

## ***Interactive comment on “Heterogeneous freezing of droplets with immersed mineral dust particles – measurements and parameterization” by D. Niedermeier et al.***

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We would like to thank the referee for the constructive comments and suggestions made to improve the manuscript. Our responses to each comment are given below.

### **General comments**

*I have an understanding problem with the temperatures given in the paper. The authors mainly talk about the wall temperature of the LACIS chamber, which leads than to the supercooling temperature,  $T_s$ . However, I guess one wants know the real temperature within section 6 and 7 of the chamber, where the ice freezing occurs. Do the particles reach there equilibrium and thus have the same temperature as the ice on the walls?*

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*If so, then  $T_s$  is the temperature in the chamber, right? If not, then the authors have to give the real temperatures in the chamber. Is it possible that the information is given in the Hartmann et al. (2010) draft (unpublished results)?*

The numerical simulations (see new Figure 3, also in the supplementary information) show that the supercooled droplets which do not freeze, reach the set wall temperature in the second cooled section (after about 1.6 s). That means the particles have the same temperature as the ice on the inner tube walls. To show this the axial temperature profile of the particle beam was inserted into the manuscript. It is clearly visible that the temperature falls very steeply within the first cooling section and reaches the adjusted wall temperatures in the second freezing section.

*In the discussion section, I would be nice to have a comparison with other studies together with the possible atmospheric implications of the results. I believe that such a discussion would increase the depth of the paper.*

A comparison with Archuleta et al. (2005) was inserted into the manuscript (see Fig. 10, also in the supplementary information). This publication deals with nucleation rate coefficients of mineral dust cores (hematite and corundum) in a size range of 50 – 250 nm. Their determined rate coefficients show a similar increase with increasing supercooling and they are in same order of magnitude compared to our results.

Also, some atmospheric implications were added to the manuscript: “In general, particle treatment did not lead to an increased IN ability compared to the pure ATD particles. One can conclude that chemical aging processes (i.e., through coatings) in the atmosphere will also not lead to an increased IN concentration for heterogeneous freezing processes. The opposite case seems to be more likely, i.e., the decrease in IN concentrations by up to one order of magnitude for the temperature range investigated.”

### **Specific comments**

*Page 15828 lines 7: Do the authors know the temperature in the chamber so precisely?*

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*The investigated temperature range primarily addresses to mixed-phase clouds activation temperatures. Can the same conclusions be drawn also for cirrus temperatures?*

The uncertainty of the temperature setting was added to the manuscript. It is  $\pm 0.30$  K. We focused on immersion freezing for mixed phase cloud temperatures, and no experiments for cirrus temperatures were performed. The sentence was rewritten: "Ice fractions at mixed-phase cloud temperatures ranging between 233.15 K and 240.65 K ( $\pm 0.30$  K) were determined for all types of particles acting as IN (Ice Nuclei)."

*Page 15828 lines 13-16: I had a hard time to understand that sentence. All experiments were investigated in dilute solutions, and thus the water activity of the droplets is always close to 1. And now you conclude that water activity is not related to the investigated freezing process? Please rephrase that sentence.*

The sentence was removed from the abstract and a rephrased version of the sentence was inserted in the results and discussion part. "A freezing point depression due to the soluble material on the particles (and therefore in the droplets) can not explain this observation as the supercooled droplets were highly dilute before freezing occurred"

*Page 15829 lines 25 -30: This discussion could be more detailed. On what base do Meyers et al. J. Appl. Meteorol 1992 conclude that deposition mode can also occur at water saturation? Why do the authors doubt that condensation freezing takes place at all?*

Due to the definitions of deposition nucleation (ice formation for any states exceeding ice saturation) and condensation freezing (CCN initiates freezing at sufficient low temperatures, water supersaturation required) one can conclude that deposition nucleation can also occur at water supersaturated conditions. Meyers et al. (1992) conclude that without special experiments the two nucleation processes can not be distinguished at water supersaturated conditions. There are a lot of measurements dealing with this problem, but they are not consistent. Additionally, Meyers et al. (1992) used a single expression to parameterize deposition nucleation and condensation freezing because

