Responses to the referees:

Referee 1:

The manuscript by Nagare et al. describes a comparison between immersion and contact freezing in the ETH Collision Ice Nucleation Chamber and the Immersion Mode Cooling Chamber/Zurich Ice Nucleation Chamber. Unlike previous studies, an enhancement of contact mode over the immersion mode was not seen.

I am supportive of publication. That said, there is some ambiguity in the way that the freezing efficiency is defined and/or used in the paper that should be clarified. In addition, I think that the authors should discuss the discrepancy between their measurements and those of other groups in more detail.

*We thank the reviewer for the careful reading of the manuscript and the suggestions for improvement. We address the comments below point by point (in italic):*

## Freezing efficiency

I think I am not quite following how $FE$ is defined and used. In the text $FE$ is defined as

$$FE = \frac{FF}{N} \tag{1}$$

where $FF$ is the fraction of droplets that have frozen and $N$ is defined as the number of collisions between a droplet and aerosol particles. If I combine the definition of $FF$ and equation 1, the result is

$$FE = \frac{freezing\ events}{total\ droplet{-}aerosol\ collisions} \tag{2}$$

which can be interpreted as the probability that a single collision between an unfrozen droplet and an aerosol particle results in a freezing event. This is the interpretation, used for example, in Hoffmann et al. [1] and Niehaus et al. [2]. My confusion is from the discussion around the case when the first collision between aerosol and droplet results in a freezing event. If that is the case, then intuitively, $FE = 1$. I dont understand the point of Equation 4 in the manuscript. The denominator is defined as the fraction of unfrozen droplets after $N$ collisions, but $1 - e^{-N}$ is defined in Nagare et al. (2015) [3] as $FF$ (see Equation 19). If the denominator *is* $FF$, then Equation 4 in the manuscript makes sense because it reduces to $FE = 1$.

*There is an ambiguity in the freezing efficiency determined by the CLINCH experiment when the droplet collides with more than 1 particle while it passes through the chamber, because in this case, it is not clear which collision is responsible for freezing. A second or a third collision might occur although they are not needed to freeze the droplet when it has frozen already on the first collision. To convert from FF to FE, only collisions of particles with liquid droplets should be counted. The reviewer is right that*

*Eq. 4 should only be used when FE = 1. This is the case for AgI at temperatures for which the plateau condition applied in Nagare et al. (2015) is valid. Using Eq. (1), FE at the highest AgI concentration is lowest. A result that is not easily explained. Therefore, we introduced Eq. (4) for this case.*

*From this it can be concluded that experiments should be run such that the average number of collisions is close to but below one. In this case, Eq. (1) of the manuscript can always be used. We have improved the discussion of Eqs. (1) and (4) in the revised manuscript.*

I am also confused by the statement in lines 6 and 7 on page 6. "...$FE$ should be independent of residence time when..." Shouldnt $FE$ always be independent of residence time? The number of freezing events will depend on the residence time, since a longer residence time is a greater probability that the droplet will collide enough particles to catalyze freezing, but once you have normalized by the number of droplet-aerosol collisions, $FE$ should be a probability, which is independent of time.

*In the case of collisional contact freezing, FE should be indeed independent of time. However, in the case of immersion freezing and adhesion freezing, FE depends on time. This is why we use FE(4s) > FE(2s) as criterion against collisional contact freezing. We have improved the text in the revised manuscript to make this clearer.*

Figure 4 is also a source of confusion for me. How is $FE > 1$ possible, as is shown in panel b for $T < 245$. If I understand the definition of $FE$ correctly, this implies that there are more freezing events than there are aerosol-droplet collisions. Under the assumption of panel b, shouldnt all these data points collapse to 1 for $T \leq 245$? I am also not understanding how $FE$ is a function of the aerosol concentration. $FF$ should be a function of the concentration, but the point of normalizing by the number of collisions is to remove that dependence.

*FE > 1 is due to homogeneous freezing and measurement uncertainties. We add this statement to the revised manuscript. Indeed, FE should not be a function of concentration.*

## Immersion vs. contact freezing

Based on a difference in the freezing efficiency with a residence time of 2 seconds vs. 4 seconds, the authors conclude that contact freezing is not enhanced over immersion freezing, at least not for the Arizona Test Dust, and perhaps not for silver iodide. This claim is also supported by the comparison to immersion freezing results using IMCA/ZINC. (See my discussion above concerning confusion about $FE$ and a time dependence.)

This is a striking result, considering the previous work in the field. Gokhale and Goold [4] tested AgI for contact freezing, and showed that freezing was initiated at temperatures close to -5 °C in the contact mode while temperatures closer to -15 °C were necessary for immersion mode freezing. Sax and Goldsmith [5] also tested AgI, in a cold room with freely suspended droplets, and saw indications of a shift to lower temperatures for the onset of freezing for contact vs. immersion freezing. These results are directly relevant to the experiments described here. While the freezing efficiency is not reported in either of these papers, they do discuss a shift in the onset freezing temperature, which can be compared, for example, to Figure 1 in this paper, which unambiguously shows that droplets begin to freeze at about -8 ˚C in the immersion mode and only at -13 ˚C in the $\boldsymbol{FE}(4s)$ experiments in the contact mode. (See also Gokhale and Spengler [6] and Gokhale and Lewinter [7]. Tests with AgI were conducted in both of those studies as well.)

*We expected to observe a higher freezing efficiency for AgI in CLINCH than in IMCA/ZINC. We were very astonished that we observed the opposite. We went therefore back to literature and studied the previous work. Because so many studies have been performed with AgI as ice nucleus, we decided that a profound discussion of all this literature would make the paper too long. Therefore we wrote a companion paper, which reviews ice nucleation studies with AgI. This paper is now also published in ACPD: Marcolli C., Nagare, B., Welti, A., and Lohmann U.: Ice nucleation efficiency of AgI: review and new insights, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-142, 2016.*

*In this paper, we refer to the literature mentioned by the reviewer. On page 4, we write:*

*Gokhale and Goold (1968) performed contact nucleation experiments by sprinkling AgI particles on supercooled droplets on a hydrophobic plate. They observed that the particles (5 – 400 µm in diameter) remained on the surface of the drops and initiated freezing at the initial stage temperature of 268 K. However, they did not quantify the number of particles present, which precludes an evaluation in terms of surface area. They performed similar experiments for an AgI smoke produced from an AgI string generator with particle diameters from 50 – 100 nm. These particles initiated freezing of 50 % of droplets at 263 K when the stage was cooled at a rate of 1.3 K/min. Gokhale and Goold (1968) concluded that these freezing temperatures are 5 – 10 K higher than the ones observed by Hoffer (1961) for droplets embedded in an oil with immersed AgI particles and attributed it to an enhanced freezing probability for dry particles on a surface compared with particles immersed in the droplet. However, a strict comparison is not possible because in both studies, information is lacking to quantify the surface area present per droplet. In a follow-up study, Gokhale and Lewinter (1971) monitored the freezing process of 2 mm water droplets with a movie camera and observed that nucleation was initiated at the point of particle contact and continued from there over the entire surface of the drop. The interior of the drop froze at a much slower rate.*

*On page 5, we write:*

*Sax and Goldsmith (1972) performed contact and immersion freezing experiments in a cloud chamber. Freely falling droplets with diameters of 40 – 160 µm (average: 100 µm) intercepted a horizontal aerosol stream of $5\cdot10^{6}$ $cm^{-3}$ AgI particles with 30 nm diameter (size range from 10 – 40 nm) for 0.04 s*

*(1 cm in vertical extent). The aerosol was produced by heating an AgI-coated resistance wire to T = 700°C in a nitrogen stream. For contact freezing experiments the droplets were brought in thermal equilibrium before intercepting the aerosol stream. After coagulation with the AgI particles, the droplets proceeded into an observation chamber where frozen droplets were distinguished visually from liquid ones. Coagulation of 100 µm droplets with 30 nm particles were dominated by Brownian motion. Assuming a collision efficiency of ca. 0.3, around 100 particles would be captured by the droplet (note that this number is higher than the collection of only 1 particle estimated by Sax and Goldsmith, 1972). For immersion freezing experiments, the droplets passed the aerosol stream at T > 273 K, before they were cooled to the target temperature. Residence time in the chamber was around 4 s. Immersion freezing occurred at 2 K lower temperature than contact freezing.*

*In Marcolli et al. (2016) we give possible explanations why FE in IMCA/ZINC was higher than in CLINCH. To avoid telling the same in two papers, we do not want to extend the discussion in the present manuscript but prefer to refer to the companion paper.*

Similarly, Pitter and Pruppacher [8] tested kaolinite in a wind tunnel and found a clear shift to lower temperatures for the onset of freezing when changing from contact to immersion mode experiments. Niehaus et al. [9] report that they ran experiments in which a freezing event occurred, then melted the droplet and cooled it back to the original temperature. No freezing events occurred. Niehaus et al. concluded that these tests, in which the same aerosol were compared against themselves, that contact freezing was more probable than was immersion mode. (ATD was among the substances they tested.) Though AgI, kaolinite, nor ATD was tested in the study, in an even more convincing case of an enhancement of contact freezing over immersion mode, Durant and Shaw [10], visually confirmed a shift in the freezing temperature when a particle was at the air-water interface. (See their Figure 1.)

*Thank you for pointing out the study of Pitter and Pruppacher. We now refer to it in the revised manuscript. We referred to the Niehaus et al. (2014) paper in the introduction and discussed it in Section 5.5. We add in the revised manuscript that Niehaus et al. concluded that contact freezing was more probable than immersion freezing for the ice nuclei that they investigated.*

As noted above, I am in favor of publication because I believe that more information on these systems will help the community to unravel the complexities and, perhaps, make a determination as to just how important contact freezing is in Earth' s atmosphere. That said, I believe that the authors should place their results more clearly in the context of previous work.

## Other comments

**Discussion of uncertainties:** The authors discuss the uncertainty in the frozen fraction as stemming from the classification uncertainty of the IODE detector (see, e.g. the caption to Fig. 5.). Shouldnt the uncertainty in the number of particles that have collided with the droplet be included when showing $FE$? I realize that different values of $N$ are used, depending on the value of $CE$, but even so, there is an uncertainty in $CE$ and thus $N$. An indication of that uncertainty would help in interpreting these plots.

*We agree that the main uncertainty for the comparison of freezing mechanisms results from uncertainties in CE. We think that it is more transparent to show results with different assumptions of CE rather than to draw huge error bars. To make it clearer that the uncertainty of FE is due to the uncertainty of CE, we added the following sentence to the Section 4.3 in the revised manuscript: "The difference in FE between panels (c) and (d) must be considered as an uncertainty in FE due to the lack of reliable theoretical values of CE in the investigated temperature and particle size range." In Section 4.4 we add: "For panel (a) the theoretical formulations were used, while panels (b) and (c) give the upper and lower limit of FE, respectively."*

**Discussion of contact freezing mechanisms:** Pg. 8, line 29. "This mechanism was refuted by Fukuta (1975b). "Refute" implies that he disproved Cooper's mechanism. I think he rejected it, but did not disprove it.

*Thank you for pointing this out, we change it as suggested.*

Pg. 9, line 18. "This indicates that collision itself does not increase $FE$..." There is evidence that the collision can increase $FE$. Davis et al. [11] recently showed that salt particles can initiate efflorescence upon contact with a supersaturated solution of a different salt. Niehaus and Cantrell [12] observed freezing events initiated by soluble salts at temperatures above the eutectic. Finally, Yang et al. [13] have observed freezing which may be in response to the movement of the triple line, as from a collision.

*Thank you for pointing out these papers. Niehaus and Cantrell indeed made plausible that the collision triggered freezing. To have an effect, the particles that collided with the droplets needed to be large so that the impact led to a mechanical disturbance. For 10 µm NaCl particles no effect was observed. Therefore, this process is likely not active in our experiment. However, we mention this study in the revised manuscript to illustrate that the collision may induce freezing when the impact is large enough. Davis et al. investigated contact efflorescence by bringing soluble salts in contact with supersaturated solution droplets. In this case, nucleation has to occur immediately after contact before the salt particle dissolves in the solution droplet. There is no immersion mode setup conceivable to compare the freezing efficiencies. Therefore it cannot be concluded whether the collision itself is responsible for freezing. In the experiment by Yang et al., no collision was involved in ice nucleation but a movement of the three-phase contact line when the droplet adjusted to the changing electric field.*

pg. 13, line3 28-29: "One reason for this may be that in CLINCH and IMCA/ZINC experiments the particles are free to realize the energetically most favorable position in or on the droplet." This may be true, but it is also true for many of the other experiments noted above.

