Homogeneous ice nucleation in adsorbed water films: A theoretical approach – Responses to RCs

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February 2025

We thank the editor for handling the review of our work. Our detailed responses to the RCs are provided in the following sections using blue font; magenta font indicates new text added in the manuscript.

1 Response on RC1

We thank the referee for the thorough and very positive review of our manuscript and the detailed comments and questions, which will be addressed point by point below.

Comments:

Comment 1: Line 28: Here and throughout the manuscript: You use monolayers, films and multilayer films. This may need more careful definition. One would assume that a water film consists of several monolayers of water. But what is meant by a multilayer water film?

Response: We have clarified this on line 29: ... multilayer films (i.e., films that consist of more than one monolayer) ...

Comment 2: Line 44 and following: I feel the expression of “film-wise” is unfortunate. I would try to find a better wording what is meant here.

Response: We replaced ”film-wise” (which by the way is standard terminology used, e.g., in film-wise condensation as opposed to drop-wise condensation) by ”multilayer”.

Comment 3: Lines 65 -70: Here, we have A(T) and A’. The latter is then switched to A. This juggling of parameter definitions is also done on line 202 (there you use A for $A_w \dots$). Frankly speaking, it took extra effort to keep track of which parameters are temperature dependent and which not. I suggest not substitute but stick with a fix set of parameters, like A(T) and $A^{298}K$, etc. This would facilitate reading of the manuscript. On line 68, I assume you meant the A parameter?

Response: We have streamlined the notation. We removed the sentence on line 68-69 about the A-values referring to 298 K because there is a similar sentence in Subsection 4.1. We rewrote Eq. (2) as $\ln S = -A(T)N^{-B}$ and replaced the A’s in the following paragraph by $A(T)$’s. We added the following after Eq. (13): where we have left out the argument (T) from A_w and A_i for convenience as well as the following in the first paragraph of Subsectiopn 4.1: Note that the A_w values shown below refer to 298 K and are denoted by A_{298}; the values of A_w for liquid water at other temperatures are obtained from Eq. (4) and the A_i values for ice from Eq. (23).

Comment 4: Lines 94-97: Maybe provide references for studies that show single and/or multiple monolayer water adsorption on substrates below 100% relative humidity.

Response: We have added the following references: McCafferty and Zettlemoyer [1971], Pashley and Kitchener [1979], Ibrahim et al. [2018], Viisanen et al. [2024].

Comment 5: Line 98-99: What is the difference between bulk ice and hexagonal ice? Can hexagonal ice form in a thin water film? As you outlined below, it needs some extra layers. If the film has the same number of water molecules, the ice film is larger in surface area? I assume this does not matter when treating it as truly 2D? So, is it a postulate or an assumption to make things work?

Response: With "bulk" we refer to macroscopic amounts of ice (which could in certain temperatures and pressures be in some other form than hexagonal, e.g. cubic). We postulate that the most stable form of an adsorbed ice film would be hexagonal ice at atmospheric temperatures and pressures. We have added the following in the manuscript: Thin films of hexagonal ice have been created in the laboratory by vapor adsorption at low temperatures (< 140 K; Thürmer and Nie [2013]), by heating adsorbed glassy ice films that transition to hexagonal ice [Leist et al., 2003] and by letting thicker ice overlayers on mineral surfaces sublimate until a thin film is left [Yeşilbaş and Boily, 2016] .

Upon freezing, the thickness of the film increases and so does the surface area; we account for this explicitly in our computer code (i.e., we do not treat the films as 2D).

Comment 6: Could you provide references for typical LJ values?

Response: We used the values of [Kulmala, 1988]. See our response to comment 6 by Referee 2.

Comment 7: Lines 150, Eq. 23: Please explain further why you can just replace the exponent "3" with "B". Above you argue that B=3 for liquid and solid phase. Why can you substitute and allow for its variation in this case? Is it for the sake of having a free parameter?