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"the results representing the contributors of both mechanisms can be parameterized with little error as a simple function of ice supersaturation". Due to that (inconsistent measurements, single parameterization for both mechanisms) we think that both processes can not be distinguished sufficiently. Consequently, to avoid any speculations and since we do not focus on deposition nucleation, the following part was removed from the manuscript: "The occurrence of some modes is discussed controversially and partly doubted. For example, Meyers et al. (1992) suggest that deposition nucleation occurs at water supersaturated conditions, too. Therefore, it is difficult to distinguish between freezing in deposition and condensation modes."

*Page 15831 lines 1-2: Which of the mentioned studies do contradict each other and why?*

The phrase "contradict..." is maybe too strong. The sentence was rewritten and an example added: "Taken together, the studies are partly difficult to compare, and even when certain results can be compared they are not entirely consistent. For example measurements concerning deposition nucleation of mineral dust particles performed by Archuleta et al. (2005) (Asian Dust,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  particles), Knopf and Koop (2006) (Arizona Test Dust (ATD) particles) and Möhler et al. (2006) (ATD particles) give an inconsistent picture. For temperatures at about 240 K, Möhler et al. (2006) and Knopf and Koop (2006) determined similar ice onset supersaturations. For lower temperatures, Möhler et al. (2006) observed ice onsets at lower ice supersaturations compared to ice onsets determined by Knopf and Koop (2006) and Archuleta et al. (2005). The explanations given by Knopf and Koop (2006) can partly resolve the observed difference but the question remains why the results are similar for higher temperatures and differ for temperatures below 235 K."

*Page 15831 line 25: Why 300 nm? Is that the mean diameter of the ATD size distribution?*

The following part was inserted in the manuscript (see particle generation section):

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"This particle size was chosen because in the atmosphere the absolute majority of IN is generally found below one micrometer (Mertes et al., 2007). To avoid a major contribution of doubly-charged particles, also care was taken that the maximum of the generated particle size distribution was at a size smaller than the selected particle size, i.e., the maximum appeared at about 200 nm."

*Page 15831 line 25: Which additional instrumentation? Since the two cited papers are unpublished papers, I would like to get here some additional information.*

The corresponding sentence was removed from the introduction. The additional instrumentation includes three Aerosol Mass Spectrometers (AMS, from Research Center Jülich, Germany and Max Planck Institute for Chemistry, Mainz, Germany and from IFT), a High-Humidity Tandem Differential Mobility Analyzer (HH-TDMA, Hennig et al. (2005)) and a Cloud Condensation Nucleus Counter (CCNC, DMT, Boulder, Colorado, USA, Roberts and Nenes (2005)). The corresponding sentence is written in the particle generation section.

*Page 15833 Eq.3 How well does the right term of the equation agree with the vapour pressures given by Murphy and Koop Q. Murphy, D. M.; Koop, T. Q. J. R. Meteorol. Soc. 2005? Why did the authors use the expression by e.g., Rogers and Yau 1996, when both vapour pressures are well parameterized? What about the uncertainty and temperature dependence of  $l_f$ ?*

It was added to the text: "From the existing expressions describing the vapor pressures of supercooled water and ice, we chose this expression because the parameterization is to be a function of supercooling temperature,  $T_s$ , which is as simple as possible and describes the freezing results as accurately as needed." The molecular latent heat of fusion  $l_f$  depends on temperature changing by about 10

*Page 15833 line 15: Why did the authors take  $\Delta F$  and  $v_i$  as constants? There are parameterizations given in Zobrist et al. JCP 2007 paper.*

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The goal of the parameterization is to get a simple tool to describe the freezing process. Since the interval for which the parameterization is valid is about 9K, we can assume that  $\Delta F$ ,  $l_f$  and  $v_i$  are almost constant. The following statement was inserted in the manuscript "For  $\Delta F$  and  $v_i$  parameterizations also exist (Zobrist et al., 2007) but given that the absolute temperature  $T$ ... ."