*Indeed, the experimental conditions have to be considered in detail. In case of AgI, a detailed discussion is given in the companion paper.*

pg. 14, line 5: “Own observations...” I think you mean to start that sentence with “Our”.

*Thank you for pointing this out.*

Table A1: Include $N$.

*We add N in the revised manuscript.*

# Bibliography

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[13] F. Yang, R. A. Shaw, C. W. Gurganus, S. K. Chong, and Y. K. Yap. Ice nucleation at the contact line triggered by transient electrowetting fields. *Applied Physics Letters*, 107(26):264101, 2015.

*Referees 2:*

***We thank Alexei Kiselev and Nadine Hoffmann for their careful reading of the manuscript and the suggestions for improvement. We address the points raised by them below (in italic).***

The manuscript of Nagare et al. describes contact freezing experiments conducted with supercooled droplets freely falling through the chamber containing ice nucleating (IN) aerosol particles. At the first glance, this seems to be the ideal experimental setup to study the evasive phenomena of contact freezing. The temperature regime, humidity, droplet and particle size are all atmospheric relevant.
Already the second glance reveals the difficulties in measuring the magnitudes in question (collision efficiency, CE, and freezing efficiency, FE) and interpreting the observation results. Most puzzling, the authors report no enhancement of contact freezing compared to the immersion freezing conducted with the same IN particles and in similar setup. We share the attitude of the Reviewer 1 that the manuscript should be published to provide the basis for the discussion of the presented measurements and data interpretation. There are some issues, however, that could be improved at the stage of preparation of the final manuscript that we would like to discuss here.

To our opinion, the main conclusion about the role of contact freezing made in this paper is a direct consequence of the method used to measure the CE and the approach used to compare the contact and immersion freezing behavior. We discuss these issues below followed by more specific remarks.

1. The uncertainty in interpretation of contact freezing results is obviously related to the uncertainty of determination of collision efficiency. The CE experimentally determined for 0.2 μm AgI particles (0.13) was reported being 14 times larger than calculated theoretical value. What could be the reason for such a high discrepancy? The degree of control of the experimental parameters (temperature, humidity, size and evaporation rate of the droplets, particle number concentration, droplet charge etc.) is very high, and all known interaction forces seem to be taken into account. On the other hand, the sensitivity of experimental observables to the value of the CE is very strong (see equation 19 and discussion of figure 4 in (Nagare et al., 2015), so that its knowledge is crucial for drawing a conclusion about the role of the contact freezing.

***We discussed collision efficiency in Nagare et al. (2015) and concluded that the discrepancy should come from phoretic forces that seem to be not well constrained at low temperature. Indeed, we presented in Nagare et al. (2015) the first dataset of CE acquired at sub-zero temperatures.***

One of the possible explanations would be the depletion of the IN particle concentration within the volume swept by the droplet train. Water droplets generated with 100 Hz frequency and falling with 0.186 m/s terminal velocity would be separated by 2 mm distance or 0.01 s time lag. The RMS diffusion displacement calculated for 0.2 μm diameter particle (Hinds, 1999, equation 7.18) is about 2e-6 m. Assuming the CE for 0.2 μm AgI particles equal to 0.13, the radius of the cylindrical volume where a falling 80 μm droplet experiences collisions with aerosol particles is

$$r_{drop} \times (CE)^{0.5} = 4 \times 10^{-5} m \times (0.13)^{0.5} = 1.4 \times 10^{-5} m,$$

seven times larger than the RMS Brownian displacement of the AgI particle within the droplet inter-arrival time. This essentially means that the particle number concentration reduced due to the scavenging by falling droplet will not return to equilibrium before the next droplet arrives. Reduced number concentration has to be compensated by higher apparent freezing efficiency (according to equation 19 from (Nagare et al., 2015) to describe the observed fraction of frozen droplets. This back-of-the-envelope calculation shows that the depletion of aerosol in the droplet train zone is quite possible and might affect the calculation of the collision efficiency. For larger aerosol particles the depletion can be even larger.

***We discussed CE in depth in Nagare et al. (2015). We concluded that the distance between droplets should be large enough to avoid any interference. If depletion of IN particles between droplets occurred, the injected concentration of aerosol particles would be higher than the one experienced by the droplet. This means that we insert a too high concentration into Eq. 19 from Nagare et al. (2015). When we insert the correct lower concentration into Eq. 19, CE would need to be even higher to realize the measured FF. This would not decrease but increase the difference between measured and calculated CE.***

2. We share the confusion of reviewer 1 with respect to the discussion of freezing efficiency calculated with equation 1 or equation 4 (Section 4.1). In your preceding paper (Nagare et al., 2015) the CE has been calculated with equation 19, which is just equation 4 of this manuscript under assumption that FE = 1. To my understanding, with the CE defined in this way the FE should be derived using equation 4 and not with the equation 1. It is correct that the time independence of FE should indicate the contact freezing but it has nothing to do with the number of collisions required to induce the freezing, it can happen on the first collision or after several dozens of them and still have to be the dominant mechanism. Surely the choice of equation could not be helpful to decide which freezing mechanism is dominating the apparent freezing rate of the droplets.

***Eq. (4) applies when the first of several collisions leads to freezing. This is the case for the plateau condition that we used in Nagare et al. (2015) to derive CE for AgI. However, this is not always the case. With other setups one can observe the number of collisions that is needed for freezing (e.g. Hoffmann et al., 2013a; 2013b; Niehaus et al. 2014). If indeed several collisions are needed to induce freezing, Eq (1) leads to a more accurate number for CE. Therefore, one has to decide from case to case whether Eq. (1) or (4) applies. This introduces an additional uncertainty in the derivation of FE. See also answer to reviewer 1. Since reviewers 1 and 2 were confused by our procedure to derive FE, we improve the text in the revised manuscript by adding before Eq. (1):***

***"If a droplet freezes after more than one particle hit it, it is not clear which particle induced freezing. Assuming that all collisions were needed for freezing leads to the following equation:"***

3. Why is the freezing induced by a particle adhering to the surface of the droplet called "freezing inside-out" throughout the paper? In the original paper (Durant and Shaw, 2005) the IN particle was penetrating the surface from inside of an evaporating droplet, hence the name. In the present manuscript this name is used to describe the situation where an IN particle adheres to the surface and is only partly immersed into the droplet, as compared to the fully immersion freezing mode in IMCA/ZINC. To our understanding, partial immersion does not imply a new nucleation mechanism different. As have been shown in (Hoffmann et al., 2013a), the contact freezing efficiency of mineral dust IN particles is proportional to the surface area of the particle. We argue there that the term "contact freezing" does not imply freezing on a point contact but a considerable fraction of particle surface has to be involved into the freezing process. The term "freezing inside-out" was used to highlight the process of penetration of the droplet surface, and is not fully applicable in the present manuscript. Please consider removing this term from the paper.

*By calling freezing induced by a particle adhering to the surface "contact freezing inside-out", we wanted to discriminate it from collisional contact freezing and emphasize the similarity to contact freezing inside-out. While in the experiments performed by Durant and Shaw, 2005 the position of the particle with respect to the droplet was fixed, in our experiment the particle is free to take the energetically most favorable position in or on the droplet. Similar to Durant and Shaw, we claim that the position on the surface may be able to induce freezing at a higher temperature than if the particle is totally immersed. We recognize the difference to "contact freezing inside-out" and will therefore call it "adhesion freezing" in the revised manuscript.*

4. Based on the comparison of FF and freezing onset temperatures you conclude that the contact freezing is a not dominant freezing process. This conclusion seems questionable, because to our opinion the true value of a contact FE for AgI cannot be derived from the experiment. A better way to compare the two freezing process is based on their characteristic times, as suggested in (Hoffmann et al., 2013b). There we have introduced a characteristic residence time $t_{im}$ of a supercooled droplet experiencing collisions with the IN particles as

$$t_{im} = \frac{2 \cdot FE_{contact}}{J_{imm}},$$

where $J_{imm}$ is the rate of freezing due to immersion freezing and can be estimated from the IMCA/ZINC measurements using the relationship between the number of unfrozen and total number of droplets:

$$\frac{N_{unfrozen}}{N_{total}} = 1 - FF = \exp(-J_{imm} \cdot t)$$

and the residence time in ZINC of $t = 3\,s$. At T = 255K the FF for the AgI 0.2 µm particles in the immersion freezing experiment (we refer to figure 1) is ≈0.95 for number concentration of 5000 $cm^{-3}$ and therefore $J_{imm} = 1s^{-1}$. The meaning of this is that on average, droplets would freeze in immersion mode 1 second after collision with 200 µm AgI particle at this temperature.

*We had expected the same but inspection of Fig. 4 shows that this is not the case: For both residence times and all concentrations but the highest one, FE is below the detection limit in CLINCH while it is around 0.95 in IMCA/ZINC. This led us to have a closer look at heterogeneous ice nucleation with AgI. See companion paper: Marcolli C., Nagare, B., Welti, A., and Lohmann U.: Ice nucleation efficiency of AgI: review and new insights, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-142, 2016.*

Even if we assume the $FE_{contact} = 1$ (in the figure 4 it is rather 0.3 to 0.5) the characteristic time would be $t_{im} \approx 2s$, comparable to the shortest residence time used in your experiment, and thus the condition

$$FE_{contact} \gg \frac{1}{2} J_{imm} t$$

required to observe the dominance of contact freezing is not fulfilled. This simple analysis show that at least for silver iodide particles both freezing mechanisms are competing and there is no way to derive the FE for both mechanisms separately on the time scale of the experiment.

As it is immediately follows from these considerations, the freezing on-set in purely immersion mode should be always observed at higher temperature just due to the fact, that in INCA/ZINC droplets are entering the cold zone carrying the IN particles inside, whereas time is needed in CLINCH for droplet first to collect an IN particle and then freeze due to one of the freezing mechanisms.

*We think that because of the uncertainties to derive FE from FF in CLINCH, we need a clear difference in onset temperatures instead of just a difference in nucleation rate to state that either immersion or contact freezing is more efficient. Also, in contrast to the reviewers reasoning, the onset temperature of freezing for kaolinite in IMCA/ZINC was lower than in CLINCH.*

*We do not derive FE for specific mechanisms but for the two different instruments CLINCH and IMCA/ZINC. So we have an FE for the CLINCH and an FE for the IMCA/ZINC experiments. We needed further analysis, e.g. the comparison of the FE for 2s and 4s residence times in CLINCH to reach conclusions concerning the freezing mechanisms. If FE observed for the IMCA/ZINC experiment with 3 s residence time and FE for the CLINCH experiment with 4 s residence time are similar, this indicates that freezing in CLINCH might occur in immersion mode after the droplet has captured the particle. To discriminate between collisional contact freezing and immersion freezing we compared FE(2s) and FE(4s).*

5. Difference or equality of FE at different reference times is discussed throughout the manuscript. However, the difference in FE for different aerosol concentrations (as seen in the figure 4) is neglected. This behavior cannot be explained by interplay of the immersion vs. contact freezing as it is done for the residence time dependence.

*Only for AgI aerosols, experiments with different particle concentrations could be performed due to experimental reasons. Our analysis in Nagare et al. (2015) showed that at temperatures for which the plateau condition is valid, freezing efficiencies for all concentration are the same within experimental error. At temperatures for which the plateau condition is not valid, freezing efficiencies were higher for experiments where the number of collisions N > 1. This is discussed in the paper.*

## Specific comments

1. There is an apparent contradiction between two statements (page 6, lines 21-25).: "*Panel (a) of Fig. 4 shows that FE does not exceed 0.5 for C =5000 cm−3 because it is assumed that on average 2.35 collisions are necessary to freeze a droplet. This led us to Eq. (4) to calculate FE, which assumes that already the first collision induces droplet freezing*". If more than one collision is needed to freeze the droplet, the freezing could occur on any of the subsequent collisions, couldn't it?

