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Interactive comment on “Particle-area dependence of mineral dust in the immersion mode: investigations with freely suspended drops in an acoustic levitator” by K. Diehl et al.

Anonymous Referee #3

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The manuscript titled “Particle-area dependence of mineral dust in the immersion mode: investigations with freely suspended drops in an acoustic levitator” by K. Diehl et al. , reports freezing temperatures of water droplets containing montmorillonite K10, illite IMt1 and illite NX as ice nuclei (IN) using an acoustic drop levitator (AT) and vertical wind tunnel (WT). Median freezing temperatures and frozen fractions are presented. Time dependent and time independent description are used to derive heterogeneous ice nucleation rate coefficients, J_{het} , and the surface density of active sites, n_s , respectively. The authors find a clear time dependence of heterogeneous freezing for these IN, and that derived J_{het} and n_s are consistent with measurements of Broadley et al.

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[Interactive Discussion](#)

[Discussion Paper](#)



(2012) using much smaller droplets and IN surface area. Results from AT and WT experiments are also consistent with each other.

In general, results and the freezing dataset are highly valuable to the ice nucleation community, extending J_{het} and n_s toward warmer temperatures. There are, however, many points in the manuscript when the discussion and interpretation of the results are unsupported and unbalanced. Unfortunately, there are a number of instances when the authors make claims that are not supported directly by their data. For example, the authors do not use an electrodynamic balance or investigate the effect of electrical charges on droplet freezing, but claim that electrical charges affect freezing. They do not provide data, nor do they provide a citation to support their contention. Specifically, Diehl et al. claim that other methods are “lacking” in their design because droplets are not freely suspended. The authors are urged to either remove this vaguely statement and any others along the same lines, or provide specific advantages and disadvantages of other methods with concrete citable evidence to back up their claims.

Additionally, in order to put their results into the proper perspective, the authors should compare their data with all available data previously acquired. For example, the analysis by Knopf and Alpert (2013) which use a water activity based description of freezing kinetics of the same type of illite and the same range in temperature and surface area would be appropriate to be compared to the data reported here. Finally, the readability of this manuscript could be greatly improved by combining many of the individual figures as panels. Following 21 figures is overwhelming for a reader! For example, figure 3, 4 and 5 can be combined in a three panel figure, and together represent a nice description of experimental temperature trajectories and how freezing temperatures are defined. Figure 6, 7, and 8 can also be combines to compare the AT dataset for the three IN types. Figure 10 and 11 are exactly the same as Fig. 14 and 15, there is no need for repetition. Similarly, figures with multiple panels having the same y-axis, J_{het} and n_s , and temperature could be combined.

Over all, this paper provides a valuable ice nucleation dataset and I am in favor of it

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being published, however, the authors should address my concerns above and specifically respond to comments below before publication of this paper.

Major Comments: Abstract - p. 12888, l. 4-5 “without electrical charges thereby avoiding any electrical influences which may affect the freezing process.” The authors do not measure the effect of electrical charges on freezing and so any mention of this in the abstract should be removed. More importantly, Krämer et al. (1999) already showed that electrical charges do not affect droplet freezing.

p. 12888, l. 14-16, Here is an example of when the authors do not use their own data to make a clear claim about their results. A major conclusion from this study is that freezing continues when the temperature is held constant and thus, a time independent description is not supported. This should be clearly stated in the abstract. It is fine that both time dependent and time independent descriptions are used to compare results of the current study with previous studies. However, the ‘correctness’ of the time dependent data should be added to the abstract.

p. 12889, l. 13-23, some “lack” in the previous ice nucleation experiments is not measured by the authors or cited in the manuscript . Specifically, what “lack” are the authors referring to here? The references cited, for example Zuberi et al. (2002) and Knopf and Rigg (2011), show that their techniques can measure homogeneous ice nucleation, surely a verification of the correctness of their approach. I will not go into advantages and disadvantages of all experimental techniques, but the authors are not justified in saying that when an experiment does not suspend a droplet in air, this is a “lack”. The authors are free to talk about advantages and disadvantages of any method including their own, but they must do it accurately and specifically with clear citations and descriptions. Along the same lines, why is it so important that a drop should or needs to be levitated? At the end of the paragraph the authors argue that the AT or WT techniques are superior, but again they do not provide any references to support their contention.