*Page 15833 line 19:  $\Delta F$  is no longer treated as a function of temperature, as mentioned above. So the T-dependence is redundant.*

That is correct; it was changed in the equation.

*Page 15834 line 16: How does the temperature gradient within the LACIS influences the results? See also general comments.*

The radial temperature gradient is non-relevant because the particle beam is 2mm in diameter and is positioned in the middle of the tube. To show the axial temperature gradient, a Figure 3 was changed in the manuscript (see supplementary information). As visible, some ice nucleation events will take place during the cooling cycle. But the lower the temperature the more nucleation events should occur. Shortly after the first freezing section, the temperature of the particle beam reaches the set wall temperature (the lowest temperature). In the second freezing section the temperature is almost constant. Therefore most of the freezing will take place in the last section.

*Page 15834 lines 20: Why is  $j_{het}$  almost constant?*

The lower the temperature the higher is the nucleation rate. For one set wall temperature the particle beam reaches this temperature after the first freezing section and is almost constant in the second freezing section. Therefore the nucleation rate reaches its highest value after the first freezing section and is almost constant in the second freezing section. The corresponding sentence was rewritten: "Assuming that the major part of ice is formed in the region inside LACIS where the supercooling temperature is highest and constant (see the temperature profile inside LACIS in Fig. 3) Eq. (6)

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simplifies to:"

*Page 15835 line 3: The validity of Eq. 8 does not cover the entire investigated temperature range.*

The validity of the parameterization is caused by the measurements themselves. For supercooling temperatures lower than 34 K the determined ice fractions are underestimated (Therefore these points were removed from the manuscript.). For supercoolings above 38 K homogeneous freezing occurs additionally and is the main freezing process for temperatures above 39 K. That means the validity of the parameterization covers the small investigated temperature range  $34\text{ K} \leq T_s < 38\text{ K}$ . The discussion about the validity of the parameterization was moved from the theoretical part to the discussion section for better understanding.

*Page 15838 lines 26-28: So the simulation can calculate the hygroscopic growth, but not the ice nucleation. But the goal of this study is to investigate ice nucleation. What does "half quantitativ" mean? I don't see the direct gain of the simulations for this study.*

The model simulations are necessary to understand the measurement results. For the chosen measurement setup the simulations (see Figure 3, also in the supplementary information) are used to determine where the droplets are generated inside LACIS, how the droplet diameter increases and at which point the droplets start to evaporate and where they are evaporated reaching hygroscopic growth regime. Due to these simulations we know that the ice fractions determined for temperatures higher than 239.15 K are not accurate, since the droplets are evaporated before they reach the end of the tube. Therefore these points were removed from the manuscript. The "Half-quantitative" statement will be removed from the manuscript and the simulation results are interpreted as stated.

*Page 15839 lines 9-10: This means that the particles are completely dry again. What are the thermodynamic conditions within the LACIS for a given wall temperature? See also comment below and general comments.*

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The RH with respect to liquid water is below 100% at the end of the tube. That means the hydrophobic ATD particles will be completely dry at the end. But the coated particles will evaporate until they reach their equilibrium diameter. The corresponding sentence was changed to: "... evaporate, become deactivated and reach their equilibrium diameter towards the end of the second freezing section ..."

*Page 15839 lines 13-17: What is the temperature within LACIS for a wall temperature of 233.15 K? Since homogeneous ice nucleation should start at 235 K.*

The set wall temperature (i.e. 233.15K) and the temperature of the particle beam are nearly identical in the second cooled section. Additional freezing measurements with highly diluted ammonium sulphate solution droplets showed that freezing was apparent only for temperatures below 235.15 K and these results are inserted into Fig. 7. (see supplement information) The corresponding sentence was changed in the manuscript: "Since experiments are performed for temperatures below 235.15 K, even homogeneous freezing would be possible."

