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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Time dependence of immersion freezing" *by* A. Welti et al.

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Response to the Comments of Anonymous Referee 2

General comment *The authors have investigated the time dependence of immersion freezing of kaolinite particles at several temperatures. This dataset provides an excellent test for different parameterizations used to describe ice nucleation. I congratulate the authors for carrying out elegant experiments that appear to be carefully done. Although the results are excellent, the writing and discussion should be improved before publication in Atmospheric Chemistry and Physics. Below are specific comments.*

We would like to thank the referee for the helpful comments and suggestions. We reply to the individual points below.

Specific comments

1. *The experiments look at freezing from approximately 5% frozen to 95% frozen. Although useful, this does not necessarily cover all atmospheric conditions. For example, under some conditions only a small percentage of the dust particles in the atmosphere may be activated as ice nuclei (IN). Do the results for these measurements at high fraction frozen extrapolate to low fractions frozen? This should be discussed.*

   Although we are not able to directly observe lower frozen fractions with the current experimental setup, the proposed fit curves can be used to derive such. We now mention this in the text.

2. *Some of the references don't seem appropriate. For example, on page 12625, lines 25-29, the authors have the following sentence: "In summary, many major mixed-phase cloud characteristics (light scattering, precipitation formation, chemistry) depend on the size of the cloud droplets, which in turn is linked by the Bergeron-Findeisen process to the rate at which ice nucleates in the interior of the supercooled cloud droplets (Tabazadeh et al., 2002)." Tabazadeh et al. 2002 focuses on surface nucleation of water droplets, so this reference doesn't seem appropriate. Please carefully check all references to ensure only appropriate references.*

   Tabazadeh et al., 2002 discuss the importance of cloud glaciation in the introduction. We agree that it is not the focus of their article but used to motivate their work. We restructured this part of the introduction and removed the citation. The other references have been checked and revised where needed.

3. *In the introduction the authors do mention briefly that others have experimentally investigated the stochastic and singular component in immersion freezing. However, the authors could do a better job of describing what has been done previously and how their experiments are different than previous work. For example have others looked at time dependent freezing of mineral dust, and do the conclusions from the current study differ from previous conclusions?*

   There are recent and older studies that addressed time dependence of immersion freezing. The main difference to this study is that it is the first to show a time dependence in a laboratory experiment measuring single immersed particles under atmospherically relevant conditions (droplets suspended in air). We extended the discussion of recent results on time dependent freezing of mineral dust immersed in droplets in the introduction.

4. *Abstract, line 17-20. Should this sentence read "... yields an equivalent effect of -1K temperature shift for an increase in time scale by a factor of 10"?*

   We changed the sentence to: "... yields an equivalent effect of -1K temperature shift for an increase in times scale by one order of magnitude. This suggests that temperature is more important than time."

5. *Is it possible that in your experiments some of the kaolinite particles are not activated as CCN? This is probably discussed in Lüönd et al. (2010), but it is worth repeating this discussion here.*

   Yes, it is possible that a small faction of kaolinite particles did not activate as CCN even at 120% RH_w and 300K. Lüönd et al. (2010) discussed the possibility that a small fraction of particles might exit the IMCA section unimmersed what could lead to a small contribution from deposition nucleation to the total ice fraction. Based on experiments with the same kaolinite in the deposition mode we know that the fraction of unimmersed particles able to serve as IN is below 10% in the investigated temperature range and at water saturation. Ice crystals forming

   via the deposition mode can therefore be expected to be very rare. Therefore their contribution can be neglected. In addition the unimersed particles do not interfere with the dorplet or ice crystal signals detected by IODE because they are too small in size and number. This is discussed in Lüönd et al. (2010) at the end of section 2. Since the contribution is very minor we assume that all particles activate as CCN in the current work. See response to comment nr. 3 of Gabor Vali.