Full Screen / Esc

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Interactive Discussion

Discussion Paper

Additional comments on the Intro - stochastic and singular descriptions are not even mentioned. How can it be that a major part of the results and discussion are dedicated to this but these approaches to processing the data are not introduced? These descriptions should be stated and reviewed, I suggest referencing Niedermeier et al. (2010), Alpert et al. (2011), Rigg et al. (2013), or Murray et al. (2011) as these papers are most closely in line with the analysis presented in the manuscript. Assumptions, caveats, and hypotheses in line with the presented research should be provided. For example, the singular description assumes time-independence. If it is found that ice nucleation process proceeds with time, then a singular description is fundamentally not valid.

Finally, Knopf and Alpert (2013) describe a water activity based immersion freezing approach which is applicable for pure water droplets. They also present new immersion freezing data for illite and find agreement with results given by Broadley et al. (2012). Therefore it would be appropriate for the data presented here to also be described by the description and analysis in Knopf and Alpert (2013). This comparison should also be included in the introduction as well as the in the section where the freezing data presented in the current manuscript is analyzed. It would be very interesting to see if the AT or WT could also be described by a time-dependent water activity description. This comparison would greatly benefit the discussion and paper.

Experiment - p. 12890, l. 14, two figures are not necessary to show the experiment since these were used previously. It would be better to have these combined as a two panel figure. This can also help to reduce the number of figures.

p. 12892, l. 16-19 this result requires much more emphasis. The authors are selling themselves short by not discussing homogeneous freezing. Up to this point in the manuscript, there is no evidence that their AT and WT experiments actually work correctly. No comparative data or validation using previous data studies is provided. Measuring homogeneous freezing would be a strong evidence for a properly working experiment. I suggest that the authors calculate the expected homogeneous ice nucle-

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ation temperature and rate coefficient (Riechers et al., 2013; Koop et al., 2000; Koop and Zobrist, 2009). My feeling is that homogeneous freezing will be in agreement with classical nucleation theory, validating the experimental approach. This analysis will only help the paper and method.

p. 12893, l. 21-22 is it important for atmospheric ice nucleation? Do previous studies claim that ventilation and heat transfer affect ice nucleation? Since AT and WT give comparable results, Diehl et al. would be right to claim that this is not important. The authors can remove this statement or alternately state that their study shows evidence that ventilation and heat transfer are not important for ice nucleation under the investigated conditions.

Results - p. 12897, l. 25, to reiterate, Knopf and Alpert (2013) measured freezing with a similar range of surface area and time scales as Diehl et al. and with the same particle type. Therefore, their data should be included in this comparison.

p. 12898, l. 16-19, this is not a good representation of the singular and stochastic descriptions. More effort should go into providing a few reasons behind analyzing data in these ways. Especially here, it is necessary to describe exact advantages and disadvantages of these descriptions. A recent study by Rigg et al. (2013) has done this so it is only necessary to include a few sentences. Also refer to Niedermeier et al. (2010). Some key points should be included. First, a stochastic description is based in classical nucleation theory and thus represents a physical description. It can therefore be applied outside the range of surface areas and time scales investigated in the laboratory. The singular hypothesis is not a physical description and has no theoretical construct therefore it is only a fit to some data and cannot be used outside of the range of laboratory conditions. Atmospheric timescales and the range of particle surface area per cloud droplet are very different than used in this study. Please include this discussion here.

p. 12900, l. 10-12, this is not supported by the data. A single nucleation site type is

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[Interactive
Comment](#)

a non-sequitur here. The results all are in agreement with classical nucleation theory, in that nucleation can take place anywhere on the IN surface and not on a single site. Why then talk about sites which are not observed or measured? There is no physical description of these sites. The result is that heterogeneous ice nucleation follows a time-dependent freezing process and this is completely missing here.

p. 12902, l. 5-7, if the experimental results are inconsistent with the singular description, why is the singular description used to analyze the experimental results? It must be stated here that immersions freezing of these IN types does not follow a singular description. Also, it should be stated that the only reason that a singular description is used, is that previous studies have done so. Still, I find it very curious that the authors are using an analysis which by their own admission is incorrect, to analyze their own data. A justification for this decision should be carefully made.