*Page 15841 lines 12-14: What is the size of the drops? Could you mark in Fig.4 where the ice starts to occur for the first time? Could the authors add in Fig. 4 also the temperature within LACIS?*

Figure 4 seems to be misleading and misunderstood. It does not contribute to the comprehension of the measurement procedure. Therefore figure 4 will be removed from the manuscript. But to answer your question: Concerning a one section measurement, the droplets inside LACIS are larger than  $1\mu\text{m}$  for temperatures below 239.15 K. As stated before, the temperature of the particle beam reaches the set wall temperature in the second freezing section. Therefore the given wall temperature in Fig. 4 and the beam temperature are identical.

*Page 15845 line 5: So what is the typical water activity of such a particle?*

For temperatures below 239.15 K the droplets inside LACIS are larger than  $1\mu\text{m}$ . Con-

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sidering the coating amounts, water activity is about 1.

*Page 15845 line 9: What means almost constant temperature? According to Fig. 11,  $j_{\text{het}}$  can increase up to one order of magnitude within 1 K (e.g., red curve), so,  $j_{\text{het}}$  is very sensitive to temperature.*

You are right that,  $j_{\text{het}}$  is very sensitive to temperature. But in the context here it is meant that for one set wall temperature, the temperature of the particle beam is almost constant after the first freezing section (see Fig. 3). That means for this fixed wall temperature  $j_{\text{het}}$  is almost constant after the first freezing section. The sentence was rewritten for better understanding: "... the assumption underlying this parameterization is that the major part of ice is formed in the second freezing section where the supercooling temperature reaches its highest value and is almost constant and where, therefore,  $j_{\text{het}}$  is almost constant."

*Page 15847 lines 19-21: This conclusion is drawn without showing the water activity data. So either show the data or omit that sentence. Could you investigate more concentrated solutions to prove that conclusion? This would be great data.*

The numerical simulations and the one section measurements show that the droplets are highly diluted. We could investigate more concentrated solutions, but we are more interested on the influence of surface changes on the freezing behaviour of the particles. The corresponding sentence in the conclusion part was rewritten: "For the investigated temperature range the droplets inside LACIS are activated and highly diluted before freezing occurred. That means a freezing point depression caused by the soluble coating material was not observed during FROST."

*Page 15847 lines 27-28 : Do you really believe that the total surface is considerably changing due to a small coating?*

This is a hypothesis we made which based on the parameters we obtained from our stochastic approach. However, we now stated in the text: "However, we have to be

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careful with this conclusion made because the simplified parameterization itself may lead to an overrated interpretation of the fit parameters  $a$  and  $f_{\text{het}}$ ." Additionally, we inserted the singular hypothesis to the manuscript showing that surface changes due to the coating procedure could also be viewed as active sites getting blocked, changed or destroyed.

*Page 15858 Fig.5: Can you give the size of the particles or droplets and not the log(channel)? Page 15859 Fig.6.: See comment Fig.5.*

For the whole size distribution this would be difficult, because the size of the ice crystals and seed particles can not be expressed accurately (different refractive indices for the dust particles, droplets and ice crystals, irregular shape of the dust particles and ice crystals). Since the ice crystal and seed mode size is not necessary for calculation of the ice fraction, we would prefer to leave it as it is.

*Page 158639 Fig.10.: How sensitive are the experiments with respect to  $f_{\text{ice}}$ ? How many droplets are investigated for one  $T_s$ ?*

Per temperature around 1000 to 10000 particles were measured and each measurement was performed at least 3 times. Very good repeatability (relative uncertainties about 10%)

*Page 15864 Fig. 11: I was wondering about the different slopes of  $j_{\text{het}}$  for the differently coated ATD particles as a function of temperature. The results indicate the some IN are better at low temperatures and some at higher temperatures. Do the authors have any idea why? The slopes are clearly smaller than that for homogeneous ice nucleation rate of pure water, which can increase by roughly one order of magnitude decreasing the temperature from 237K to 236.5K (e.g., Benz et al. J. Photochem. Photobiol. 2005). Possible reasons?*

To answer the first part of your question: The different slopes of  $j_{\text{het}}$  for the differently coated ATD particles result from the determined ice fractions. For low supercoolings