*Yes, this introduces indeed an additional uncertainty when the number of collisions in the chamber exceeds 1. To make this clearer in the revised manuscript, we now write on pages 6/7: "For this concentration and residence time 2.35 collisions occurred in the chamber and freezing might have been induced by any of these collisions. Eq. (1) assumes that indeed all collisions are necessary to freeze a droplet and gives a lower limit of freezing efficiency. An upper limit is obtained using Eq. (4), which assumes that the first collision induces freezing."*

2. (page 6, lines 25-26).: "*This reinforces the assumption that the first contact leads to droplet*

*freezing in this temperature range and confirms the plateau condition used in Nagare et al. (2015) to derive CE."* This is a confusing statement: in your previous paper the CE was derived from the measurements of FF under assumption that FE = 1 (in the plateau region, at T < 245K), and now you derive the FE value from essentially the same measurements under assumption of known CE? In this case you can't obtain any other value of FE but 1.

*Yes, indeed. This result is expected. It just shows the consistency of the approach.*

3. (page 10, line 28) Could you clarify why is the solubility of silver iodide important for the contact freezing experiments reported in this paper and what do mean by the statement "*Moreover the freezing ability depends on the surface charge on AgI particles*" (page 11 line 1).

*For an explanation of this, we refer to the companion paper (Marcolli et al., 2016), which has been published in ACPD. This paper is a review of the ice nucleation ability of AgI and discusses the questions raised by the reviewer in detail.*

## References

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Referee 3:

*We would like to thank the reviewer for careful reading the manuscript and the suggestions of improvement of readability. The responses to the comments and questions are given below in italic.*

My major comment is that main conclusions of the paper are not visible. Some revision is needed to enhance the readability, and also it is necessary to clarify what are the major conclusions of the paper. It is also not clear why this study is important, and what the atmospheric implications are. Some more discussion is needed to understand why AgI, ATD and Kaolinite particles were used, why natural dust or soil dust particles were not chosen as these are more atmospherically relevant. This is nice study, overall contact freezing is not well understood, but main message is buried. Below some comments may help to revise this paper further.

*It is important to know whether contact freezing is more efficient than immersion freezing for parameterization in atmospheric models and for the microphysical understanding of the different heterogeneous ice nucleation processes. We emphasize this now more in the abstract by adding on line 4:*

*"To date, direct comparisons of contact and immersion freezing with the same INP, for similar residence times and concentrations are lacking."*

*We preferred to first study INPs that have been investigated before. This is the case for AgI, ATD, and kaolinite. Moreover, these samples represent different types of ice nuclei. ATD is a mixture of different minerals, while AgI and kaolinite contain one main component. AgI induces ice nucleation at a rather high temperature and shows a close lattice match with ice, while kaolinite does not have a close lattice match and induces freezing at much lower temperature. In future this study could be extended to investigate natural mineral dust or soil dust samples.*

-What is the typical size of supercooled droplets observed in mixed phase clouds? How often 80 um droplets are observed. Atmospheric relevance of droplet size should be discussed.

*For heterogeneous nucleation, droplet size is not important. The relevant quantity is the surface of the INP, which is in our experiments in the atmospherically relevant range.*

-Following two sentences (i and ii) needs to be elaborated. Bulk liquid water properties are different from individual water droplet properties. Please define what you mean by sprinkling. Do particles were size-selected, how many particles were used, what is the temperature of the liquid water, do water is pure or distilled or regular lab supply grade, how long this experiment was performed, do all particles sediment, and how this observation was made (visual observation, microscope).

(i) "When we sprinkled ATD on a water surface, most particles immediately immersed and sank to the bottom. This suggests that when ATD particles collide with water droplets, the particles become immediately immersed such that in immersion freezing and contact freezing experiments the immersion mode is probed."

(ii) "When we sprinkled kaolinite powder on water, we observed that some particles floated on the surface while others became totally immersed and sank to the bottom."

*We give the requested information in the revised manuscript in the new Section 2.3. These were very simple experiments to confirm the wetting behavior predicted by evaluating the contact angles between water and the particles. There should be no difference between a droplet surface and a bulk water surface as long as the Kelvin effect is not important, which is the case for droplets larger 1 µm, i.e. all cloud droplets.*

***We add to the observations for kaolinite the timescale:"… some floated on the surface for hours while others became totally immersed and sank to the bottom within seconds."***

-It is mentioned that "A particle on the surface can induce ice nucleation in the immersion mode with the part immersed in water or in contact mode with the part exposed to air." How this can be assumed, what is the basis for this?

***We refer here to the contact freezing process occurring when a particle adheres to the surface of a droplet. In the ACPD version of the manuscript we referred to this process as contact freezing inside-out. In the revised manuscript we change the terminology to "adhesion freezing" because naming it "contact freezing inside-out" was criticized by reviewers 2. If the part of the particle that is exposed to the surface is less efficient at nucleating ice than the part of the particle immersed in the droplet, the freezing efficiency should still equal approximately the one observed for cases when the particle is totally immersed in water.***

-Section 5.6: It is not clear what results are discussed. This section looks like reading a literature review. There is only one sentence (The immersion and contact freezing studies compiled in Fig. 6 suggest that contact freezing is more efficient than immersion freezing with an onset temperature that is about 3 K higher), which describes the results, but there is no discussion. I suggest use present results to discuss the figure 6, but not previous results (as they have different instrument platform to study Kaolinite properties). For example XRD analysis of Kaolinite particles differ from group to group because of the XRD instrument sensitivity issues, and also impurities within the Kaolinite samples. Note that Kaolinite from different vendors have different properties, also shown by Wex et al (http://www.atmos-chem-phys.net/14/5529/2014/acp- 14-5529-2014.pdf) who shown ice nucleating properties are sensitive to the particles procured from different vendors.

***We are aware of the different qualities of kaolinite depending on the vendor. For our experiment we used Fluka kaolinite from Sigma Aldrich (K-SA). We therefore compare to studies, which also used Fluka kaolinite. This is the case for Wex et al. (2014) and Tobo et al. (2012). This comparison is therefore justified. It is well known that Fluka kaolinite is not pure. This is why the composition determined by XRD is important. The information given in this section is relevant for the interpretation of the results. Reviewer 1 even asked us to "place our results more clearly in the context of previous work".***

-Section 5.6: Second paragraph. How this is applicable to the present study. This material is not relevant, if yes please discuss how. As mentioned above this reads like a literature review.

***We need information about the morphology and surfaces of kaolinite to discuss whether kaolinite particles adhere to the surface of the droplet or whether they are immersed. A discussion of previous literature is needed. Reviewer 1 even asked for a more profound discussion of kaolinite and suggested inclusion of more previous work.***

-Please see Section 5.5 too. Discuss the present results. There is lot of discussion on previous studies, but how they are related to this study. It is not clear why these studies are discussed. I suggest move this material to Intro section to increase the readability.

***In this section the results for ATD are discussed and put in context with previous studies on ATD. Such a discussion is necessary.***

-Last three sentences from Conclusion section (page 14, line 8-11). Do authors performed any experiments to conclude this, or these are the conclusions from previous studies. If later then I suggest move this to intro section.

***These are the conclusions of the present study. We make this clearer in the revised manuscript by writing: "Our experiments and calculations…"***

-Can majority of Section 5.2 (except page 17, line 17-23) and Section 5.3 be moved to Intro section? They do not discuss any results.

*We moved Section 5.2 to the introduction and Section 5.3 to an appendix.*

-It may be a good idea to combine section 4 and 5. Section 5, for dust particles, has lot of discussion concerning previous studies and may help to increase the readability.

*We prefer to keep the results and the discussion of the results apart.*

***Manuscript with changes marked:***

# Comparing contact and immersion freezing from continuous flow diffusion chambers

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**Abstract.** Ice nucleating particles (INPs) in the atmosphere are responsible for glaciating cloud droplets between 237 K and 273 K. Different mechanisms of heterogeneous ice nucleation can compete under mixed-phase cloud conditions. Contact freezing is considered relevant because higher ice nucleation temperatures than for immersion freezing for the same INPs were observed. It has limitations because its efficiency depends on the number of collisions between cloud droplets and INPs. To date, direct comparisons of contact and immersion freezing with the same INP, for similar residence times and concentrations are lacking. This study compares immersion and contact freezing efficiencies of three different INPs. The contact freezing data was obtained with the ETH CoLlision Ice Nucleation CHamber (CLINCH) using 80 $\mu m$ diameter droplets which can interact with INPs for residence times of 2 s and 4 s in the chamber. The contact freezing efficiency was calculated by estimating the number of collisions between droplets and particles. Theoretical formulations of collision efficiencies gave too high freezing efficiencies for all investigated INPs, namely AgI particles with 200 nm electrical mobility diameter, 400 and 800 nm diameter ATD and kaolinite particles. Comparison of freezing efficiencies by contact and immersion freezing is therefore limited by the accuracy of collision efficiencies. The concentration of particles was 1000 $\mathrm{cm}^{-3}$ for ATD and kaolinite and 500, 1000, 2000 and 5000 $\mathrm{cm}^{-3}$ for AgI. For concentrations $< 5000\,\mathrm{cm}^{-3}$, the droplets collect only one particle on average during their time in the chamber. For ATD and kaolinite particles, contact freezing efficiencies at 2 s residence time were smaller than at 4 s, which is in disagreement with a collisional contact freezing process but in accordance with immersion freezing or adhesion freezing. With adhesion freezing, we refer to a contact nucleation process that is enhanced compared with immersion freezing due to the position of the INP on the droplet and discriminate it from collisional contact freezing which assumes an enhancement due to the collision of the particle with the droplet. For best comparison with contact freezing results, immersion freezing experiments of the same INPs were performed with the continuous flow diffusion chamber IMCA/ZINC for 3 s residence time. In IMCA/ZINC, each INP is activated into a droplet in IMCA and provides its surface for ice nucleation in the ZINC chamber. The comparison of contact and immersion freezing results did not confirm a general enhancement of freezing efficiency for contact compared with immersion freezing experiments. For AgI particles the onset of heterogeneous freezing in CLINCH was even shifted to lower temperatures compared with IMCA/ZINC. For ATD, freezing efficiencies for contact and immersion freezing experiments were similar. For kaolinite particles, contact freezing became detectable at higher temperatures than

immersion freezing. Using contact angle information between water and the INP,  it is discussed how the position of the INP in or on the droplets may influence its ice nucleation activity.

## 1 Introduction

Aerosol particles influence the climate system in different ways. They scatter or absorb the incoming solar radiation or can absorb thermal radiation. Aerosol particles also play a role in cloud formation by acting as cloud condensation nuclei (CCN) and as ice nucleating particles (INPs). INPs help in ice nucleation depending on their physical and chemical properties, temperature of the environment and presence of supercooled droplets. Heterogeneous ice formation may take place with the help of INPs between 237 K and 273 K in the mixed-phase clouds regime. In this regime, three pathways of ice nucleation are differentiated, namely, immersion freezing, condensation freezing and contact freezing. In condensation freezing, water vapor condenses on the INP at temperatures $<$ 273 K to form a liquid droplet which freezes instantaneously. Immersion freezing (IF) takes place when an INP acts as CCN and the formed droplet freezes when the temperature is lowered. In contact freezing the INP collides with the droplet followed by freezing. Contact freezing (CF) in the original sense is defined as the process in which freezing of a supercooled droplet results from the collision with an aerosol particle (Ladino Moreno et al., 2013; Vali, 1985). This view of collisional contact freezing has been complemented by Durant and Shaw (2005) who found higher ice nucleation temperature compared with the immersion mode, when an INP was in contact with the water-air interface of a droplet, from either the inside or the outside (Durant and Shaw, 2005; Gurganus et al., 2014; Fornea et al., 2009; Murray et al., 2012; Shaw et al., 2005). In the following, we refer to a contact nucleation process as adhesion freezing when the position of the INP on the water surface enhances the ice nucleation efficiency compared with immersion freezing and discriminate it from collisional contact freezing, which assumes an enhancement due to the collision of the particle with the droplet.

