Responses to Referees, "Deposition mode ice nucleation reexamined at temperatures below 200 K" By E. S. Thomson et al.

We appreciate all of the submitted comments, which have been instructive and illuminated several areas for improvement within our manuscript. We have prepared a revised manuscript that thoroughly addresses the questions and comments that have been posed. Furthermore, below we explicitly address and/or point to changes in the text that address each of the items raised in the comments. The responses are presented in an order corresponding to the order of their respective submissions.

In some way each commenter individually suggests that there is a lack of discussion of the relevance of the findings for higher temperature. We acknowledge this as a problem and therefore have added text to §4 (text for final 2 ¶s moved and supplemented) and rephrased the final sentence of the abstract. In essence we hope these additions make clear that these results are most relevant in the cold upper troposphere (to wit, the lower stratosphere). It is less clear how the low temperature data can be extrapolated to higher temperatures. However, a successful theory should be able to to capture and predict observational data for the full range of temperature. Thus the low temperature data may help to establish a more complete general understanding for deposition freezing.

Anonymous Referee #2

• The Figure 2 caption has been modified as the referee suggests.

• Figure 3 has been remade as suggested by Referees #1 and #2. The figure caption has been changed accordingly, as have references within the text.

• The author's thank the referee for drawing our attention to the Loeffler and Chen (2013) paper. This is an interesting reference of which we were not previously aware. It is now included in §3.2 for completeness. There we add the sentence, "Similar conclusions have been drawn from simulated Lennard-Jones systems, where the barrier to nucleation is found to decrease with an increasing strength of the surface interaction potential (Loeffler and Chen, 2013)."

However, from a free energy perspective the theoretical treatment presented in that paper is identical to the standard CNT (that we also present and summarize in §3.1). The written form may appear more 'simple' only due to the fact that only the critical free energy barrier height is presented. That is simply the $\Delta G^* f$ term within the exponential of our equation (8). Loeffler and Chen (2013) go on to derive $f(\theta)$ using the picture of a truncated droplet (their FIG. 1) which is analogous to the $f(m) \equiv f(\cos\theta)$ we present and is found in numerous references. Section 3.3 is a detailed discussion of the physical meaning of this contact angle term and in Fig. 5 we present solutions for single valued contact terms. To make the shortcoming of using a single valued contact angle more explicit within the text, the sentence, "Thus the observed nucleation behavior cannot be captured with the choice of a single valued contact angle.", is added to §3.3.

• The Figure 6 caption has been modified as the referee suggests.

• The suggested change of "can be well explained" to "can be replicated" on page 23726, row 12 has been made.

Short comments by Michel J. Rossi

MJ Rossi brings up points of concern regarding details of the experiments, which were left out of the manuscript in an attempt to be concise (in general these specifics can be found in previously published papers cited throughout our manuscript). For experts with intimate knowledge of such apparatuses like Rossi some of these details may help to complete the story and thus we include a didactic discussion here, and have made a few augmentations to the text to assure the readers that we have tested what may have appeared to be experimental assumptions.

With regards to the the steady state versus equilibrium distinction – we do not obtain equilibrium conditions largely because the gas temperature outside the ice surface is close to but not exactly the ice temperature. However, using three lines of thinking we have clear evidence that the achieved steady state is an essential equilibrium.

I. First and foremost it is important to reassert what has been stated in the text. The measured supersaturation values are always determined as a ratio of two empirically determined H_2O vapour intensities (pressures) – that required to nucleate ice I_{nuc} and at the same temperature the value for vapor in coexistence with macroscopically thick bulk ice I_{eq}. This ratio should not be affected by the parsing of the equilibrium.

II. We have directly measured k_{esc} at the experimental temperatures, by filling the environmental chamber with H_2O vapor, closing the inlets and fitting the decaying H_2O signal. Measured values were found to be between 0.1-0.2 s^{-1}. Using Rossi's own equation we see clearly that this yields a ratio $r = 1$. The discrepancy with Rossi's well meaning estimation originates from an incomplete understanding of the system geometry. Rossi has miss-estimated the internal dimensions of the environmental chamber and identified an extra escape orifice. The laser beam propagates through a glass window that is part of the chamber wall.