Conclusions - p. 12904, l. 5-6, please read Krämer et al. (1999). Again, this manuscript has nothing to do with testing how electrical charges affect ice nucleation. Any mention of this should be removed from the conclusion.

p. 12904, l. 7, are there other advantages of AT and WT techniques? It should be stated that droplets can be held at a constant temperature, a significant advantage. Anything else?

p. 12905, l. 4-15, I am confused reading this now. Why is this not mentioned in the intro or discussed and in the results sections? The authors are strongly suggested to clearly state advantages and disadvantages (l. 4-5) of their two techniques. This would be very beneficial to the reader. Why conclude that the experiment could be placed in a table top cold box (l. 9)? This conclusion regarding the benefits and adaptable of these techniques should be more emphasized earlier.

Finally, the conclusion section should include the major findings: 1) The WT and AT reproduce homogeneous ice nucleation of 1 mm sized droplets. 2) Ice nucleation proceeds with time and so the singular description is not valid. 3) A stochastic description

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is supported and verifies that illite, and montmorillonite follows classical nucleation theory. 4) Data is in agreement with previous studies and extends the temperature range of J_{het} and n_s .

Minor Comments: Abstract - p. 12888, l. 6,10 “two types”, “one particle type” Please be specific and states what these are.

p. 12888, l. 8, temperatures down to -28C do not simulate the tropospheric temperature range. It gets colder than that. Please reword.

p. 12888, l. 9, what does remotely mean? Be specific and state what this means, or remove it.

p. 12888, l. 10, “indicated” Indicated by what? This sentence is confusing in terms of what is measured and needs rewording. Please be more specific.

p. 12888, l. 12-14, both sentences essentially say that surface area was used for interpreting freezing. There is repetition and these two could be combined.

Intro - p. 12889, l. 21,22 “two types”, “one particle type”, please specifically state them.

Experimental - p. 12890, l. 3-7, it is not necessary to describe what the experiment was used for in previous studies here, just that details can be found in peer-reviewed literature. Simply stating instrument capabilities is sufficient.

p. 12890, l. 14,15,16, are piezoelectric oscillator and radiator the same thing? This is confusing.

p. 12890, l. 20-21, it is nice that you state what the experimental capabilities are, but please also clearly define what sizes are actually used for which experiment here.

p. 12890, l. 23 - p. 12891, l. 10, the sequence here is a little disjointed. I found myself jumping back and forth between instrument names, function, calibration procedures, etc. . . It would help to spend a little more time to make this section read a little more smoothly.

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p. 12891, l. 13, could ambient particles impact the 1 mm droplet? Is the levitator flushed with particle free air?

p. 12891, l. 11-12, is this why the droplets are 1 mm, because you detect temperature for a 1 mm spot size? If you had a smaller spot size for detection, would you be able to apply smaller droplets in the AT? It is suggested to remove any mention of the WT in this paragraph, it distracts from your explanation of the AT.

p. 12891, l. 18-20, the input power and radiation-reflector distance seem like the key parameters here. A range of these values/metrics should be given so future studies using these techniques can reproduce the data. Please give some sort of specific number here. Frequency, wavelengths, intensities?

p. 12892, l. 2-3, there should be a solution kept in a bottle or tube that fed solution to the needle. Where was the bulk solution and what was its temperature?

p. 12892, l. 5, “signals of the video camera” these are images. Please change.

p. 12892, l. 6-10, please clarify optical detection of freezing and the infrared detection of freezing. It reads like infrared detection was used to determine temperature. If so what was the camera for? What is the freezing temperature exactly? Here would be a good place to say, because at this point I am wondering if it is when the onset of crystallization was identified with the movies, or some distortion in the infrared signal. . . Only in the next section I get my answer, that it is a sharp drop in surface temperature.

p. 12892, l. 13, I did not read that this was mentioned above, see comment for p. 12891, l. 11-12.

p. 12892, l. 16, what parts of the levitator were cleaned? Why does it matter that these were cleaned? I was under the impression that a droplet is freely levitated so a clean surface is not really important? Is there any evidence that by not cleaning the levitator, freezing temperatures are affected? If so, then that would be valuable information for future studies.