Response: When the FHH adsorption isotherm was first derived, it was soon discovered that it rarely works for the adsorption of real gases or vapors (nitrogen, water) with $B = 3$, the value that is obtained from the LJ 12-6 potential, but it works surprisingly well if B is treated as an adjustable parameter (that corresponds to a LJ 12-(B+3) potential). We follow the same logic here. Regardless of the value of B, be it 3 or something else, it should be the same for the liquid and solid phases of the adsorbate since it depends only on the intermolecular potential, and the potential does not change with solidification of the adsorbate. These issues have been clarified as follows:

When the FHH theory was first derived, it was soon discovered that it rarely works for the adsorption of real gases or vapors (nitrogen, water) with $B = 3$, but works surprisingly well if B is treated as an adjustable parameter ([Halsey, 1948, Hill, 1952]). We thus replace exponent 3 in Eq. 22 by B and have

$$A_i = A_w \left(\frac{d_w}{d_i}\right)^B + \frac{\pi \epsilon_w \varsigma_w^{B+3}}{3kTd_i^B}(v_w^{-B/3} - v_i^{-B/3}).$$

We also noticed an error in equation (23); the correct exponent of ς_w is $B + 3$, not $2B$. Fortunately, correction of this error in our computer code caused only a very minor change in the results.

In addition, we wanted to clarify the sentence saying we have reduced the number of free parameters from four to two by combining two preceding equations into one: Inserting Eq. 23 in Eq. 17 leads to

$$\Delta\mu_A \approx \Delta\mu_{iw} + kTN_w^{-B}\left\{A_w\left[\left(\frac{v_w}{v_i}\right)^B - 1\right] + \frac{\pi\epsilon_w\varsigma_w^{B+3}}{3kTd_w^B}\left(\frac{v_w}{v_i}\right)^B\left(v_w^{-B/3} - v_i^{-B/3}\right)\right\}.$$

In this way, we have reduced the number of parameters of our system from four (A_w,B_w,A_i,B_i) in Eq. 16 to two (A_w,B) in Eq. 24.

Comment 8: Line 158, 160: Explain how you derived those two equations. Just looking at the above equations, it is difficult to follow.

Response: We rearranged the text at the beginning of Subsection 2.4 as follows: We make the assumption that all other variables except the chemical potential difference are the same for adsorbed and bulk water. Thereby we obtain expressions for the homogeneous nucleation rate and the radius of the critical nucleus in adsorbed water simply by replacing $\Delta\mu_{iw}$ in Eqs. (8) and (9) by $\Delta\mu_A$:

Comment 9: Line 164 and following: We would assume that Jhom and ice properties are not decoupled from the water saturation vapor pressures. Can you use different sets of parameters for ice nucleation and properties of water and ice? Espinosa et al. is somehow only chosen to yield better Jhom? In this regard, there might be an even better description of Jhom (Knopf and Alpert, 2023).

Response: Nucleation rate is certainly not decoupled from the vapor pressure; however, in practice the expression for the vapor pressure and other relevant properties used in the nucleation rate calculations only need to be sufficiently accurate within a narrow temperature interval where J_{hom} increases by 30 orders of magnitude. Besides, an expression for J_{hom} that works well could also result from fortuitous cancellation of errors. In any case, we chose the Espinosa parametrization only because it reproduces experiments well. Note that we are not using the parametrization from Espinosa et al. [2016], which is shown in Knopf and Alpert (Fig. 2), and yields about 3 orders of magnitude higher rates than the one based on Barahona [2018] Our parametrization is from Espinosa et al. [2018] (dashed line in their Fig. 2) and it gives rates very close to the Barahona-based parametrization.

Comment 10: Line 202: See comment above on parameter naming.