6. *Figure 4 shows a curve for homogeneous freezing. How was this calculated and what are the uncertainties of this calculation? The homogeneous curve overlaps slightly with the heterogeneous freezing data at 236 K. Has this been taken into account when fitting the heterogeneous data? If not please explain why it is valid to ignore this overlap.*

   The homogeneous freezing curve is derived from the nucleation rates reported in Earle et al. (2010). There might be a contribution to the measured frozen fraction at 236K due to homogeneous freezing. However no discontinuity is observed which could be attributed to the onset of homogeneous freezing. Therefore we conclude that the theoretical calculated droplet size over predicts the real size of the droplets formed in IMCA and the shown homogeneous freezing curve is rather conservative. One reason why the calculation over predicts the real droplet size could be that the calculation does not include a droplet nucleation process but only diffusional growth.Reference measurements with an equivalent experimental setup using $(NH_4)_2SO_4$ particles (reported in Hoyle et al. (2011)) showed the onset of homogeneous freezing to take place at 235K. We changed the given line in the figure accordingly.

7. *Page 12630, line 19-21. Please quantify what you mean by minor. Less than 1%?*

   As the droplets are cooled down to the experimental conditions in ZINC, they

reach temperatures suitable for immersion freezing on kaolinite particles (below 245K) 1-2 seconds before the conditions are stable in the experiment. The reported nucleation times might therefore be biased by that time towards shorter residence times. We now wrote: " The nucleation events during the cooling of the particles to the experimental temperature prevailing in ZINC induces a systematic uncertainty in the reported nucleation time of up to 2 seconds where nucleation might occur at higher temperatures."

8. *Page 12630, line 24. Please quantify what you mean by small. Less than 1%?*

   Nucleation might be shut off 1 seconds before the frozen fraction is detected. The data reported to be measured after 21.4s might therefore rather correspond to 20.4s. We calculate the droplet temperature to reach the set experimental temperature within 0.3 seconds. Now we wrote: " The reported time for nucleation might therefore be 1s shorter what could lead to a small systematic bias... ."

9. *Page 12632, line 22-24. "Compared to homogeneous freezing however, immersion freezing has a gentler slope in the frozen fraction. This indicates a temperature dependent increase in the reduction of the energy barrier to ice nucleation." I struggled to understand what the authors are trying to say in the second sentence. Please restate to make this point more clear.*

   We intended to say that the nucleation kinetics becomes more important towards homogeneous freezing temperatures and surface features aiding the nucleation process become more important towards higher temperatures. We reformulated the statement to

10. *Page 12633, line 1-3. Please state here what the error bars represent in the figure and how they were determined.*

    The error bars represent an uncertainty in the frozen fraction due to the classification (liquid or ice) uncertainty originating from the measurement errors of the

IODE detector. Particles are classified to be ice crystals or water droplets due to the depolarization ratio of backscattered polarized incident laser light. A threshold depolarization ratio has been determined experimentally (reported in Lüönd et al. (2010)). Each depolarization signal is classified according to the depolarization threshold. However, the depolarization ratio of each detected particle is allocated with an uncertainty due to electronic noise. If the depolarization threshold lies within a one sigma standard deviation of a signal, the particle is counted as potentially misclassified. Error bars are calculated as the ratio of potentially miscounted droplets or ice crystals in minus and plus direction respectively. We added a short explanation and reference to the description given in Lüönd et al. (2010).

11. *Page 12638. The authors should also state that although the alpha-pdf model gave the best fits, this model was not able to fit all the data within experimental error. This probably should also be mentioned in the conclusions and the abstract.*

    We agree that it has to be stressed that non of the models was able to fit the measurements within the experimental error. We added that to the conclusion.