Various theoretical mechanisms underlying contact freezing have been proposed as explanations for the higher freezing efficiency in contact compared with immersion mode. They have been reviewed by Ladino Moreno et al. (2013). Here we discuss them in brief. Cooper (1974) proposed that ice embryos formed on INPs in vapor are able to nucleate supercooled water upon collision with a droplet. His explanation relies on the classical nucleation theory and is based on the prediction that the critical radius of an ice embryo for deposition nucleation is about 4-5 times larger than that for immersion freezing. Therefore a particle inactive as a deposition nucleus in the vapor, may nevertheless possess ice embryos larger than the critical size for an embryo immersed in water on it's surface. Such an embryo may induce freezing when immersed in water. This mechanism was rejected by Fukuta (1975b). Fukuta (1975a) proposed a similar mechanism but with subtle differences. Similar to Cooper (1974), Fukuta (1975a) assumed that subcritical ice clusters form on the particles by vapor deposition. However, he rejected that these clusters remain active, once they are immersed in the droplet as proposed by Cooper (1974). Instead, he assumed that freezing occurs during the wetting process when the water front moves over the particle, because this process gives rise to a transient high free energy zone which facilitates nucleation. This process should be only valid for hydrophobic nuclei. While the older theories focus on a collisional contact freezing mechanism, the more recent ones concentrate on adhesion freezing. Indeed, experimental studies by Shaw et al. (2005) and Fornea et al. (2009) have shown that an INP that is not completely immersed in the droplet can trigger ice nucleation at higher temperatures. From simulations, Sear (2007) found that the nucleation rate is 4 orders of magnitude higher along the contact line where the water surface meets the surface of the particle. Based on classical nucleation theory, he considered this result as generic. Suzuki et al. (2007) found from their experiments with water droplets on silicon surfaces coated with various silanes that the temperature at which nucleation occurs at a contact line depends on the contact angle between water and the substrate. On the other hand, Gurganus et al. (2011, 2013) investigated the freezing of droplets deposited on clean and coated silicon wafers and did not observe any preference of nucleation at the contact line. The same group also studied this phenomenon on catalyst substrates with imposed surface structures and found that the preferred nucleation site was the contact line in the case of nanoscale texture but not for microscale texture (Gurganus et al., 2014). (Djikaev and Ruckenstein, 2008) proposed that the line tension associated with the three phase contact line may indeed play an important role. On the other hand,**?** investigated soluble INPs for contact freezing. They showed that ionic salts can trigger freezing of moderately supercooled water. They concluded that this freezing effect must depend on collision between water droplet and INP since the particles they have used dissolve when they become immersed in water.

Ladino Moreno et al. (2013) reviewed experimental studies on contact freezing and also pointed out large discrepancies in the available experimental data. Quantification of the number of INPs required for contact freezing, time dependence of contact freezing, dependence on particle type and size were listed amongst the most uncertain parameters. Hoffmann et al. (2013a, b), and Niehaus et al. (2014) attempted to quantify the number of INPs required to freeze a droplet by contact freezing for their respective experiments. In Hoffmann et al. (2013a, b), an highly electrified droplet is suspended in an electrodynamic balance. The freezing probability of a droplet on a single collision was shown to be a steep function of temperature. Nine collisions were necessary to freeze the droplet at 244 K while a single collision was sufficient to freeze the droplet at 239 K for illite particles with a mobility diameter of 750 nm. They conclude that contact freezing is the dominant mechanism over immersion freezing (Hoffmann et al., 2013a). Niehaus et al. (2014) found that for mineral dust from different origins $10^3$ to $10^5$ particles had to collide with a droplet deposited on the glass slide in the temperature range of 253 K to 258 K. Moreover, they ran experiments in which they melted a droplet after having observed a freezing event. When they cooled it back to the original temperature, no freezing event occurred. From this, they concluded that contact freezing was more probable than immersion freezing and that the particle-droplet collision was responsible for freezing. Contact freezing and immersion freezing have been previously compared by Levin and Yankofsky (1983) for bacterial cells where onset temperatures for contact freezing were shown to be 2 K higher. However, they did not state how many particles were needed to collide with the droplets to initiate freezing. Also Ladino et al. (2011) concluded that there are some hints that contact freezing is more efficient than immersion freezing for kaolinite particles. They attempted to derive the freezing efficiency per single particle using theoretical formulations of collision efficiencies to calculate the number of collisions between droplets and particles and obtained unrealistic freezing efficiencies on the order of 10 to 100 for 26 μm diameter droplets and 400 nm kaolinite particles. The too large values of the freezing efficiency were attributed to the overestimation of droplet size in calculating $CE$. They also were mistaking liquid droplets as frozen droplets because multiple droplets were simultaneously present in the laser beam of the detector (Ladino Moreno et al., 2013).

The relevance of contact freezing for the atmosphere depends on the collision rate and the freezing efficiency. The collision rate between particles and droplets is a function of the collision efficiency which is not well determined in the accumulation mode size range as pointed out by Nagare et al. (2015). Collision efficiency ($CE$) is defined as the fraction of particles in the cylindrical volume swept out by a falling droplet that collide with it. $CE$ depends mainly on particle size and droplet size. Other factors which influence $CE$ are relative humidity of the environment and charges on droplets and particles. For Aitken mode particles, Brownian motion of the particles is usually the dominant collision process and $CE$ can exceed 1 because of the high mobility of the particles in this size range. For coarse mode particles, impaction and interception of particles are the dominant contributors to $CE$. The minimum of $CE$ (Greenfield gap) is in the accumulation mode where thermophoresis and diffusiophoresis may also contribute to $CE$ (Nagare et al., 2015).

In order to compare the efficiency of immersion freezing and contact freezing, we performed a series of experiments with silver iodide, kaolinite and Arizona Test Dust (ATD) in immersion and contact freezing mode. Silver iodide is known to be a very good ice nucleus (Vonnegut, 1949) inducing ice nucleation up to 269 K, while ATD and kaolinite become efficient ice nuclei only at lower temperatures. Silver iodide has been reported to be more efficient as INP in contact than in immersion mode (DeMott, 1995). Kaolinite and ATD have been widely tested in laboratory studies as immersion freezing nuclei. Kaolinite is a clay mineral and accounts for 13 % of dust mass in the atmosphere (Atkinson et al., 2013). It has been studied previously in immersion freezing (e.g., Welti et al., 2012) and contact freezing studies (e.g., Ladino et al., 2011; Svensson et al., 2009). ATD has been previously studied for immersion freezing by Marcolli et al. (2007) and Niedermeier et al. (2010) and for contact freezing by Niehaus et al. (2014). ATD is composed of quartz, feldspar, carbonate, illite, kaolinite and other clays (Broadley et al., 2012).

## 2 Experimental setups and procedures

### 2.1 Instrument description

#### 2.1.1 CLINCH setup

Contact freezing data was obtained with the ETH CoLlision Ice Nucleation CHamber (CLINCH). This instrument has been used previously by Ladino et al. (2011) for a contact freezing study with kaolinite as INPs. In CLINCH, aerosol and water droplets collide and may freeze by contact. The extension of the chamber length from 40 $\mathrm{cm}$ used by Ladino et al. (2011) to 80 $\mathrm{cm}$ for the current study makes it possible to observe the frozen fraction of droplets ($FF$) i.e. the ratio of number of frozen droplets to total number of droplets, at residence times of 2 s and 4 s with 80 $\mu\mathrm{m}$ diameter droplets compared to 26 $\mu\mathrm{m}$ droplets used by Ladino et al. (2011). The droplet diameter is changed from 26 to 80 $\mu\mathrm{m}$ in order to increase the geometrically swept out volume by the droplet and to avoid significant change in the droplet size due to evaporation in the chamber. $80 \pm 3$ $\mu\mathrm{m}$ diameter droplets are generated with a droplet generator (Ulmke et al., 2001) at the top center of the chamber with a frequency of 100 $\mathrm{Hz}$. The droplets are generated with pure water (Milli-Q, 18.2 $\mathrm{M\Omega}$) at a temperature of 281 K. The relaxation time for a droplet to reach its terminal velocity (0.186 $\mathrm{ms}^{-1}$) is 0.2 s and the time needed to reach the target temperature is about 0.1

and 0.6 s when the chamber is kept at 261 and 235 K, respectively (Nagare et al., 2015). While performing the experiment, the walls of the chamber are coated with a thin layer of ice creating an ice saturated environment inside the chamber.

Aerosol particles enter the chamber at the top in air streams from both sides with a flow velocity of 1 LPM and can interact with the droplets inside the chamber. $FF$ can be determined with the in-house developed Ice Optical DEtector (IODE) (Nicolet et al., 2010; Lüönd et al., 2010) which discriminates water droplets from ice crystals by measuring the depolarization of the backscattered light of a laser beam. In order to avoid the presence of several droplets simultaneously in the laser beam, a new laser was installed (402 nm, Schaefter + Kirchhoff laser Makroliniengenerator13LTM) providing a rectangular instead of a circular laser beam. At each temperature, a blank experiment without aerosol particles was performed before the aerosol stream was turned on. A more detailed description of the instrument and experiment is given in Nagare et al. (2015).

### 2.1.2 IMCA/ZINC setup

Immersion freezing experiments were performed using the IMCA/ZINC setup (Welti et al., 2012). This setup combines the Zurich Ice Nucleation Chamber (ZINC) (Stetzer et al., 2008) with the vertical extension Immersion Mode Cooling chAmber (IMCA) (Lüönd et al., 2010). In brief, the aerosol particles are activated as CCN in the IMCA part at a relative humidity with respect to water $> 120\ \%$ and temperature $> 300$ K. These activated droplets are then cooled down in the IMCA part and reach the target temperature for freezing when they enter the ZINC chamber. The droplets are $18-20$ µm in diameter when they leave the IMCA part and enter the water saturated environment in ZINC which is created by ice coatings on the parallel walls, which are kept at different temperatures. $FF$ can be determined using the depolarization detector IODE at different residence times from 1 s to 21 s. A more detailed description of the instrument and experiment is given in Welti et al. (2012). Characteristics of the IMCA/ZINC and the CLINCH experiments are compared in Table 1.

## 2.2 Aerosol generation and sampling

Silver iodide was precipitated by mixing 0.1 M solutions of potassium iodide and silver nitrate. The aerosol particles were generated by atomizing this suspension and dried (for details refer to Nagare et al. (2015)). The suspension was usually prepared the day before a measurement series was started and used for a measurement series performed during typically 2 days. Between measurements the suspension was kept in the dark. Kaolinite (Fluka, Sigma Aldrich GmbH) and ATD (Powder Technology Inc.) particles were aerosolised in a fluidized bed aerosol generator (TSI Model 43400A). The aerosol stream was passed through a cyclone to remove large particles. Aerosol particles were selected based on their electrical mobility with a Differential Mobility Analyzer (DMA TSI 3081) with an upstream impactor. These size selected particles were used for either contact or immersion freezing experiments in the respective experimental setups. The concentration of particles in CLINCH was measured at the end of the chamber using a condensation particle counter (CPC, TSI 3772).

### 2.3 Particle sprinkling experiment

We sprinkled polydispersed particles of AgI, ATD, and kaolinite gently on a water surface to observe optically whether they adhere to the surface or sink to the bottom. The particles were sprinkled on Milli-Q water at room temperature by gently shaking a spatula loaded with a small portion of the powders.

## 3 Experimental results

Figure 1 shows the $FF$ observed for silver iodide as INP in CLINCH (triangles) as a function of chamber temperatures for droplet residence times of 2 s in panel (a) and 4 s in panel (b) for different concentrations of silver iodide. The gray shaded area is the experimentally determined homogeneous freezing regime of droplets in CLINCH from blank experiments. The black horizontal line marks the lower reliability limit of differentiation between ice and water determined from blank experiments. As the temperature of the chamber decreases to $<$ 250 K, the $FF$ starts to rise and then remains constant. The frozen fraction due to immersion freezing from IMCA/ZINC experiments with 3 s residence time in the ZINC chamber is shown as circles for comparison with contact freezing. Silver iodide particles produced by our method are found to be much more efficient INP in terms of onset temperature in immersion than in contact freezing mode. The onset temperature for silver iodide particles as INP is 265 K while for contact freezing significant frozen fractions were observed only below 250 K except for the highest concentration and 4 s residence time. For the highest concentration used in our experiment, the onset temperature for contact freezing is 258 K.