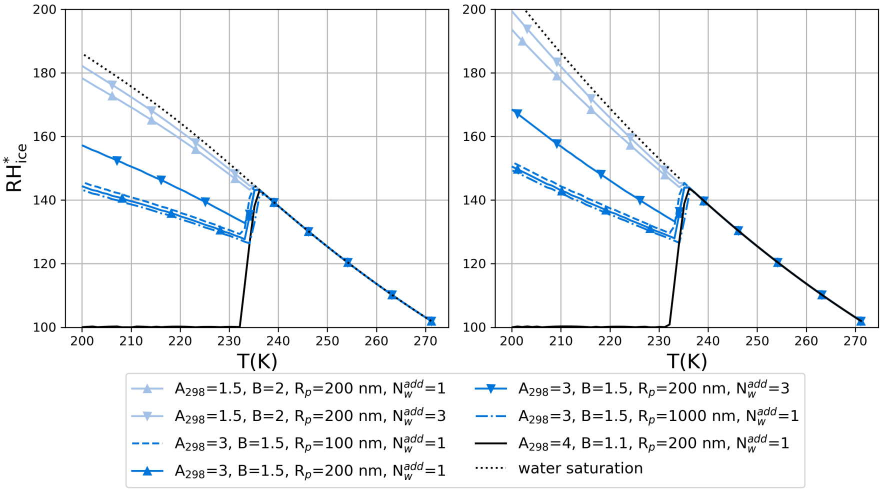
Response: Fixed.

Comment 11: Line 260: What do you mean by "where V_A denotes the volume of adsorbed water on a single ice nucleus"? How is this volume defined? Does it include additional layers of water?

Response: This is a very good point. V_A in the manuscript (and in our original code) refers to the total volume of water (supercooled liquid) adsorbed on an ice nucleus before freezing, but should, of course, refer to the adsorbed volume minus the additional water layers. We fixed the code and the results did not change much because the nucleation rate increases so steeply with temperature. We added the following in discussion of the additional layers: Note that we subtract the volume of the additional monolayers from V_A in Eq. (26); this volume depends, of course, on whether the additional monolayers are adjacent to the surface of the adsorbent particle (which we assume in the calculations) or if they are at the liquid-vapor interface. However, in practice, subtracting the additional volume from V_A has very little effect on the numerical results because the nucleation rate is a very steep function of temperature.

Comment 12: Figure 8: The discussion of Fig. 8 does not mention much the difference in results in response of using Murphy and Koop vs. Wagner and Pruss saturation vapor pressures. In the former case, the critical humidity drops to 110% for some cases but not when applying the latter. Is this just because the water saturation line by Wagner and Pruss is a bit steeper at lower temperatures? This is surprising. So, it is very sensitive to the saturation vapor pressure? Would you expect this?

Response: Thank you for pointing this out; we found an unfortunate error in our computer code, and the results shown in the left panel of Fig. 8 are not correct. The error has now been fixed and as can be seen from the corrected figure below, the difference is much more like what one would expect.



Comparison of critical relative humidity with respect to ice (RH^*_{ice}) as a function of temperature (T) for different parameter sets.

Comment 13: Line 287-289: Above you mentioned to ignore the Kelvin effect for this study. Did you account for the Kelvin effect when modeling 100 nm particles (Fig. 8)?

Response: We have accounted for the Kelvin effect in all our calculations; it is the Laplace effect that we did not account for.

Comment 14: Figure 9 discussion: Your model sensitivity to R is stated as quite weak: an order of magnitude change in R for 3% RHice variation. However, the measurement points have more than 10% RH uncertainty. In other words, uncertainties in R cannot explain the trend in the data. It "has to" be due to variation in A and B parameters and amount of water present? Maybe this could be clearer stated.

Response: The sensitivity to dry particle size that we show in the figure is based on the theory, and it would of course be valuable to repeat the experiments using monodisperse aerosol with a few different diameters between 100-1000 nm. Regarding the theoretical slopes, see our answer to comment 15 below. We added discussion to the end of Subsection 4.5 as follows:

One factor in the promising agreement of our model with the experimental data, especially at lower temperatures (below 235 K), is the incorporation of the equilibrium vapor pressure equation derived by Wagner and Pruss [2002]. This equation improved the performance of our model relative to the vapor pressure equation of Murphy and Koop [2005] by making the critical supersaturation curves somewhat steeper (see Fig. 8). However, as discussed in the previous subsection, the temperature dependencies of a number of variables that affect the slopes remain uncertain, especially below 235 K. These uncertainties should be diminished in order to obtain a better understanding of the agreement (or disagreement) between experiments and theory. In addition, experiments should be repeated using monodisperse aerosols with a few different dry sizes.