12. *Page 12640, lines 219-25. "The rapid change in the frozen fraction for increasing residence time, calculated for the active site model is unexpected, as this model, although also based on CNT, is conceptually closer to the singular model than the alpha-pdf or the stochastic model." To me this is not surprising. Both the alpha-pdf and the active site model can approach the stochastic model depending on the parameters used in the model. In your case, the fits have given parameters that make the active site model closer to the stochastic model compared to the alpha-pdf model.*

    For the α-pdf this is true but the probability density function (taken form Marcolli et al. (2007)) which is inherent in the active site model prevents an attribution of

a constant contact angle to all the active sites. The function predescribes a steep increase in the probability of larger contact angles. We would have expected, that the rare, small contact angles attributed to the small surface area of an active site would initiate ice nucleation in a small temperature range followed by little additional freezing with time initiated by particles which do not contain the efficient active sites. Therefore we prefer to leave that statement as is.

13. *Please include references for Equations 13 and 14.*

    Equations 13 and 14 are deduced from the so called d^2-law for the evaporation of droplets put forward by Maxwell. We added a textbook reference. In addition there was a factor of 2 missing in equation 13. This has been corrected.

14. *Page 12640, lines 23. "Probably the assumption of a 6nmËĘ2 active site area and the resulting number of active sites generated per particle is too high." I don't think this discussion is necessary and could be removed especially since it is speculative.*

    This is a possible explanation for the statement already mentioned in comment 12 i.e. that the high number of active sites causes the surface to appear on average more homogeneous therefore resulting in the active site model appearing stochastic-like where only one contact angle is assumed. We think this is an interesting conclusion that single active sites might not be the most important feature that trigger ice nucleation but rather the stochastic cluster formation aided by a larger number (surface area) of average active sites.

15. *Page 12642, line 9. Do the authors have a reference to show that mineral dust is partly hydrophobic.*

    A recent atomic force microscopy (AFM) study by Yin and Miller (2012) demonstrated the hydrophobic property of the silica tetrahedral face of kaolinite whereas the aluminum octraedral face did not exhibit hydrophobic properties. We added the reference.

16. *Page 12642, line 15-16. "Also the observable time dependence of the frozen fraction would be distinctly different for different IN, as can be already seen in the variance between the two tested particle sizes." I don't see how the variance between the two tested particle sizes necessarily tells you anything about the possible difference between particles with different chemical compositions. The authors have not proven that the differences they observed between the two sizes is due to a difference in chemical composition.*

    Previous studies have shown different freezing efficiencies of different substances e.g. Pinti et al. (2012) and also different freezing efficiencies of the same substance dependent on particle size (Lüönd et al., 2010). The time dependence is less pronounced in the 800 nm sample. However, if a 400 nm particle sample of a more efficient IN (due to a different chemical composition) was used, this would also hinder the observation of time dependence in the first 22 s much like what we observed with the 800 nm kaolinite particles. In one case the increased IN efficiency is due to an increase in particle size and the other due to a more favorable IN species (of different composition compared to kaolinite). In other words, depending on the temperature where ice nucleation can be observed the relative importance of surface features and of nucleation kinetics vary in the way that surface features are more important at higher temperatures. This effect is evident when comparing the experimental data for 400 and 800 nm particles. The time dependence is less pronounced for larger particles as higher frozen fractions are already reached at higher temperatures. Therefore we conclude that if another mineral dust species is active at a higher temperature the time dependence would be less pronounced in the first 22 s of nucleation, whereas for a less efficient IN the kinetic effect dominates and as ice formation would be observed at lower temperatures it would appear more stochastic. For clarification we added: "Small ice clusters are formed with a higher probability. With decreasing size of the critical ice embryo towards homogeneous freezing temperatures, surface features (that would be different for different IN samples and particle sizes) which can reduce

the number of molecules needed for a stable ice cluster become less important."

17. *Page 12642, line 18-19. "The IN activity could also be an impermanent feature, as from the moment the aerosols are released into the atmosphere until they become active in clouds they are exposed to sunlight and chemical compounds in the air that might lead to loss or increase of their nucleation activity..." The authors could add references here.*

    We added some references. (Cziczo et al., 2009; Yang et al., 2011; Chou et al., 2012)

18. *Page 12642, line 25-26. "Therefore we recommend to include a time-dependence in numerical calculations of the evolution of mixed-phase clouds." It should be mentioned that this recommendation is based on only the current study, which utilized one mineral from one vendor, whereas mineral dust in the atmosphere can contain many different minerals. At this point the authors could also discuss if all other studies carried out with mineral dust are consistent with this recommendation.*

    We included a discussion of the results by Murray et al. (2011), Broadley et al. (2012) and Ervens and Feingold (2012) and we state that the recommendation is based on the results of the current study.

