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Atmospheric Chemistry and Physics Discussions

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 reponses are given below.

Major concerns

The manuscript gives, as far as I can see, no information at all about the actual temperature and humidity profiles the dust particles experience in the nucleation sections. This information is a prerequisite for e.g. judging the applicability and suitability of classical nucleation theory (CNT) for data evaluation and interpretation. Also, what about radial temperature and humidity gradients in the aerosol center flow? Is the tempera-

ture known at the saturation point? In other words, is the temperature range known the droplets are exposed to?

There are radial temperature and humidity gradients in the tube but they are negligible for the aerosol flow, because the particle beam is narrow (diameter of 2 mm) and is situated in the middle of the tube. The axial temperature profile for three different set wall temperatures was added to the manuscript (see new Fig. 3, also in the supplement information). It is clearly visible that the temperature of the beam decreases within the first freezing section reaching the set wall temperature in the second freezing section. The saturation profiles with respect to ice and liquid water for LACIS measurement conditions are not presented here (but in Hartmann et al. (2010)) but in Fig. 3 it is clearly visible that the temperature range the droplets are exposed to is known. Additionally, immersion freezing is mainly driven by the temperature of the water drops, being not explicitly dependent on supersaturation with respect to liquid water Connolly et al. (2009).

And what about the nucleation time? Was the nucleation time varied to prove that a stochastic nucleation rate approach, i.e. a time dependent formulation appropriate to fit the experimental data? Such an approach implies that the nucleation conditions, here mainly the temperature, stay constant throughout the nucleation time period with a constant formation rate of ice. This obviously is not the case in the LACIS setup. Instead the droplets form at some temperature and are further cooled to the temperature which is taken as the supercooling or freezing temperature in the manuscript. What if a significant fraction of ice is already formed or nucleated during this 'cooling path'? Can this really be excluded? If not the CNT approach would only provide lower limits of the nucleation rate.

At the current stage nucleation time was not varied to prove the stochastic approach. This approach was used because it is a simple method to describe and interpret the determined freezing result in terms of CNT. As visible in the temperature profile added to the manuscript the temperature decreases in the first freezing section and reaches

the set wall temperature in the second freezing section. The assumption underlying this parameterization is that for one set wall temperature 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 therefore $j_{\mathrm{het}}$is almost constant. This assumption is reasonable because: a) The lower the temperature the higher is the nucleation rate, i.e., for one set wall temperature the nucleation rate is highest and almost constant in the second freezing section. Our determined heterogeneous ice fractions are clearly below 1, indicating that most of the freezing should occur in the second freezing section where the temperature is lowest and almost constant and therefore the nucleation rate is highest and also almost constant. b) The ice fraction values increase with increasing supercooling. That means the increasing ice fraction when going from e.g. $T_{\mathrm{s}} = 34\,\mathrm{K}$ to $T_{\mathrm{s}} = 35\,\mathrm{K}$ should be the result of the increased nucleation rate when going from $T_{\mathrm{s}} = 34\,\mathrm{K}$ to $T_{\mathrm{s}} = 35\,\mathrm{K}$. Since the axial temperature profile for both supercoolings are similar in the first freezing section, the difference in the ice fraction should be caused by the temperature difference in the second freezing section where the beam temperature is almost constant. However, to improve the message of the manuscript the singular hypothesis using the polynomial fit function introduced by Connolly et al. (2009) was added to the manuscript so that both limit cases (stochastic and singular) are in the manuscript. As a result both approaches (stochastic and singular) can be used to sufficiently describe the experimentally determined results. From both parameterizations it can be concluded that the coating of the particles lead to a modification of the particle surface influencing the nucleation efficiency.

As far as I see the CNT analysis as used by the authors also assumes that all particles have the same probability to carry active sites for heterogeneous ice nucleation. Is this a reasonable assumption for mineral particles? The particle and generation procedures are only uniform with respect to particle mobility size and probably also coating layers. But the aerosol is still a complex mixture with respect to e.g. mineralogy and surface morphology. Therefore it can be assumed that not only one surface site but a mixture of different sites with different activation energies (or contact angles) are present in the

aerosol. A larger fraction of ice particles observed at lower T may also be interpreted partly by a larger number fraction of aerosol particles to carry sites with higher activation energy and therefore lower activation temperature (singular hypothesis). Both the time dependent and singular hypothesis approaches can be found in the recent literature to evaluate and parameterise laboratory measurements of heterogeneous ice nucleation (see e.g. Marcolli et al., ACP, 7, 5081, 2007 or Connolly et al., ACP, 9, 2805, 2009), and it is not yet clear which one applies best or if a mixture of both should be used. I think that LACIS is a promising new setup to gain such information just by systematically varying particle sizes, number concentrations and nucleation times. Unfortunately, the manuscript in its current version lacks of such information. Therefore the experimental data seem to be over-interpreted in terms of conclusions for CNT parameterisation and I recommend the authors to be more careful with statements about the comparability with or between other measurements (e.g. on page 15831, lines 3 to 8 or page 15846, lines 22 to 26).