Comment 15: Line 327: I am not sure, if "promising agreement" is the right wording. I appreciate that the authors clearly state the caveat that this apparent agreement can only be achieved by using the vapor pressure equation derived by Wagner and Pruss [2002], though the vapor pressure equation of Murphy and Koop [2005] has held up well for ice nucleation studies across many disciplines. Would it be worthwhile to consider uncertainties in those vapor pressure formulations and perform some sensitivity tests? What does it mean for the theory, if somehow greater vapor pressures are needed below the homogeneous freezing limit to achieve apparent agreement? Which parameters are affected by this? This discussion could point to further research needs.

Response: See our responses to two previous comments. The low-temperature agreement between model and experiments is improved by using the Wagner-Pruss equation, but it is not the only factor. The slopes of our theoretical curves are also impacted by the temperature dependences of surface and interfacial tensions and density of water, and the temperature dependence of the A-parameter. All these T-dependences are uncertain, especially below 235 K and clearly it would be of great interest to perform a sensitivity study using the experimental ice nucleation results as a constraint. However, that would be quite a large task, and we therefore leave it for the future. Nevertheless, we added discussion of the matter to Subsection 4.4 as follows: It should be noted that the slopes of our theoretical curves below 235 K are affected not only by the saturation vapor pressure equation used in the calculations, but also by the temperature dependencies of surface and interfacial tensions and the density of water, and the temperature dependence of the A_w parameter. All these temperature dependencies are uncertain, and it would be of interest to conduct in the future a sensitivity study using experimental ice nucleation results as a constraint.

2 Response on RC2

We sincerely thank the referee for their careful and positive evaluation of our manuscript, as well as for the detailed questions and comments, which we address in detail below.

Comments:

Comment 1: It is a lot of formulas to process when reading that paper, and a lot of jumping around between formulas. It would have made reading a lot easier if there were a variable list in the appendix, with the variables, names, and units. Especially, the units would make it clearer in some equations to fully grasp them.

Response: We have added an appendix with the suggested list.

Comment 2: The naming of the variables are sometimes a bit confusing, for example switching A to A' for temperature independence, the difference between μ_{ia} and μ_A, the x in equation 19 for the two variables that are the same for water and ice (while for v one has to replace x with w or i).

Response: Regarding the A parameter, see our response to comment 3 by Referee 1. We modified Eq. 19 as follows: The constants C_w and C_a are given by

$$C_w = \frac{\pi \epsilon_w \varsigma_w^6}{3 v_w}; \qquad C_a = \frac{\pi \epsilon_a \varsigma_a^6}{3 v_a}$$

where ϵ_w and ς_w are the LJ energy and length parameters for water-water interactions, respectively, ϵ_a and ς_a are the LJ parameters for water-adsorbent interactions, and v_a is molecular volume of the adsorbent. Furthermore, we modified the text after Eq. 21 as: where $C_i = C_w(v_w/v_i)$ (note that the LJ parameters are the same for water and ice). By eliminating ...

Comment 3: Some concepts used and mentioned are not explained. I would suggest adding some explanations to some basic concepts/terms since the readers for this paper might come from a variety of fields and might not have the background on all terms, e.g., CCN, CCN activation, LJ molecules, adsorption isotherms, Laplace pressure, Nitrogen adsorption isotherms.

Response: We removed "CCN" and replaced "CCN activation" by cloud drop formation. We replaced "LJ molecules" by molecules interacting via the LJ potential. We replaced "Laplace pressure" by the increase of the internal pressure of a droplet caused by surface tension, which is greater for smaller droplets (the Laplace effect). We clarified "adsorption isotherms" as follows: (which show the amount of adsorbed gas or vapor on solid surfaces as a function of saturation ratio at constant temperature). We added the following after "Nitrogen adsorption isotherms": showing the amount of adsorbed N_2 as a function of saturation ratio.

Comment 4: One aspect of the paper, which is a bit unclear to me as a reader, is the definition that B=3 and when/where it is used and where not. In Eq. 18 for example, it is directly replaced while other equations keep the B. Then there is a sensitivity for different B values in a lot of plots, which is kind of contradicting that it was assumed to be 3 in some derivations? This could be better explained.

Response: See our response to comment 7 by Referee 1.

There are many assumptions made in the course of the paper. This is necessary and often clearly explained, but some assumptions I found difficult to follow:

Comment 5: Why is there a 1/T dependence assumed in eq. 4?