19. *Page 12643, lines 23-26 and page 12644, lines 1-12. This section was confusing to me. On one hand, this paper shows that a single contact angle and classical nucleation theory cannot describe the experimental data well, but on the other hand, in this section the authors are using a single contact angle and classical nucleation theory to derive a surface tension. It is not clear to me that the surface tensions from this analysis have any physical meaning.*

    Using a single temperature dependent contact angle might be less costly to implement in a model than a contact angle distribution or active sites. It is also

    widely accepted that the surface tension is a temperature dependent factor what leads to the conclusion that a temperature dependence of the contact angles could be a physically meaningful extension and should be pursued in future attempts to use CNT to parameterize ice nucleation. We state that: "This test confirms that it is plausible to attribute a change in contact angle to a change in surface tension with temperature. However, to conclude on the physical meaning of this finding, is out of scope of this study."

20. *Page 12644, lines 13-17. It would be interesting to see a comparison between predictions with the average active contact angle of the population and the time dependent data, similar to the comparisons shown in Figure 7. Otherwise it is hard to judge the accuracy of the average active contact angle of the population.*

    The discussion of a temperature dependent contact angle is meant to show the possibility of a different approach than in the four models presented in the result section and not a main result. However the comparison is shown in Figure 1. A temperature dependent contact angle allows to adjust the steepness of the nucleation rate as shown below in Figure 1 in the response to the comment of referee 1, therefore improves the fit curves compared to a single contact angle model. We will provide the figure as a supplement for the interested reader.

21. *Section 6.2. The authors do not refer to any figures in this section. Does the discussion refer to figure 10?*

    Yes. We clarified that.

22. *Figure 2. I assume the data shown in this figure is based on calculations. This should be stated and references to the calculations included. Do the calculations for droplet radius assume monodispersed droplets?*

    Figure 2 shows results from a Fluent simulation of the experimental conditions. We clarified that in the figure caption. The droplet radius is calculated assuming

diffusional growth without accounting for a droplet nucleation process resulting in monodisperse droplets. The real droplet size is overestimated due to this assumption and a droplet size distribution can be expected. The droplet size was calculated to confirm that droplets survive the transition from IMCA to ZINC.

23. *Figure 3. I don't see a black line in this figure.*

    We increased the line thickness to make the line more visible.

24. *Figure 4, 5, and 7. Please clarify what the error bars represent in these figures. Do the error bars represent the standard deviations of the measurements (one sigma or two sigma) or do they represent confidence intervals.*

    The error bars represent the variability in the frozen fraction due to potentially miscounts of particles as being ice crystals or droplets due to the set depolarization threshold which is described in Lüönd et al. (2010). section 3.2. See response to comment 10.

Technical corrections

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References

Broadley, S. L., Murray, B. J., Herbert, R. J., Atkinson, J. D., Dobbie, S., Malkin, T. L., Condliffe, E., and Neve, L.: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust, Atmos. Chem. Phys., 12, 287–307, 2012.

Chou, C., Stetzer, O., Tritscher, T., Chirico, R., Heringa, M. F., Kanji, Z. A., Weingartner, E., Prévôt, A. S. H., Baltensperger, U., and Lohmann, U.: Effect of photochemical aging on the ice nucleation properties of diesel and wood burning particles, Atmos. Chem. Phys. Discuss., 12, 14 697 – 14 726, 2012.

Cziczo, D. J., Froyd, K. D., Gallavardin, S. J., Moehler, O., Benz, S., Saathoff, H., and Murphy, D. M.: Deactivation of ice nuclei due to atmospherically relevant surface coatings, Environ. Res. Lett., 4, doi:10.1088/1748-9326/4/4/044013, 2009.