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p. 12893, l. 26-27, “Air sucked in from outside” Please change this. Was it compressed air? Was airflow generated by an air blower? What type of filter was used and what were the specs? Was it verified that the air was particle free (homogeneous freezing results would be good here to show that there was no effect of the air flow on freezing).

p. 12894, l. 16-p. 12895, l. 2, all of this should be verified. As freezing was visual determined here, why not visually determining the size to verify that calculations based off terminal velocity are correct? Why not use infrared detection to measure the temperature to verify that equilibration time is calculated correctly? What is the size of the initial injection droplet, how long does it take to shrink due to evaporation to a size when you start your experiment, how much longer to shrink so small that it blows away in the WT? These should be stated.

p. 12895, l. 12-14, didn't Broadley et al. (2012) do composition measurements too? This should be compared.

Results - p. 12896, l. 5, this is not a sufficient explanation of how the surface area per droplet was calculated. A particle concentration is not a surface area. Was spherical particles assumed? Was BET specific surface area used and calculated weight fractions of mineral dust? What is your uncertainty in estimating surface area? It feels like this first paragraph should go in the experimental section.

p. 12896, l. 10 “The results” Which figure is being talked about? Is this some conclusion statement about the results of the whole study put in the beginning of the paragraph? The structure should be reworked here.

p. 12897, l. 11, median freezing temperatures is a little confusing here because the WT method is essentially a constant temperature experiment. It may help to clarify that this means that half of the droplets freeze within a 30 sec observation time. Of course if the experiment is longer, the median freezing temperature would change. Also, it should definitely be stated how many droplets make up a single data point in Fig. 9. What are the vertical error bars? Generally speaking for all figures, how are vertical error bars

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for frozen fraction determined?

p. 12899, l. 21-24, this also means that J_{het} is not a function of surface area and time, only that J_{het} scales with surface area and time. J_{het} is unique for each material involved and scales with temperature according to classical nucleation theory.

p. 12900, l. 15, why was 1 K chosen? Is there a sensitivity analysis for this? What is the error is assuming this? I feel some discussion is missing.

p. 12899, Eq. 4 and p. 12901 Eq. 8 and 9. The authors claim Eq. 4 is valid only for constant temperature, but this does not seem right because frozen fractions, f_{ice} , surface area, s , and time, t can be calculated for a temperature interval and therefore, so can J_{het} . This is exactly what Murray et al. (2011) does. Please carefully determine if this is the case and change if necessary. Zobrist et al. (2007) has a method of calculating J_{het} from experimental data for constant cooling rate experiments. Why would you not use that and with a smaller temperature step than 1 K?

p. 12903, l. 14, extrapolation would not meet each other. If the 3rd order polynomial was extrapolated toward lower temperatures, then it would diverge away from data by Broadley et al. (2012). Is it meant here that both datasets follow a similar exponential trend? This would be a much simpler statement and one that could be easily understood.

Conclusions - p. 12904, l. 14-15, this must be a typo. The author clearly derives nucleation rates for both techniques, see Fig. 16. Conclusions - p. 12904, l. 14-15, this must be a typo. The author clearly derives nucleation rates for both techniques, see Fig. 16.

p. 12904, l. 25 - p. 12905, l. 3, it is strange to conclude that J_{het} and n_s will be used in a cloud model in a forthcoming paper, when this is not previously stated in the manuscript. Please describe how models use J_{het} and n_s data in the intro then it can be easily understood in the conclusion. As it is now, it reads a little disjointed. Also, it is strange to conclude what the INUIT campaign is about when this is not introduced.

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Please give a description of INUIT in the introduction to give the reader. Especially since this paper will be published in a special ACP issue.

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