Response: The temperature dependence of adsorption obtained from the FHH model should be in agreement with the Clausius-Clapeyron equation. Since the left-hand sides of the Clausius-Clapeyron equation (Eq. 1) and the FHH expression with temperature-dependent $A(T)$ (Eq. 3) are equivalent, $A(T)$ must be proportional to $\frac{1}{T}$ to match their right-hand sides.

We added the following before Eq. (4): The temperature dependence of adsorption obtained from the FHH model should be in agreement with the more general Eq. 1 based on the Clausius-Clapeyron relation. We therefore assume the following specific temperature dependence for the parameter $A(T)$:

Comment 6: Another assumption that I could not connect with the rest of the paper is the statement on page 6, line 152 that the LJ potential is spherically symmetric $->$ where or in which formulas does that play a role, and how does that affect the framework?

Response: Only atoms have spherical symmetry, molecules such as water do not. Therefore, their intermolecular potentials are not spherically symmetric either, and thus an LJ potential fitted to water properties is not accurate. As a consequence, the values of the LJ parameters for water are not "unique"; their values are different depending on how they have been determined (there are multiple ways). We have reworded the text as follows: In doing so, we have made some approximations; for example, the LJ potential is spherically symmetric, whereas water molecules are not, and therefore their true intermolecular potential function is not spherically symmetric either. Figure 1 shows A_i as a function of A_w at two different temperatures for B values between 1 and 5 calculated using Eq. 1. For the LJ parameters, we use the following values [Kulmala, 1988]: $\epsilon_w = 440.3 \cdot k$; $\varsigma_w = 0.31$ nm.

These values have been determined from the critical properties of water. The viscosity-based LJ energy and length parameters for water that can be found in the table of Poling et al. [2001] (along with values for other molecular species) are somewhat different from these; however, the exact values of the parameters have only a very minor effect on the numerical results as the second term on the right-hand side of Eq. (23) is small compared to the first term.

Comment 7: I would also like to have had a bit more background on the LJ values used here.

Response: See our response to the previous comment.

Comment 8: I could not derive or grasp how equations 24 and 25 were derived.

Response: We now provide an explanation on how to derive the equation. See our response to comment 8 by Referee 1.

Comment 9: In section 4.4, a threshold of AF of 1% is chosen. Is that identical to the detection limit of SPIN?

Response: This is an onset criterion for deposition ice nucleation used in many studies (although 0.1% is occasionally used also). 1% is a good value with SPIN as we can be confident that it is above the noise level.

Comment 10:

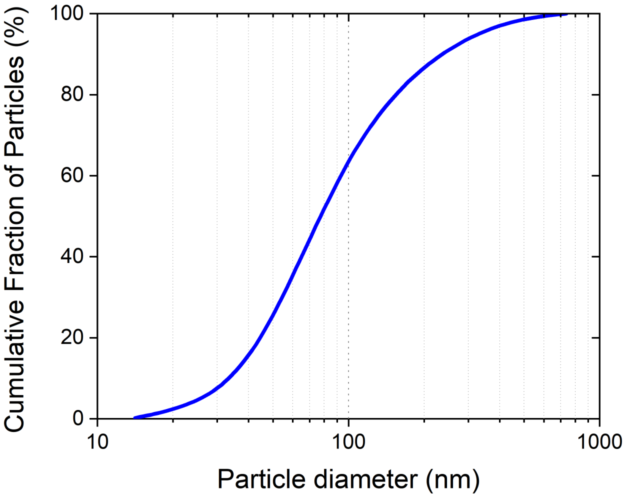
In section 4.,5 a size of 400 nm is chosen even if the size distribution looks very different from that, and a value of 70 nm (or something around 100 nm) would have made more sense. It is explained that the model is not very sensitive to that, but still, I found the value of 400 nm very arbitrary and difficult to understand. If it hardly makes a difference and there is no strong argument for the 400 nm, why not use the value from the size distribution measurements?