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the pure ATD particles exhibit the highest IN ability. For higher supercoolings ( $T_s \geq 35$  K), all particles besides the  $(\text{NH}_4)_2\text{SO}_4$  coated ones possess similar nucleation rate coefficients (within the uncertainties). These uncertainties were added to Fig. 10. So the mistaken indication that some IN are better at low temperatures and some at higher temperatures is not present anymore. The following part was added to the text: "The curves of the nucleation rate coefficients in Fig. 10 reflect the ice nucleation potential of the particles. E.g., for  $T_s \geq 35$  K the nucleation rate coefficient for  $(\text{NH}_4)_2\text{SO}_4$  coated particles is about one order of magnitude lower compared to the other coated and uncoated particles, which exhibit similar nucleation rate coefficients within the uncertainties." To answer the second part of the question: It is true that the slopes of the nucleation rate coefficients derived for heterogeneous freezing here are shallower than the curve of homogeneous ice nucleation of pure water which increases by about one order of magnitude for an increase in supercooling by 0.5 K. As an explanation for this, we think that in terms of CNT the difference is caused by the thermodynamic term because with increasing  $f_{\text{het}}$ , the slope increases reaching its maximum for  $f_{\text{het}} = 1$  for the investigated temperature range. This corresponds to the homogenous freezing case. That means the properties of the particle surface directly influence the slope of the nucleation rate coefficient curves (through  $f_{\text{het}}$ ). Nucleation rate coefficients determined by Archuleta et al. (2005) for size segregated aluminium oxide and iron oxide particles (these substances are also components of the investigated ATD particles) treated with sulfuric acid were added to the manuscript. These coefficients show a similar increase with increasing supercooling and have values comparable to our results (see Fig. 10, also in the supplementary information).

#### Technical corrections

*Page 15828 lines 15: change ". . . before the freezing occurred." to ". . . before freezing occurred."*

Thanks for your remark. The sentence was changed as suggested.

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*Page 15828 lines 18: replace ". . .allows us to determine. . ." by for example ". . . suggest ..."*

Thanks for your remark. The sentence was removed from the abstract.

*Page 15828 lines 22: Please rephrase that sentence.*

The sentence was rewritten: "Among other factors, ice containing clouds, such as cirrus and mixed-phase clouds have an impact on Earth's radiative balance by scattering and absorbing solar and terrestrial radiation (Hung et al., 2003; Zuberi et al., 2002) with ice formation processes strongly influencing cloud radiative properties (DeMott et al., 2003b)."

*Page 15829 lines 5: Either use "ice-forming nucleus" or "ice nucleus" trough out the entire manuscript. I suggest the latter one.*

Now ice nucleus is used through out the entire manuscript.

*Page 15829 lines 12: Melting point of water or of ice?*

The melting point of ice is meant.

*Page 15829 lines 12, 15 and 18: I would rather argue with super-saturation or frost point than with the melting point of water (or rather ice).*

In the manuscript, definitions were used consistently dealing with the melting point of ice. We would prefer to leave it as it is.

*Page 15831 line 12: add "ice" before "heterogeneous freezing". The author should be consistent within the publication*

We are wondering why "heterogeneous freezing" should be changed to "ice heterogeneous freezing". We would argue that "ice" and "freezing" declare the same thing. So, the "ice" before "heterogeneous freezing" seems to be redundant. Therefore nothing was changed.

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Page 15832 line 12: Give typical units for  $j_{\text{het}}$ ,  $n_s$  . . .

The typical unit for  $n_s$  was added to the text when introducing this parameter in the theory section. A typical unit for  $j_{\text{het}}$  was not added at this place because the values for  $j_{\text{het}}$  determined in this study are presented in the results part.

Page 15834 line 6: replace “. . . crystallization velocity of water . . .” by “. . . crystallization velocity of ice . . .”.

Thanks for the remark, the phrase was rewritten.

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Please also note the supplement to this comment:

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<http://www.atmos-chem-phys-discuss.net/9/C10174/2010/acpd-9-C10174-2010-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15827, 2009.

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