The particles are not completely specified with respect to mineralogy and surface morphology at the current state, but this topic as those of the influence of mineral composition will be the focus of future studies. But to allow for your comment, the following part was added to the text (see section 2.1): “Because of the narrow particle size distribution of the ATD particles (see Wex et al., 2010) and the lack of information on precise properties of single particles, we made the simplified assumption that the investigated particles feature a similar size, a similar surface and similar surface properties." Additionally, to improve the message of the manuscript the singular hypothesis using the polynomial fit function introduced by Connolly et al. (2009) was added to the manuscript so that both limit cases (stochastic and singular) are in the manuscript. The derived nucleation rate coefficients were compared with results from Archuleta et al. (2005). A comparison between the ice-active surface site densities determined by Connolly et al. (2009) and our study was not performed. The reason is that Connolly et al. (2009) measured in a higher temperature regime compared to our study. That means an extrapolation has to be performed which, we think, would not lead to reasonable

physical interpretations/results. At the current state, we are not able to clarify which approach correctly describes the immersion freezing process. Further investigations have to be performed measuring at higher temperatures and varying particle size and nucleation times to quantify if one the approaches or even a mixture of both has to be applied. Therefore the following part was added to the conclusion part: “In summary, both approaches can be used to sufficiently describe the experimentally determined results. Therefore, we can not clarify at the current state which approach correctly describes the investigated immersion freezing process. Further investigations have to be performed measuring at higher temperatures and varying particle size and nucleation times to quantify if one of the approaches or even a mixture of both has to be applied, e.g., following Marcolli et al. (2007) who could best describe their measurement results when using the singular hypothesis while keeping the stochastic concept of a nucleation rate"

Also it is not clear how the authors can exclude contributions from deposition nucleation. This question may sensitively depend on the temperature at the condensation point. It is known from many literature studies that dust particles can be active deposition mode nuclei, though normally at lower temperature compared to freezing modes. Figure 4 indicates ice formation before droplet activation occurs in the first cooling ramp. I would suspect that the uncoated and slightly coated cases are affected by deposition nucleation, whereas the thicker coatings suppress deposition mode IN but still allow the freezing modes (can be condensation and immersion freezing) to be active. If contributions from deposition mode nucleation can not fully be ruled out I would recommend to change the paper title.

Figure 4 is somewhat misleading and misunderstood. The extra performed measurements clearly show that ice formation caused by deposition nucleation is negligible for FROST measurement setup (see text and old Figure 8). The ice formation visible in Fig. 4 (at about 14:45, one section measurement, $T_{\mathrm{w}} = 240.65\,\mathrm{K}$) appears after the droplet activation (this conclusion is proved by the model results shown in Fig. 3). But

the droplets evaporate between the end of the tube and the inlet of WELAS so that only the seed mode and the ice crystal mode remain. Fig. 4 was removed from the manuscript to avoid misunderstandings.

The authors argue that data below 38 K supercooling is excluded from the CNT analysis. From Figure 4 it appears to me that the experiments are affected by homogeneous freezing already at a supercooling around 36 to 37 K (dark red area between 15:45 and 16:00). The droplet diameters given in Figure 2 could be used together with recent literature data for freezing rates of supercooled water to estimate the threshold temperature at which homogeneous droplet freezing starts to affect ice formation in the LACIS experiments. At this point I would like to recommend the LACIS team to conduct, if not yet done so, freezing experiments with supercooled water in order to demonstrate the feasibility of the LACIS setup for quantitative ice nucleation rate measurements.

Measurements, using the FROST measurement setup, concerning homogeneous freezing of highly diluted ammonium sulfate solution droplets were performed. This was stated in the text before! For clarification the determined ice fractions are now added to Fig. 6. It is clearly visible that homogeneous freezing starts to be detectable for supercoolings larger than 38 K, being the dominant process for supercoolings above 39 K.

The authors refer to several related papers 'in preparation' which will address issues of coating thickness either directly measured with aerosol mass spectrometers or derived from CCN activation measurements. I strongly suggest to include some experimental information about coating thickness also in the present manuscript.

The axial temperature profile was added to the manuscript. Additionally, the coating thicknesses derived from CCN activation measurements are added to the text (ranging between 1 to 10 nm).

Specific comments

First statement of introduction: It is not only the ice containing clouds that affect the climate by light absorption and scattering.

In the manuscript, it is not written that only ice containing clouds affect climate. But to avoid misunderstandings, the sentence was changed to "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)."

p.15829, l.7: I recommend to avoid the term 'deposition freezing', and suggest instead to distinguish between deposition nucleation (vapour to ice) and freezing modes (supercooled liquid to ice) of ice formation.

Thanks for the considerate observation. This mistake was corrected in the whole manuscript.

p.15829, l.16: Numerous previous studies clearly showed that dust particles act as freezing nuclei in case of droplet activation below -35°C (see e.g. a recent paper by Connolly et al., ACP, 9, 2805, 2009 and references therein).