Response: The cumulative size distribution (Fig. 2 below) shows that 1% of the particles are larger than about 550 nm. As it is very likely that the largest particles activate at the lowest supersaturations, and the onset criterion is activation of 1% of the particle population, we believe that using a dry size of 100 nm or even less in the calculations would be unwarranted. The difference between the critical supersaturations calculated using 400 and 550 nm is very small; nevertheless, we re-calculated the lines in Fig. 9 using a dry size of 550 nm to be consistent with the 1% criterion. We added the cumulative size distribution to Fig. 2, and the following sentence in discussion of the dry size selected for the model calculations: Furthermore, the 1% fraction of the particles that activate at the critical supersaturation are likely to be the largest particles; 1% of the particles are larger than about 550 nm (see the cumulative size distribution in Fig. 2).

Comment 11: Sometimes, there could be more reflection on the assumptions used and the consequences. I was surprised by the big difference between the left and the right plot in Fig. 8 - especially the curve for A=3, B=1.5 that bends down when using Murphy and Koop. I would like to see a bit more discussion on this and the related uncertainties (in section 4.4), since Wagner and Pruss was used for Fig. 9 (?, see below).

Response: There was an error in the figure that has now been corrected. See our response to comment 12 by Referee 1.

Comment 12 Section 4.5: It is not mentioned nor explained (why) that the e_w equation from Wagner and Pruss is used (?)



Cumulative size distribution (percentual) of the silica particles used in the IN experiments.

Response:We added an explanation and discussion on the matter. See our response to comments 14 and 15 by Referee 1.

Comment 13 Code and data availability: I suggest making this public and not upon request.

Response: We will make the code and the data publicly available when the final version of the ms is accepted for publication.

Comment 14

Some figures have a slightly different style in the axis labels, legends, units/variables (italic or not), e.g., Fig. 2 vs. 3, but also the legend has a different size for Fig. 7 a and b. Make it uniform.

Response: Fixed.

Comment 15 If possible, replace ”references therein” by the most important references needed for your context.

Response: We removed the phrase and added a few references in one instance (Murphy and Koop 2005), but left the phrase in the other instance (Barahona 2018) because there are very many references and it would be hard to pinpoint the more important ones.

Comment 16 Can you give some context on the film thickness? What are ”typical values” and why did you choose what you did?

Response: We added the following in discussion of Fig. 4: The liquid water film thicknesses considered are 1.5 and 3.0 nm (the latter value corresponds to about 10 monolayers; thicker films are occasionally seen in adsorption measurements at high saturation ratios but are quite rare).

Comment 17 Can you add some more explanation on A and B and what it means, also in the discussion, for example, on page 10 (line 233-235).

Response: The physical meaning of the parameters is already explained in the text right after Eq 2; see also our response to comment 33.

Comment 18 page 3, line 75: This sentence is a bit difficult to read since the formula (= for equals) is breaking up the sentence. Also, I was wondering if an adsorbed layer means one adsorbed layer?

Response: We added an "is" before the equation. The text reads "adsorbed monolayer", not "adsorbed layer".

Comment 19 - Eq. 12 and 13: add that $P_w/e_w = S_w$ and $P_i/e_i = S_i$.

Response: Done.

Comment 20 Eq. 16: I had a bit of trouble understanding this equation (maybe related to the naming of the chemical potentials and some confusion on my side). If possible, add more explanation/steps here.

Response: We reworded the text preceding Eq. (16) as To be able to calculate the freezing nucleation rate in adsorbed water, we need an equation for the chemical potential difference between adsorbed water and adsorbed ice, which we denote by $\Delta\mu_A$. By subtracting Eq. 13 from Eq. 12 and rearranging the terms, we obtain

Comment 21 Eq. 19: v_x is the molecular volume?

Response: Yes. We now provide the equations for both constants in Eq. 19 to make it clearer. See our response to comment 2.

Comment 22 page 6, line 151: split up this very long and complex sentence.

Response:The sentence has been reformulated. See our response to comment 6.

Comment 23 page 7, line 171: be more specific equations for ... .

Response: We rewrote the sentence as: This could be done, for example, using equations for chemical potential as a function of pressure [Němec, 2013, Marcolli, 2020].

Comment 24 page 9, line 200: $P_w = P_i$ is also true at the phase boundary? It is the more trivial argument in my opinion.