Figure 2 shows the frozen fraction of droplets when ATD was used as INP in contact and immersion freezing mode. The frozen fraction due to immersion freezing shown are for 800 nm particles and 3 s residence time in the ZINC chamber. There is no significant difference in onset temperature for immersion and contact freezing for ATD. Figure 3 shows the frozen fraction for experiments performed with kaolinite. For this INP, the onset temperature of contact freezing is 3 K higher than for immersion freezing. Possible reasons for this will be discussed in Sects. 5.5 and 5.6.

## 4 Freezing efficiencies

### 4.1 Calculation of freezing efficiency from frozen fraction

The frozen fraction measured by CLINCH depends on the collision efficiency and the freezing efficiency. For a further evaluation and comparison of contact freezing and immersion freezing $FF$ has to be converted to $FE$ . If a droplet freezes after more than one particle have hit it, it is not clear which particle induced freezing. Assuming that all collisions were needed for freezing leads to the following equation:

$$FE = \frac{FF}{N} \quad (1)$$

where $N$ is the number of collisions for a droplet with the aerosol particles and can be calculated as (Ladino et al., 2011)

$$N = CE \times C \times L \times \pi \times (R + r)^2 \tag{2}$$

where $C$ is the concentration of the particles, $R$ and $r$ are the radii of droplets and particles, respectively, and $L$ is the effective length experienced by the droplet given as

$$L = \frac{U(R)l}{U(R) + V_{flow}} \tag{3}$$

where $l$ is the geometrical length traced by the droplet, $U(R)$ is the terminal velocity of the droplet and $V_{flow}$ is the flow velocity of the carrier gas in CLINCH.

Eq. (1) assumes that the droplet has collected $N$ particles and freezes due to the last particle that it has collected. However, the droplet can freeze on collision with the first particle and then collect other particles. Assuming that one collision is enough for ice nucleation, leads to the following expression for $FE$:

$$FE = \frac{FF}{1 - e^{-N}}. \tag{4}$$

Here the denominator indicates the fraction of unfrozen droplets after N collisions with the particles. We use this formula in the case of AgI, because we expect for this ice nucleus $FE$ = 1 at T < 245 K (Nagare et al. 2015). While Eq. (1) gives a lower limit of $FE$, Eq. (4) gives the upper limit.

Since $FE$ is derived by normalizing $FF$ with respect to $N$, $FE$ should be independent of the residence time when the number of collisions is < 1. If freezing efficiencies of 2 s $(FE(2s))$ and 4 s residence times $(FE(4s))$ are the same within the experimental uncertainty, this can be considered as an indication of immediate freezing when the first particle collides with a droplet. Conversely, $FE(4s) > FE(2s)$ suggests that freezing is not immediate when a particle hits a droplet but that more time is needed on average. Such a time dependent freezing process would be in accordance with an immersion freezing mechanism assuming that the droplet only freezes when the particle becomes immersed. A time dependence is also expected for adhesion freezing when the particle adheres to the surface of the droplet. If $N < 1$, it is unlikely that $FE$ is influenced by the number of collisions and we will interpret $FE(2s) = FE(4s)$ as a criterion for collisional contact freezing and $FE(4\text{s}) > FE(2\text{s})$ as a criterion for freezing in immersion mode or adhesion freezing.

### 4.2 Freezing efficiency of silver iodide particles

We derived a collision efficiency $CE = 0.13$ for 200 nm diameter AgI particles with 80 $\mu\text{m}$ droplets in our previous study (Nagare et al., 2015). This number is an order of magnitude higher than the values calculated with commonly used theoretical formulations of collision efficiencies. Figure 4 shows $FE$ of 200 nm diameter silver iodide particles for droplet residence times of 2 s (open symbols) and 4 s (filled symbols) calculated using Eqs. (1) (panel a) and (4) (panel b). The number of collisions for the different particle concentrations range between 0.1 and 2.35 as listed in Table 3. Panel (a) of Fig. 4 shows that $FE$ does not exceed 0.5 for $C = 5000\ \text{cm}^{-3}$ for 4 s residence time. For this concentration and residence time 2.35 collisions occurred in the chamber and freezing might have been induced by any of these collisions. Eq. (1) assumes that indeed all collisions are necessary to freeze a droplet and gives a lower limit of freezing efficiency. An upper limit is obtained using Eq. (4), which assumes that the first collision induces freezing. Panel (b) of Fig. 4 shows that this assumption leads to a grouping of $FE$ data around 1 for T $<$ 245 K for all particle concentrations and residence times of 2 s and 4 s. This reinforces the assumption that the first contact leads to droplet freezing in this temperature range and confirms the plateau condition used in Nagare et al. (2015) to derive $CE$. We ascribe data points with $FE > 1$ to homogeneous freezing and measurement uncertainties. For T $>$ 252 K, $FE$ values significantly different from zero are only reached for concentrations of 5000 $\mathrm{cm}^{-3}$. This would imply that above this temperature more than one collision is necessary for droplet freezing in CLINCH. For T $<$ 245 K, $FE$s for 2 s and 4 s residence times are the same within measurement uncertainties suggesting that ice nucleation occurs immediately when the particle hits the droplet. At higher temperatures the data points are quite scattered impeding a clear conclusion. Also shown are immersion freezing measurements with IMCA/ZINC with AgI particles that were prepared the same way as the ones for the contact freezing experiments. Residence time in the ZINC chamber was 3 s. Surprisingly, the onset temperature and the efficiency for immersion freezing are significantly higher than for contact freezing. This observation is further discussed in Sect. 5.2.1.

### 4.3 Freezing efficiency of ATD particles

Figure 5 shows $FE$ in contact freezing mode for 800 nm ATD particles calculated using Eq. (1). $N$ is calculated based on 4 different assumptions for $CE$. For panel (a), $CE = 0.0033$ from the theoretical formulation by Park et al. (2005) and Wang et al. (1978) was used. Details of the calculations are given in Nagare et al. (2015), where discrepancies between theoretical calculations and experimental observations have been addressed. For 200 nm silver iodide particles, the experimentally determined $CE$ is 14 times higher than the calculated one. In order to adjust $FE$ better to the theoretical upper limit of $FE = 1$ and due to lack of other available experimental values, the calculated collision efficiency was multiplied with the factor of 14 to calculate $N$ for panel (b). For a lower limit the experimentally derived $CE$ for 200 nm AgI particles ($CE = 0.13$) was used to calculate $N$ in panel (c). In panel (d), $CE = 0.061$ was used which shifts $FE$ of 800 nm ATD particles close to 1, which is in accordance with the assumption that each collision leads to droplet freezing. The calculated $CE$ shown in panel (a) leads to unrealistically high $FE$. This was also observed by Ladino et al. (2011). Using a correction factor of 14 for $CE$, still yields $FE$ values $>$ 1. Panels (c) and (d) give best estimates of lower and upper limits of freezing efficiency. The difference in $FE$ between panels (c) and (d) must be considered as an uncertainty due to the lack of reliable theoretical values of $CE$ in the investigated temperature and particle size range. The number of collisions for the different assumptions of $CE$ is listed in Table 2. For the lower limit case with $CE = 0.13$, $FE$ reaches values up to 0.5 for data points that can be unambiguously assigned to heterogeneous freezing. Contact freezing experiments do not show significantly different onset temperatures compared with immersion freezing experiments carried out with the IMCA/ZINC setup, where every droplet contains one particle. The active site parameterization developed by Marcolli et al. (2007) based on DSC experiments is shown as brown line in Fig. 5. It agrees well with the immersion freezing experiments carried out with 800 nm particles in the IMCA/ZINC chamber. Taking $CE = 0.061$ (panel d), contact freezing might be slightly more efficient than immersion freezing. Taking $CE = 0.13$

(panel c), contact freezing and immersion freezing seem to be similarly efficient. We did not convert the frozen fraction of 400 nm ATD particles to freezing efficiency because $FF$ is close to the detection limit. For all assumed values of collision efficiencies, the freezing efficiency at 4 s residence time is almost twice the value at 2 s residence time. As listed in Table 2 the number of collisions is < 1 for both residence times. While the uncertainty associated with the measurements at 2 s is quite large, this data still seems significantly lower than the 4 s residence time freezing efficiencies. An increasing freezing efficiency with increasing residence time is expected for immersion freezing (Hoffmann et al., 2013b; Welti et al., 2012) and adhesion freezing. Therefore, it is likely that freezing occurs due to one of these mechanisms rather than collisional contact freezing.

### 4.4 Freezing efficiency of kaolinite particles

Figure 6 shows freezing efficiency for 800 nm diameter kaolinte particles for 2 s (open triangles) and 4 s (filled triangles) residence times. The frozen fraction measured for 400 nm particles was not significant, therefore, we do not convert this data to freezing efficiency. Panels (a), (b) and (c) use three different assumptions to calculate $N$ as explained in the previous section for ATD. For panel (a) the theoretical formulations were used, while panels (b) and (c) give the upper and lower limit of $FE$, respectively. Shown as brown circles in Fig. 6 are the immersion freezing results of 800 nm Fluka kaolinite particles for 3 s residence time in the ZINC chamber. Freezing efficiencies are in good agreement with the previously published $\alpha$-pdf parameterization by Welti et al. (2012) derived from immersion freezing experiments performed with the same setup (brown line). In Wex et al. (2014) immersion freezing experiments with 700 nm kaolinite (Fluka) particles were performed with LACIS (shown as blue diamonds) and with a CFDC (shown as green diamonds). In the LACIS instrument, INPs are activated to droplets at $T = 257 - 260$ K while cooling to the targeted temperature. They are at the experimental temperature during 1.6 s while they evaporate. This lower residence time may explain the lower freezing efficiency observed in LACIS compared with IMCA/ZINC. Slightly higher freezing efficiencies than in LACIS but still lower than in IMCA/ZINC were observed for 700 nm Fluka kaolinite particles in the CFDC (orange stars: Tobo et al. (2012); green diamonds: (Wex et al., 2014)). The contact freezing efficiencies from CLINCH are clearly higher for the lower limit of $CE = 0.046$ and slightly higher for the upper limit of $CE = 0.13$.

## 5 Discussion

### 5.1 Collision efficiency

Collision efficiency is a crucial parameter for an accurate comparison of contact and immersion freezing. Figures 5 and 6 show that freezing efficiencies of ATD and kaolinite particles calculated with theoretical formulations of $CE$ are at least by one order of magnitude too high. This corroborates the finding by Nagare et al. (2015), that $CE$ formulations need to be reassessed for temperature below 273 K. More such studies for different particle and droplet sizes are needed to improve the data base for validation of calculated collision efficiencies at subzero temperatures, subsaturation with respect to water and droplets and particles with known charges. For measurements with the AgI aerosol, $FE = 1$ could be assumed for data points at T < 245

K, because they showed constant frozen fractions and IMCA/ZINC experiments determined $FE = 1$ at T < 245 K. For ATD and kaolinite, there was no temperature range where freezing occurred with an efficiency of one. Therefore, only upper and lower limits of collision efficiency can be estimated. This limits the comparison of contact with immersion freezing. Collision efficiency is also a crucial factor to quantify the lifetime of the accumulation mode aerosol in the atmosphere because their lifetime strongly depends on the scavenging rate of particles by the droplets (Seinfeld and Pandis, 2006).

### 5.2 Contact freezing process

The higher $FEs$ for 4 s than for 2 s residence time of the CLINCH experiments with ATD and kaolinite are in agreement with adhesion freezing or immersion freezing. This indicates that collision itself does not increase $FE$ but there seems to be an effect whether the INP adheres to the water surface or is immersed in the droplet. The situation is less clear for AgI. For contact freezing experiments $FE$ at 2 s is the same as for 4 s residence time within error when on average one AgI particle or less collides with the droplet in the chamber. This result is in agreement with a collisional contact freezing mechanism, but may also result from a very high nucleation rate of immersion freezing and/or adhesion freezing at the investigated temperature.

When a particle adheres to the surface it might induce ice nucleation in contact mode by the part exposed to air and immersion freezing by the part immersed in water. When an insoluble or slightly soluble particle acts as cloud condensation nucleus (CCN), it is usually assumed that it becomes totally immersed into the droplet. However, whether the particle adheres to the droplet surface or becomes totally immersed depends on the wetting behavior of the particle (see Appendix A). The consequences for ice nucleation is discussed below for the investigated INPs.

