (2) are not defined.)
4. Figure 5a: On my computer screen brown and red segments of the water saturation curve are visible but not orange segments.

Figures 5 and 6. The various lines need clarification. The axes are temperature and RH_i (never defined). The dotted black lines are said to be from Koop (2000) for constant J (nucleation rate). However, Koop shows J as a function of temperature and water activity. The step from water activity to RH_i needs to be made explicit.

Similarly, the light blue lines are said to be calculated from Eq (1), but Eq (1) is written in terms of RH_w , not RH_i . The missing steps, easy enough to fill in, would aid the reader of an already complicated set of graphs.