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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities" *by* C. Marcolli

Anonymous Referee #2

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This paper contains so much material that a thorough review would take many months of work. Hence, the comments below focus on the core issues and on some selected portions of the paper. My rating on presentation quality is directed to the excessive length of the paper and the lack of focus.

The basic tenet of the paper is laudable. Porous materials undoubtedly present conditions where interaction with water in any of its phases is different from bulk or uniform surface situations. The idea of liquid or ice remaining in pores even below the thermodynamic equilibrium conditions has been around for a long time. This paper is a thorough examination of the consequences of that phenomenon, with special emphasis on ice in pores being responsible for what has been viewed as deposition nucleation in the atmosphere.

Homogeneous freezing in pores is the clearest example of the importance of water retained in pores. The support for this is the increased frequency of nucleation below 235 K in all experiments. The effect of the pore walls on homogeneous embryo formation within the water in the pores is assumed to be negligible. Similarly, the formation of cubic ice is assumed to have the same homogeneous nucleation threshold as hexagonal ice. These assumptions are not as fully justified in the paper as one would wish.

The paper overextends the importance assigned to pores by also claiming that many observations of heterogeneous nucleation via immersion freezing are in fact explained by the presence of pore ice. Much of that analysis is speculative and results in losing the focus on deposition nucleation and in making the paper too long. In fact, this paper is a curious mixture of a broad review of immersion freezing and a specific point of view from which to examine past work. The review is quite comprehensive and detailed but it ends up providing few definite insights on immersion freezing.

To someone not specializing in the study of porous materials, the descriptions of pore configurations (section 2.1) appears too simplistic. To what extent is it realistic to consider pores as tubes with a fixed radius, or to think of cavities as ink bottles with a round opening? Since the main properties of pores that enter into the quantitative analyses are size and contact angle, it is important to understand to what extent these are idealized quantities or true representations of the pore structures. Many references are given about porous materials; a judicious summary of the key issues would be helpful.

Schaller and Fukuta (1979) and Roberts and Hallett (1968) found ice nucleation requiring water saturation for temperatures above thresholds in the range 250-260 K with a sharp change to nucleation taking place below water saturation at lower temperatures. The discussion of these types of results in the paper (page 32, lines 7-12) focuses on temperatures near 235 K and invoke homogeneous nucleation in pores. That is untenable for the observations of Schaller and Fukuta and other similar results. Yet, the transition in behavior is an important finding and should be discussed, because the reasons for the transition near 260 K may also apply near 235 K and make it unnecessary

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to invoke pore phenomena.

Cooper (J Atmos. Sci., 31, 1832-1837, 1974) also used the idea of ice germs of subcritical size with respect to the bulk phase to interpret contact freezing. That idea is different from the PCF hypothesis but it does deserve to be recalled. There are possible extensions of Cooper's idea with pores also considered.

Comments below are referenced in the following manner: page number/line number

Abstract: Much too long. Overly detailed.

5/5-6 Is it justified to claim that deposition is always(!) pore freezing? There are numerous laboratory experiments with presumedly smooth surfaces on which deposition nucleation could be observed.

5/18 Suggest the use of "cavities" instead of "caves"

8/15; Fig 1 It would make Fig. 1 more meaningful if the range of pore diameters were indicated with error bars instead of single points for each material.

8/27 How was freezing initiated for the data shown in Fig. 3, i.e. how was an equilibrium freezing temperature determined?

10/1 What is the justification for using 1 min for this calculation?

17/13 It requires some justification that CNT parameters for hexagonal ice can be used for cubic ice.

26/7-20 Is there an explanation for 'slow freezing'? Limited by heat transfer? What else?

29/8-9 On what basis does the author rule out the possibility that other than pore structures provided the nucleation sites in these experiments? Pits? Steps? Dislocations? Etc.

29/13-14 Why is it taken for certain that pores are involved?

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29//21 Would be clearer to say "All studies except that performed on 50 nm particles . . ."

29/20 What type of solution is assumed for the black lines in Fig. 6.?

33/13-17 If pores do not offer a clear explanation, should perhaps other ideas be considered? Didn't the authors of the cited works offer some possible explanations of the observations?

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