#### 5.2.1 Silver iodide

For AgI particles, freezing efficiencies for 2 s and 4 s residence times are the same within experimental uncertainties, which is in accordance with immediate freezing after collision. However, adhesion freezing and immersion freezing cannot be excluded, if these processes occur at a high rate. Whether AgI adheres to the surface after collision or becomes totally immersed depends on the contact angle between water and the AgI surface. Billett et al. (1976) observed a dependence of the contact angle on the silver concentration in the solution. For silver iodide prepared in stoichiometric ratio, they determined $\alpha = 45° - 50°$ for the intermediate advancing angle. We observed that most of the AgI particles adhered to the surface when we sprinkled them gently on water. This is in accordance with observations by Gokhale and Goold (1968) and Gokhale and Lewinter (1971). We therefore assume that silver iodide particles remain on the droplet surface after collision in the CLINCH chamber. It is also likely that the AgI particles adhere to the droplet surface in the ZINC chamber after activation in the IMCA chamber. Therefore, in CLINCH and IMCA/ZINC experiments, the efficiency of adhesion freezing is probed and it could be expected that freezing efficiencies in both experiments are the same. However, the IMCA/ZINC freezing experiments performed with the same AgI aerosol and similar residence times shows a much higher freezing efficiency than the CLINCH experiments. This is in contrast to DeMott (1995), who reported higher freezing efficiencies in contact than in immersion mode for AgI-AgCl aerosols. However, AgI is a complex ice nucleus that appears in different polymorphic forms. Moreover, it partly dissolves in water. Depending on the production procedure, AgI is agglomerated with soluble salts. Moreover the freezing ability depends on the surface charge on AgI particles. A closer investigation of factors influencing the efficiency of AgI as an ice nucleus and reasons for the lower freezing efficiency in CLINCH compared with IMCA/ZINC are discussed in the companion paper by Marcolli et al. (2016).

### 5.2.2 Arizona test dust

The ice nucleation ability of ATD has been investigated by several groups using different setups. Niehaus et al. (2014) investigated contact freezing of deposited droplets on a glass slide, which were exposed to a flow of a polydisperse ATD aerosol (0.3 - 10 µm diameter particles). They determined that one in 1000 particles induced freezing at 253 K, and one in 100 000 at 258 K. These numbers are not directly comparable with this study, because the detection limit for frozen fractions of the IODE detector is ca. 0.05. In CLINCH we observed the onset of freezing at 247 K for 800 nm ATD particles. For 800 nm ATD particles, the freezing efficiencies in contact mode are within experimental uncertainties the same as freezing efficiencies in immersion mode measured with IMCA/ZINC at 3 s residence time. When the ATD parameterization for immersion freezing proposed by Marcolli et al. (2007) is applied to 800 nm particles with a nucleation time of 3 s, it is agreeing well with the experimental data from IMCA/ZINC. Niedermeier et al. (2010) investigated immersion freezing of ATD particles with LACIS. Experiments with ATD aerosols with diameters $<$ 560 nm yielded frozen fractions of 0.04 at 239 K and 0.1 at 236 K. The low residence time and the cutoff of particles $>$ 560 nm might be reasons for this lower freezing efficiency compared with IMCA/ZINC. When the active site parameterization by Marcolli et al. (2007) is applied to 400 nm particles, it gives too high active fractions compared to experiments. The heterogeneous mineralogical composition of ATD may be one of the reasons that smaller particles do not act as effective INPs and may even be inactive. Atkinson et al. (2013) have shown that ATD is composed of 20.3% K-feldspar, 12.4 % (Na, Ca)-feldspar, 17.1 % quartz, 7.5 % illite/muscovite, and 10 % illite/smectite. Clay mineral particles of illite/muscovite tend to be small and presumably dominate the particle fraction with diameters $<$ 500 nm, while quartz and K-feldspar may be overrepresented in the fraction with diameters $>$ 500 nm. Moreover, larger particles are often conglomerates of different minerals (Reid et al., 2003; Kandler et al., 2011) and might contain contributions of some K-feldspar while small particles are often primary particles of one mineral, which might not be very active as INP. Comparison of all measurements shows that immersion and contact freezing are similarly efficient modes of ice nucleation with ATD. Contact freezing experiments performed at 2 s residence time yielded higher freezing efficiencies than at 4 s, which is compatible with adhesion freezing or immersion freezing, but not with a collisional freezing mechanism. If particles became immediately immersed after contacting the droplet, freezing would occur in immersion mode also when a contact freezing experiment is performed. Indeed, the surfaces of many mineral dusts like quartz and feldspars are covered with hydroxyl groups, which render surfaces hydrophilic (Koretsky et al., 1997). Shang et al. (2010) measured contact angles of water droplets on clay films and found for illites a dependence of contact angles on relative humidity and on the exchangeable cations: the contact angle of Ca-illite sank from 28.3° to 21.6° when RH was raised from 19 % to 100 %. At 33 % RH contact angles ranged between $23.3^\circ - 34.2^\circ$ for illites saturated with different cations (Na, K, Mg, or Ca). Contact angles of $31^\circ - 35^\circ$ were measured for quartz (Szyszka, 2012). When we sprinkled ATD on a water surface, most particles immediately immersed and sank to the bottom. This suggests that when ATD particles collide with water droplets, the particles become immediately immersed such that in immersion freezing and contact freezing experiments the immersion mode is probed.

### 5.2.3 Kaolinite

X-ray powder diffraction showed that Fluka kaolinite (K-SA) which is used in this study, contains only 82.7 % kaolinite, but 5.4 % illite/muscovite, 5.9 % quartz, and 4.5 % K-feldspar (Atkinson et al., 2013). The clay minerals illite/muscovite and kaolinite tend to form small crystals and are presumably enriched in the particle fraction with diameters < 500 nm, while quartz and K-feldspars might be overrepresented in the fraction with diameters > 500 nm. K-feldspars and illite are known to be efficient ice nuclei (Atkinson et al., 2013; Hiranuma et al., 2015) and may dominate freezing when many particles are present in a sample (Pinti et al., 2012). When only one particle is present, this is likely to be a kaolinite particle. Kaolinite is a clay mineral with the formula $\mathrm{Al_2Si_2O_5(OH)_4}$. It has a layered structure with octahedral aluminum and tetrahedral silicon layers. It forms plate-like crystals with sizes of several hundred nanometers to micrometers and typical thicknesses of 30 - 50 nm (Hu and Michaelides, 2007, 2008). These plates have a hydrophilic octahedral Al-OH surface and a rather hydrophobic tetrahedral siloxane (Si-O) surface. The edges of the plates are terminated by oxygen atoms or hydroxyl groups and are hydrophilic. Šolc et al. (2011) computed a contact angle of $105°$ for nanodroplets on the tetrahedral siloxane surface by force-field molecular dynamics. Nanodroplets spread on the octahedral surface indicating a contact angle of $0°$. Shang et al. (2010) measured a contact angle of about $18°$ for water droplets on kaolinite films. This experimental value represents an averaged value over all kaolinite surfaces. The energetically most favorable configuration is therefore when the kaolinite particle adheres to the water surface with the siloxane surface exposed to air. Whether a kaolinite particle realizes this configuration may depend on the orientation of the particle when it contacts the water droplet. When we sprinkled kaolinite powder on water, we observed that some particles floated on the surface for hours while others became totally immersed and sank to the bottom within seconds. The lower freezing efficiency observed for 2 s residence time in the CLINCH chamber compared with 4 s is incompatible with a collisional freezing process but in accordance with adhesion freezing or immersion freezing. A particle on the surface can induce ice nucleation in the immersion mode with the part immersed in water or in contact mode with the part exposed to air. While it is likely that a kaolinite particle that hits a water droplet adheres to the surface and exposes the hydrophobic siloxane surface to air, it is less clear whether particles that underwent droplet activation stick to the surface or whether they totally immerse into the growing droplet. Which is the case may also depend on the conditions during activation like supersaturation or growth rate of the droplet. The immersion and contact freezing studies compiled in Fig. 6 suggest that contact freezing is more efficient than immersion freezing with an onset temperature that is about 3 K higher. Ladino et al. (2011) who compared their contact freezing data with immersion freezing measurements from Lüönd et al. (2010) using IMCA/ZINC concluded that there are some hints for contact freezing to be more efficient than immersion freezing. Pitter and Pruppacher (1973) compared contact and immersion mode freezing temperatures in wind tunnel experiments by exposing water droplets to kaolinite particles that were injected into the air stream. They estimated that a droplet captured several thousands of particles, which explains the much higher median freezing temperature of 261 K compared with this study. In accordance with our experiments, they found a clear shift to lower freezing temperatures when changing from contact to immersion mode experiments. Hoffmann et al.

(2013b) found that contact freezing dominates over immersion freezing for droplets levitated in an electrodynamic balance that were exposed to a flow of a kaolinite KGa-1b particles. Svensson et al. (2009) investigated contact freezing using an eletrodynamic balance to levitate droplets exposed to a flow of Fluka kaolinite particles. They observed contact freezing below 249 K for dry conditions and a freezing threshold of 267 K when the air was humidified. This value is higher than the one reported for freezing of bulk suspensions of Fluka kaolinite (K-SA) by Pinti et al. (2012).

It is not clear which surface of kaolinite is responsible for ice nucleation. Using grand canonical Monte Carlo simulations, Croteau et al. (2008, 2010) showed that the Si-O surface remained dry up to water vapor saturation, while the edges and the Al-OH surface are much more hydrophilic and absorb up to a monolayer water at water saturation. Adsorbed water on the octahedral Al-OH surface exhibits hexagonal patterns but no close lattice match with ice (Croteau et al., 2008, 2010). Simulations by Zielke et al. (2015) showed that for the Al-surface, reorientation of the surface hydroxyl groups is essential for ice nucleation. On the siloxane surface, ice nucleates via an ordered arrangement of hexagonal and cubic ice layers, joined at their basal planes where the interfacial energy cost is low. Experimentally, much higher absorption was determined showing that most absorption probably occurs on surface irregularities such as adsorbed ions or surface defects like trenches, pits, and steps (Schuttlefield et al., 2007; Tabrizy et al., 2011). Croteau et al. (2010) have shown that absorption is much higher on trenches than on the defect-free surface. Ice nucleation may therefore occur on liquid patches on an otherwise dry surface (Conrad et al., 2005). The wetting state of a nucleus may therefore be a crucial parameter for ice nucleation by kaolinite. This would be in accordance with the higher nucleation temperatures observed by Svensson et al. (2009) at humid conditions and point to a adhesion freezing mechanism.

## 6 Summary and conclusions

This study confirms the findings of Nagare et al. (2015) that theoretical formulations give too low collision efficiencies at subzero temperature for particles in the accumulation mode. In CLINCH, droplets are evaporating giving rise to diffusiophoresis and thermophoresis. Moreover, droplets and particles are charged. Freezing efficiencies calculated from theoretical formulations of collision efficiencies are more than one order of magnitude higher than the highest possible value of $FE = 1$. An assessment of the relevance of contact compared to immersion freezing is therefore limited by knowledge of collision efficiencies. To improve calculated collision efficiencies, formulations of thermophoresis and diffusiophoresis should be re-assessed.