Response: Thank you for the comment. We have rephrased the paragraph in the revised manuscript as follows:

At the phase boundary, the melting temperature is defined by the condition of zero chemical potential difference between the adsorbed ice and the liquid film, which corresponds to equality of their equilibrium vapor pressures ($P_w = P_i$). This standard phase-equilibrium condition allows calculation of the melting temperature as a function of film thickness for each pair of A_w and B.

Comment 25 Fig. 4: A symbol for the intersection point would help to see that quicker.

Response: Thank you. We have added a red diamond symbol at the intersections in Fig. 4.

Comment 26 Increase legends in Fig. 4, 8, and potentially 9 (it is the smallest/worst in Fig. 4).

Response: The legend font size has been increased and homogenized in all the figures in the revised manuscript

Comment 27 - Fig. 5: M. P. temperature is nowhere explained - use melting point temperature instead (fewer abbreviations, less confusion).

Response: We added (M.P.) to the caption instead, to avoid decreasing the y-legend font size.

Comment 28 - Fig. 5 caption: the last sentence = interpretation is not needed here.

Response: Thank you. We removed the sentence.

Comment 29 Fig. 9: Is pink vs. green a good choice when it comes to colorblind-friendliness?

Response: It shouldn't be a problem. We checked the figures before submission using a colorblind tool.

Comment 30 Fig. 9: The sensitivity bar is hard to see. Is that independent of T?

Response: From Fig. 8, that includes predictions for $R_p = 100, 200, 1000nm$ at different T it can be seen that the uncertainty is almost independent of T. We increased the thickness of the sensitivity bar in Fig. 9.

Comment 31 page 15, line 309: I don't understand why this is explicitly stated here/in the context.

Response: Just to inform the reader that the model's size dependence increases substantially when particle size decreases below 100 nm.

Comment 32 page 15, line 311: But the measurements look steeper?

Response: We modified the text as follows: At temperatures below 235 K, the experimental slope appears steeper than the individual theoretical lines; however, the measurement uncertainties are quite large at the lowest temperatures. See also our responses to comments 14 and 15 by Referee 1.

Comment 33 page 16, line 321-322: Conclusions? What do these specific values mean?

Response: It is explained in the following sentence ("Our interpretation:...). The comparison to Kumar is included in order to show that the values we determined do not deviate wildly from values obtained in a completely independent, experimental study. We added the following: For comparison, Kumar et al. [2011] obtained $A_w = 2.95$, $B = 1.36$ from cloud drop formation experiments with silica particles; as their B-value is between the two modeled values, and A_w is not markedly different from the model value either (the model is much more sensitive to B than to A_w), we believe that the modeled values are reasonable.

Comment 34 page 16, line 324: Can it not be measured or confirmed how hydrophilic the silica is here?

Response: In principle yes (by measuring water adsorption isotherms; contact angle measurements with powders are not reliable) but the question is about the comparison to the silicas used by the other groups, we do not have access to them. And even if we had, there is the problem that the surface properties (especially hydrophilicity/phobicity) of almost anything tend to change in timescales of days to months to years due to atmospheric contamination unless the samples are not stored very carefully. Therefore, the characterization of the hydrophilicity should be done simultaneously with the ice nucleation experiments.

Comment 35 Add . after equation 3, 20, 21, 22 and a comma after equation 4, 26 and double check the writing of equations (: before etc.) - this is inconsistent in the current version of the manuscript.

Response: Fixed.

Comment 36 page 5, line 116: I believe it must be Eq. 11 and 13.

Response: No, Eq. 16 follows from subtraction of Eq. 13 from Eq. 12.

Comment 37 page 6, line 149: There is a) too much.

Response: Fixed.

Comment 38 Fig. 6 caption: remove the () around the variables, inconsistent.

Response: Thank you. We removed the () around the variables in the revised manuscript.

Comment 39 Fig. 8 legend: there is a space missing between the value and unit for R_p.

Response: Thank you. We fixed the spacing issue in the revised manuscript.

Comment 40 A1, use {} for the exp function in the Murphy and Koop e_w equation to enhance readability.

Response: Fixed.

Comment 41 page 19, line 374: a space is missing after water.

Response: Fixed.

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