The ATD particles also act as IN at -35°C in the immersion freezing mode in our study, so we do not understand the comment. Therefore, nothing was changed.

p.15831, l.3: As stated above, the mobility size as well as type of coating (and probably also coating thickness) are well defined and known in the current experiments, but questions remain concerning the role of unspecified mineral composition, surface roughness and particle morphology.

It is right that the particles are not completely specified with respect to the mentioned properties, but this topic as those of the influence of mineral composition (and e.g. the above mentioned particle diameter) will be the focus of future studies.

p.15832, l.5: Why should a 'questionable theory' be applied here? Would recommend

to mention which assumptions are questionable and why the authors believe the theory to be appropriate for data evaluation or heterogeneous freezing parameterisation.

For example macroscopic properties were assumed to describe microscopic properties/processes. For some quantities in the theory, different parameterizations exist (e.g. the saturation ratio and interfacial free energy) As stated in the manuscript, CNT can be used at least in a phenomenological way to interpret observations (Shaw et al., 2005). For example, CNT provides a feasible method to parameterize homogenous and heterogeneous ice nucleation as function of temperature.

p.15832, l.14: . . . density of liquid water molecules . . .

We would prefer not to write liquid water molecules. We declare ns similar to Marcolli et al. (2007); therefore the phrase is left as it is.

p.15832, l.19: . . . second term represents . . .

The phrase was rewritten as suggested.

p.15833, l.13 to 16: Suggest to give an estimate of the range of these parameters in the given temperature interval, if possible.

The change of these parameters in an interval of 10 K (between 233.15to 243.15) is given in percent and is added to the manuscript: " ... we can reasonably take $\triangle F$, l_{f} and v_{i} as constants for the investigated temperature range. The temperature dependence of these parameters is small in the interval from 233.15 K to 243.15 K, changing by about 8%, 10% and 0.1%, respectively."

p.15835, l.13: Corona discharges are known to induce radical chemistry. Could this produce impurities to condense on the dust particles and thereby affecting the surface composition?

We were aware of the fact that Corona discharges are known to induce radical chemistry. Therefore generated particles on two ways: with and without Corona Discharger.

The result was that the freezing ability of the particles did not change! This is now mentioned in the particle generation section.

p.15839, l.8: Replace 'section one' with 'section six' or 'freezing section 1'

Section one will be changed to freezing section one (first freezing section, respectively), and section two will be changed to freezing section two (second freezing section, respectively) throughout the whole manuscript.

p.15840, l.16: Is the seed correction factor of 0.05 also valid for the coated particles?

The correction factor of 0.05 is also valid for the coated particles investigated during FROST because the size difference between the different coated particles is marginal.

p.15840, l.21: Is the correction factor CMV caused by a radial particle concentration gradient. Are such gradients the same for aerosol, droplets and ice particles? And if not, did you correct for that effect?

The reason for this correction is that (as stated in the text) the extension of the particle beam is larger than the WELAS measuring volume. A radial particle concentration gradient is not present.

p.15841, l.3: Please specify the CPC and other relevant uncertainties here.

The uncertainty of the CPC number is about $\pm$5% (given in the text now). C_{MV} and C_{seed} are given with uncertainty ranges.

p.15846, l.10: Why can surface area explain the observed increase of parameter a? I thought the diameter and therefore the surface area was kept constant in all experiments.

The initial particle diameter was kept constant, indeed. And for the determination of the nucleation rate coefficients spherical particles were assumed for calculations. But in the factor a the ice active surface is included and this is what was changed due to the coating. However, a sentence was added to the discussion part saying that we have

to be careful with the conclusion made because the simplified parameterization itself may lead to an overrated interpretation of the fit parameters a and f_{het}.

p.15853, Figure caption: Refer to Equation 8 where the parameters are defined.

The reference to the equation was added.

p.15853, Figure 4: Any explanation for the the particles in size channels around 100 between 15:30 and 15:45?

The dark red area between 15:30 and 15:45 is most likely caused by supercooled droplets which are not frozen or evaporated respectively. Again, Figure 4 leads to some misunderstanding. Therefore, this Figure was removed from the manuscript. (All necessary information is visible in the new Fig. 4 and Fig. 5 (old Fig. 5 and 6)).

p.15865, Figure 12: Are the dashed and dotted curves based on measurements? If so it would be nice to see the nucleation rates instead of ice fractions. If not, the figure should be removed (see also comments above on comparison to other literature data).

For the dashed and dotted curves the CNT type parameterization was used to detect that ice fractions would increase with increasing residence time (in case that the stochastic assumption is correct for immersion freezing). Therefore nucleation rates should be used for comparison because they are not instrument specific and generally comparable. Nevertheless, Fig. 12 was removed from the manuscript because we cannot show a time dependence of freezing with the presented data.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C10202/2010/acpd-9-C10202-2010-supplement.pdf

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