Earle, M. E., Kuhn, T., Khalizov, A. F., and Sloan, J. J.: Volume nucleation rates for homogeneous freezing in supercooled water microdroplets: results from a combined experimental and modelling approach, Atmos. Chem. Phys., 10, 7945–7961, doi:10.5194/acp-10-7945-2010, 2010.

Ervens, B. and Feingold, G.: On the representation of immersion and condensation freezing in cloud models using different nucleation schemes, Atmos. Chem. Phys., 12, 5807 – 5826, 2012.

Hoyle, C. R., Pinti, V., Welti, A., Zobrist, B., Marcolli, C., Luo, B., Höskuldsson, A., Mattsson, H., Stetzer, O., Thorsteinsson, T., Larsen, G., and Peter, T.: Ice nucleation properties of volcanic ash from Eyjafjallajökull, Atmos. Chem. Phys., 11, 9911 – 9926, 2011.

Lüönd, F., Stetzer, O., Welti, A., and Lohmann, U.: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode, J. Geophys. Res., 115, D14201, doi:10.1029/2009JD012959, 2010.

Marcolli, C., Gedamke, S., and Zobrist, B.: Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081 – 5091, 2007.

Murray, B., Broadley, S., Wilson, T., Atkinson, J., and Wills, R.: Heterogeneous freezing of water droplets containing kaolinite particles, Atmos. Chem. Phys., 11, 4191–4207, doi:10.5194/acp-11-4191-2011, 2011.

Niedermeier, D., Shaw, R. A., Hartmann, S., Wexx, H., Clauss, T., Voigtländer, J., and Stratmann, F.: Heterogeneous ice nucleation: exploring the transition from stochastic to singular freezing behavior, Atmos. Chem. Phys., 11, 8767–8775, 2011.

Pinti, V., Marcolli, C., Zobrist, B., Hoyle, C. R., and Peter, T.: Ice nucleation efficiency of clay minerals in the immersion mode, Atmos. Chem. Phys., 12, 5859 – 5878, 2012.

Yin, X. and Miller, J.: Wettability of kaolinite basal planes based on surface measurements using atomic force microscopy, Minerals & Metallurgical Processing, 29(1), 13 – 19, 2012.

Yang, Z., Bertram, A., and Chou, K.: Why Do Sulfuric Acid Coatings Influence the Ice Nucleation Properties of Mineral Dust Particles in the Atmosphere?, J. Phys. Chem. Lett., 2, 1232 – 1236, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12623, 2012.

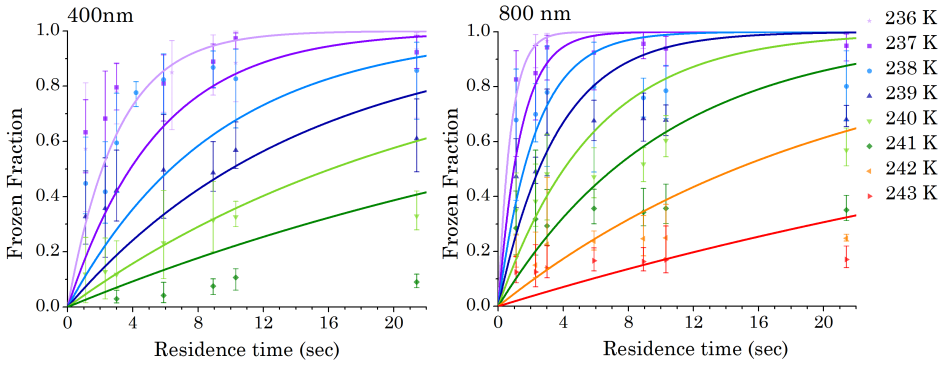

Fig. 1. Comparison of the fit curves obtained from a stochastic description of the nucleation process with a temperature dependent contact angle for 400 and 800 nm kaolinite particles to experimental data.