Comparing contact freezing efficiencies acquired at 2 s ($FE(2s)$) and 4 s ($FE(4s)$) residence times enables conclusions regarding the freezing mechanism. For contact freezing experiments with AgI, freezing efficiencies at 2 s and 4 s residence times were the same within error when the droplets collected on average only one particle during their time in the chamber. This is in accordance with a collisional contact freezing mechanism. However, adhesion freezing and immersion freezing cannot be excluded if these processes occur at a high rate. For experiments with ATD and kaolinite $FE(2s)$ was smaller than $FE(4s)$ which is incompatible with immediate freezing after contact. Therefore, immersion freezing or adhesion freezing must be at work for these INPs. The comparison of contact and immersion freezing experiments did not confirm a general enhancement of freezing efficiency in contact mode relative to immersion mode. One reason for this may be that in CLINCH and IMCA/ZINC experiments the particles are free to realize the energetically most favorable position in or on the droplet. For AgI particles the freezing efficiency in CLINCH experiments was less than in IMCA/ZINC and the onset temperature was shifted to lower values. This is further investigated in Marcolli et al. (2016). For ATD, freezing efficiencies in contact and immersion mode were similar. For kaolinite particles, contact freezing became detectable at higher temperature than immersion freezing. A specific dependence on the INP for the enhancement of contact freezing relative to immersion freezing is in accordance with Gurganus et al. (2014) who observed an increased efficiency for nucleation at the three-phase contact line in case of nanoscale but not for microscale textures. In most experiments of contact freezing inside-out, the position of the particle with respect to the droplet is fixed by the design of the experiment (Shaw et al., 2005; Fornea et al., 2009; Gurganus et al., 2014). Whether a particle adheres to the surface or becomes totally immersed in a droplet depends on the wetting of the particle with water. A contact angle of zero corresponds with complete wetting, for higher values, the wetting is only partial. Our observations of particles that were gently sprinkled on water confirmed the predictions based on contact angles. Our experiments and calculations suggest that AgI particles partition to the droplet surface for contact and immersion freezing experiments. ATD particles seem to have highly hydrophilic surfaces that lead to fast immersion of the particles so that there is no time for adhesion freezing and immersion freezing prevails. Kaolinite forms plate-like crystals with a hydrophobic siloxane surface, all other surfaces are hydrophilic. It is therefore energetically most favorable when the hydrophobic surface of kaolinite particles is exposed to air. For this configuration, adhesion freezing and immersion freezing can compete.

## Author contribution

B. Nagare carried out the CLINCH experiments and evaluations. A. Welti carried out IMCA/ZINC experiments. B. Nagare and C. Marcolli prepared the manuscript. O. Stetzer supervised the laboratory work and U. Lohmann supervised the work overall.

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## Appendix A: Wetting of particles

The wetting behavior of particles can be quantified by the contact angle $\alpha$, which is related to the surface tensions of water with air $\sigma_{LA}$ and solid with air $\sigma_{SA}$ and the interfacial tension between solid and water $\sigma_{SL}$ through the Young equation (Hołownia et al., 2008) as follows:

$$\cos\alpha = \frac{\sigma_{SA} - \sigma_{SL}}{\sigma_{LA}}, \tag{A1}$$

The change in surface tension when the particle that adheres to a surface of the droplet becomes totally immersed in the droplet is given as (Hołownia et al., 2008)

$$\Delta\sigma = \sigma_{SL} - \sigma_{SA} + \sigma_{LA} \tag{A2}$$

Using Young's equation the change of surface tension is

$$\Delta\sigma = \sigma_{LA}(1 - \cos\alpha). \tag{A3}$$

The change in the interfacial energy is given by

$$\Delta G = \Delta\sigma A \tag{A4}$$

where $A$ is the surface area of the particle exposed to air when the particle adheres to the surface of the droplet. Considering a cubic particle and neglecting the curvature of the droplet, the area to be immersed in the droplet would be the area of one face of the cube. The particle will immerse in the droplet for negative $\Delta G$ and will remain on the surface for positive $\Delta G$. As can be seen from Eq. A4, $\Delta G$ is always positive and becomes zero for $\alpha = 0°$. This means that in the absence of other forces, complete wetting of the particle surface by water is needed for total immersion of the particle into the droplet.

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**Table 1.** Instrument characteristics

| Instrument | Droplet diameter (µm) | Residence time of droplet (s) | Aerosol concentration $\mathrm{cm}^{-3}$ |
|---|---|---|---|
| IMCA/ZINC | 18 - 20 | 3 (variable) | 1 particle per droplet |
| CLINCH | $80 \pm 3$ | 2 and 4 | 500 - 5000 |

**Table 2.** Average number of collisions for 800 nm particles with a 80 µm diameter droplet in a concentration of 1000 $\mathrm{cm}^{-3}$ and residence times of 2 s and 4 s assuming different values for CE.

| Collision efficiency $CE$ | Number of collisions N | |
|---|---|---|
| | 2 s | 4 s |
| 0.003 | 0.0056 | 0.012 |
| 0.46 | 0.079 | 0.168 |
| 0.13 | 0.24 | 0.48 |

**Table 3.** Average number of collisions $N$ for 200 nm silver iodide particles with a 80 $\mu\mathrm{m}$ diameter droplet in concentrations from 500 to 5000 $\mathrm{cm}^{-3}$ and residence times of 2 s and 4 s.

| Concentration $\mathrm{cm}^{-3}$ | 2 s | 4 s |
|---|---|---|
| 500 | 0.11 | 0.23 |
| 1000 | 0.23 | 0.47 |
| 2000 | 0.47 | 0.94 |
| 5000 | 1.17 | 2.35 |

**Table A1.** List of symbols

| | | | |
|---|---|---|---|
| $A$ | Surface area of the particle $[\mathrm{m}^2]$ | $C$ | Concentration of particle $[\mathrm{m}^{-3}]$ |
| $CE$ | Collision efficiency | $FE$ | Freezing efficiency |
| $FF$ | Frozen fraction of droplets | $L$ | effective length experienced by the droplet $[\mathrm{m}]$ |
| $l$ | length of chamber $[\mathrm{m}]$ | $N$ | Number of collision between droplet and INP |
| $R$ | Radius of the droplet $[\mathrm{m}]$ | $r$ | Radius of the particle $[\mathrm{m}]$ |
| $U(R)$ | teminal velocity of droplet $[\mathrm{ms}^{-1}]$ | $V_{flow}$ | flow velocity in the chamber $[\mathrm{ms}^{-1}]$ |
| $\alpha$ | contact angle | $\sigma_{SA}$ | surface tension between particle and air $[\mathrm{Jm}^{-2}]$ |
| $\sigma_{LA}$ | surface tesnsion between air and liquid $[\mathrm{Jm}^{-2}]$ | $\sigma_{SL}$ | interfacial tension between particle and water $[\mathrm{Jm}^{-2}]$ |

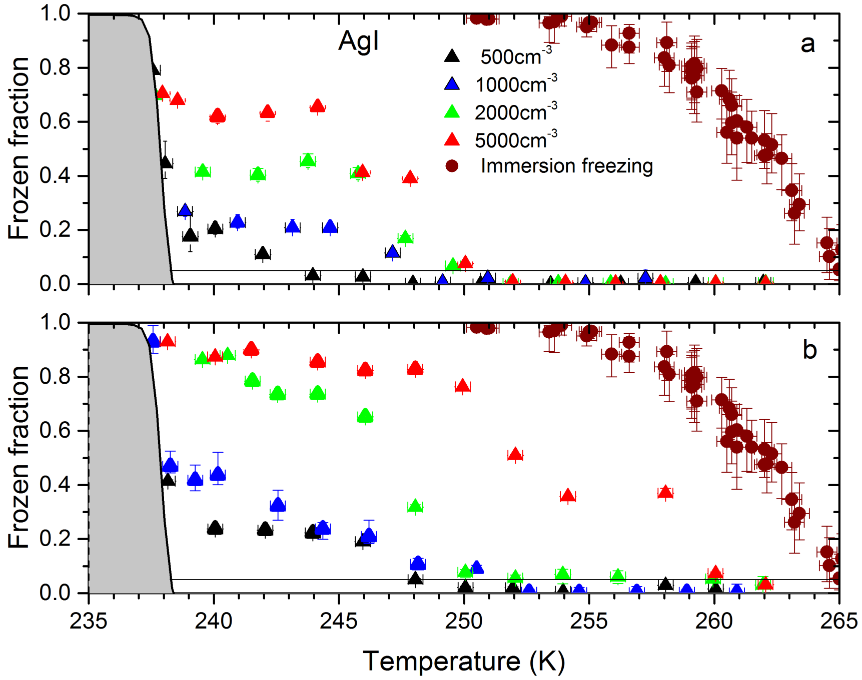

**Figure 1.** Frozen fraction against chamber temperature for silver iodide particles of 200 nm diameter. Contact freezing for aerosol concentrations from 500 $\mathrm{cm}^{-3}$ to 5000 $\mathrm{cm}^{-3}$ are given by triangles for a droplet residence time of 2 s in panel (a) and 4 s in panel (b). Immersion freezing for 3 s residence time of droplets in the ZINC chamber is shown by circles. The gray shaded area shows the homogeneous freezing of droplets determined from blank experiments (without aerosol) and the black horizontal line indicates the lower reliability limit of the measurements determined from the blank signal level observed in experiments without aerosol. Error bars represent the uncertainty in the frozen fraction due to the classification (liquid or ice) uncertainty of the IODE detector (Lüönd et al., 2010).

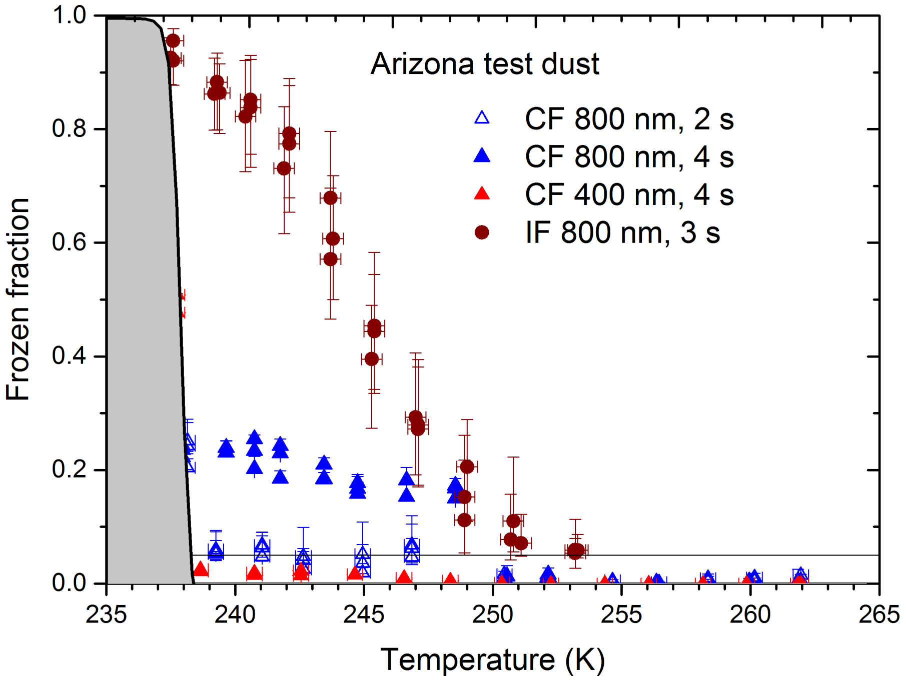

**Figure 2.** Frozen fraction against chamber temperature for ATD particles of 400 nm and 800 nm diameter. Contact freezing (CF) for aerosol concentrations of 1000 $\mathrm{cm}^{-3}$ are given by triangles for droplet residence times of 2 s and 4 s. Immersion freezing (IF from IMCA/ZINC) for 800 nm ATD particles and 3 s residence time in ZINC are shown by circles. The gray shaded area shows the homogeneous freezing of droplets determined from blank experiments (without aerosol) and the black horizontal line indicates the lower reliability limit of the measurements determined from the blank signal level observed in experiments without aerosol. Error bars represent the uncertainty in the frozen fraction due to the classification (liquid or ice) uncertainty of the IODE detector (Lüönd et al., 2010).