III. As would be expected from the first two points, we can also verify that the evaporative flux from the surface does not dominate the system. Because the background flow exceeds the surface exchange any pumping perturbation should minimally displace the achieved steady state from equilibrium.

To add clarity we have changed equilibrium to 'near equilibrium'.

• We do not dispute Rossi's statement that, "on soot there is a specific balance of polar and non-polar groups, ..., but in different proportions which will lead to different macroscopic wetting behaviour". However, the experimental systems we have investigated, and in particular the complete methanol layer on well-characterized graphite to which Rossi refers, are significantly different (e.g., homogeneous) from the soot example. The cited papers (Thomson et al., 2011; Kong et al., 2012) detail the character of that and other surfaces.

• On page 23719 the capital "V" is the extensive volume, while the lower case "v" is the volume per unit area. Line 17 has been changed to read, "...change per unit volume v expressed ..." for clarification and given that the ACPD typesetting font makes the small v difficult to distinguish from the Greek ν, which appears later.

• Certainly pre-exponential factors like that mentioned on line 12, pg. 23721 of 10^{-13} s^{-1} can vary. However, transition state *theory* (TST) tells us that for the simplest model of desorption – one-dimensional desorption of a fixed (ground state) molecule – that factor is set by the vibrational frequency that characterizes the molecules surface attachment. Likewise TST can model systems where bound molecules have more degrees of freedom and thus the desorption

process is more complex. In such systems the pre-exponential factor may deviate from 10^{-13} s^{-1} by orders of magnitude. For our purposes we have chosen the first-order approximation.

• Given the significant amount of literature dedicated to extracting and/or parameterizing contact angles in studies of nucleation, and interest from referees (see comments and response to Referee #2), we feel that the discussion of the contact parameter f is warranted.

Anonymous Referee #1

• The technique has commonality with Knudsen cell measurements (see response to MJ Rossi) and our observations support the previous findings of the Tolbert group. That group's work is already heavily referenced because of those commonalities and a paragraph of the Discussion section is devoted to discussing some of those previous findings and conclusions drawn from them. To make the link more transparent we also add discussion and reference to those results within the introduction, as per the Referee suggestion.

• A discussion of, "the difference between a macroscopic substrate and a freely suspended atmospheric particle" that includes a reference to Marcolli (2014) has been added to §4.

• The statement, "Heterogeneous *ice* nucleation may occur when (1) supercooled liquid water contacts a foreign body and subsequently freezes, or (2) when H_2O vapour is directly deposited..." was written with the intent to convey the idea that broadly ice grows from supercooled water or vapour. Thus all modes of nucleation involving the coexistence of supercooled liquid and a foreign body are subsumed within point (1). Clearly the use of the word, 'contacts' adds some ambiguity in this manner. We have rephrased the above to become, "Heterogeneous *ice* nucleation may occur when (1) an interface exists between supercooled liquid water and a foreign body that acts to initiate freezing, or (2) when H_2O vapour is directly deposited..."

• See response to Referee #2 with regard to Figure 3.

• Question mark '?' added to, "...how can surfaces with widely dissimilar hygroscopic behavior all require high supersaturations for vapor deposition ice nucleation?"

References

Kong, X., Andersson, P. U., Thomson, E. S., and Pettersson, J. B. C.: Ice Formation via Deposition Mode Nucleation on Bare and Alcohol-Covered Graphite Surfaces, J. Phys. Chem. C, 116, 8964–8974, doi:10.1021/jp212235p, 2012.

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Marcolli, C.: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities, Atmos. Chem. Phys., 14, 2071–2104, doi:10.5194/acp-14-2071-2014, 2014.

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