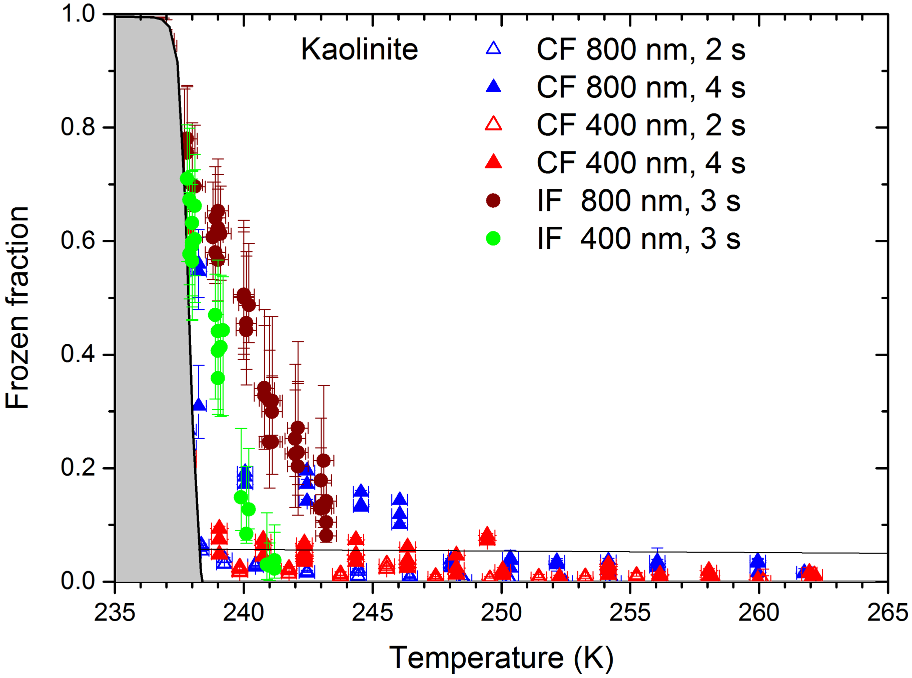

**Figure 3.** Frozen fraction against chamber temperature for kaolinite particles of 400 nm and 800 nm diameter. Contact freezing (CF) for aerosol concentrations of 1000 $\mathrm{cm}^{-3}$ are given by triangles for droplet residence times of 2 s and 4 s. Immersion freezing (IF from IMCA/ZINC) for 400 nm and 800 nm kaolinite particles and 3 s residence time in ZINC are shown by green and brown circles, respectively. The gray shaded area shows the homogeneous freezing of droplets determined from blank experiments (without aerosol) and the black horizontal line indicates the lower reliability limit of the measurements determined from the blank signal level observed in experiments without aerosol. Error bars represent the uncertainty in the frozen fraction due to the classification (liquid or ice) uncertainty of the IODE detector (Lüönd et al., 2010).

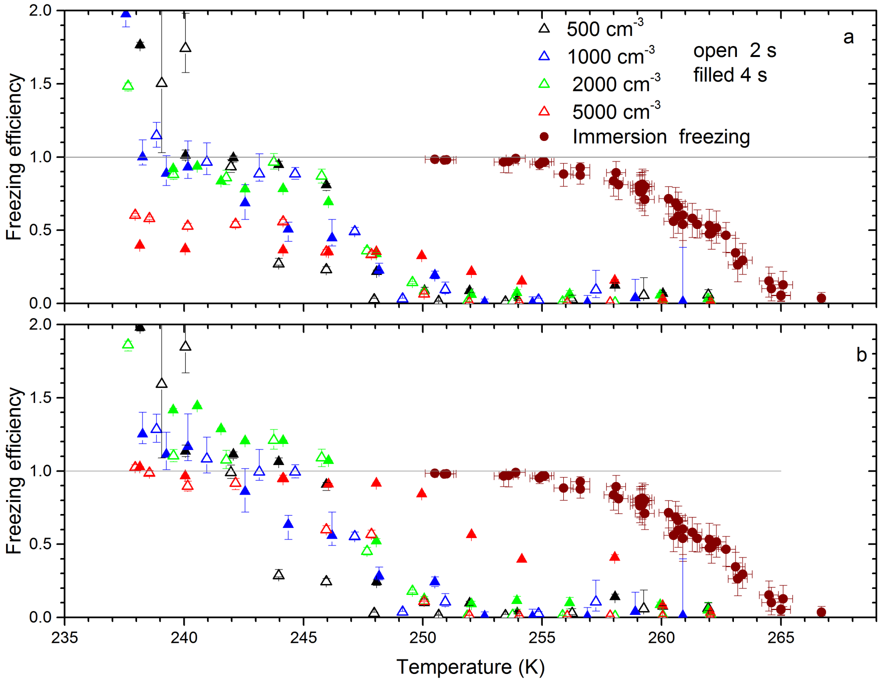

**Figure 4.** Freezing efficiency $FE$ against chamber temperature for contact freezing experiments (triangles) with 200 nm diameter AgI particles with droplet residence times of 2 s (open symbols) and 4 s (filled symbols). The concentration of silver iodide partiles varies from 500 $\mathrm{cm}^{-3}$ to 5000 $\mathrm{cm}^{-3}$. A collision efficiency $CE = 0.13$ is used to calculate $N$. $FE$ is calculated using Eq. (1) in panel (a) and Eq. (4) in panel (b). Immersion freezing of droplets in the ZINC chamber for 3 s residence time is shown as circles. The gray horizontal line indicates the maximum freezing efficiency realized when the first collision initiates freezing.

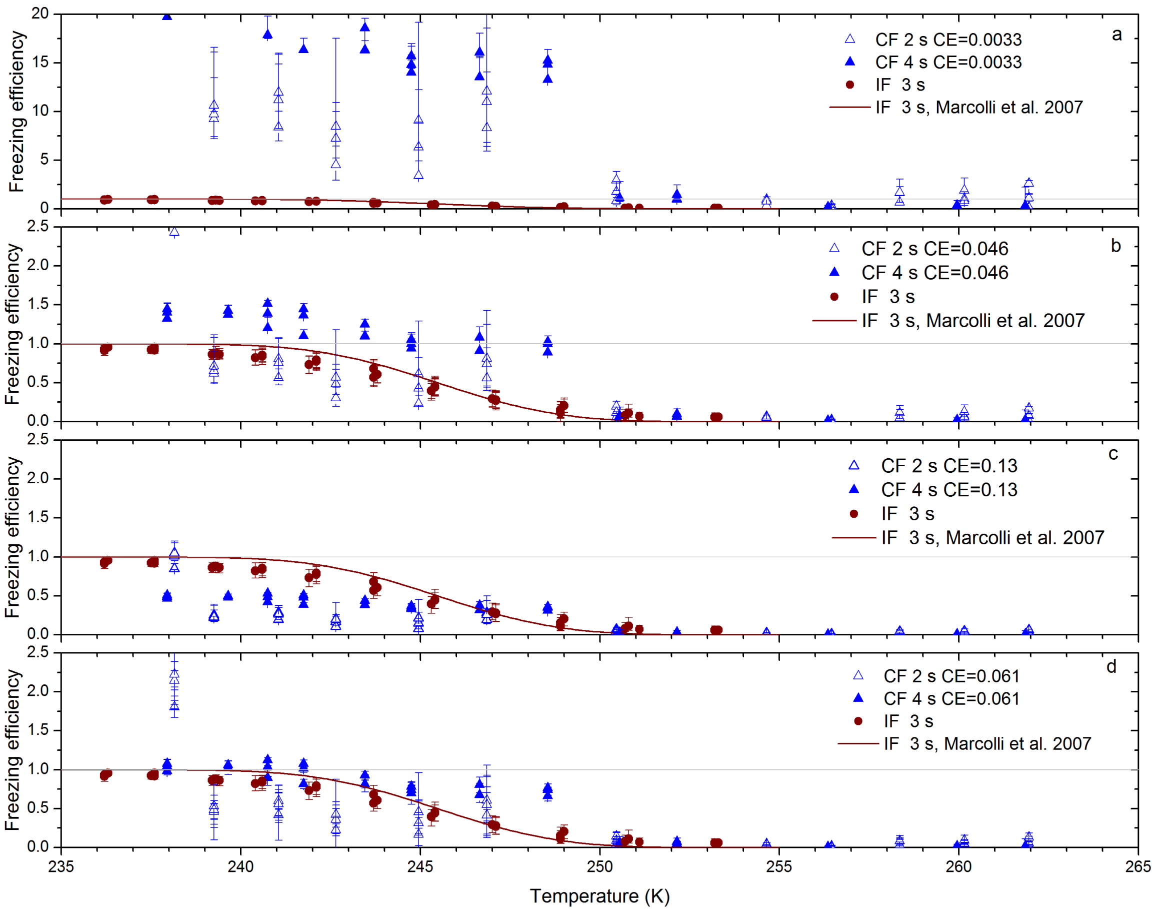

**Figure 5.** Freezing efficiency for 800 nm ATD particles with a concentration of 1000 $\mathrm{cm}^{-3}$ calculated with 4 different assumptions for $CE$: panel (a) with theoretical $CE$ from Wang et al. (1978) and Park et al. (2005); panel (b) with $14 \times CE$ from panel (a) (see text for details); panel (c) with $CE = 0.13$ (applying the value for 200 nm AgI particles for all particle sizes); panel (d) with $CE = 0.061$, shifting collision efficiencies close to 1. Filled triangles show contact freezing for 4 s residence time in the CLINCH chamber, the open triangles for 2 s residence time. Each triangle represents an independent measurement. Error bars represent the precision of the IODE detector. Brown circles show the freezing efficiency for immersion freezing of droplets in the IMCA/ZINC chamber for 3 s residence time. The brown lines show the $FF$ calculated with the active site immersion freezing parameterization from Marcolli et al. (2007) evaluated for 800 nm particles and 3 s residence time. The gray horizontal line indicates $FE = 1$. Note that the y-scale in panel (a) is different from the ones in panels (b), (c) and (d).

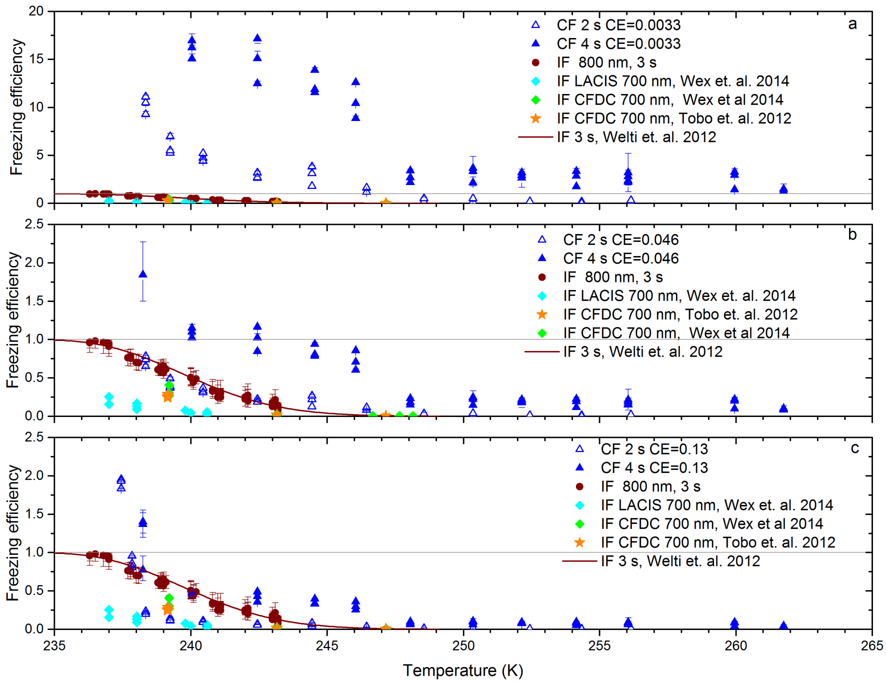

**Figure 6.** Freezing efficiency for 800 nm kaolinite particles with a concentration of 1000 $\mathrm{cm}^{-3}$ calculated with 3 different assumptions for $CE$: panel (a) with the theoretical $CE$ from Park et al. (2005) and Wang et al. (1978); panel (b): $14 \times CE$ from panel (a); panel (c) with $CE = 0.13$ (applying value of 200 nm AgI particles) for lower bound of freezing efficiency. Each triangle represents an independent measurement. Error bars represent the precision of the IODE detector. Brown circles show the freezing efficiency of droplets in ZINC for a residence time of 3 s for 800 nm kaolinite particles. Orange stars show immersion freezing of droplets activated by 700 nm Fluka kaolinite particles (from Fig. 2a of Tobo et al. (2012)). Light blue diamonds show immersion freezing of droplets activated by a 700 nm Fluka kaolinite particle (LACIS data with 1.6 s residence time (from Fig. 2 (right panel) of Wex et al., 2014). The green diamond shows immersion freezing of droplets activated by 700 nm kaolinite particles (CFDC data with 5 s residence time (from Fig. 2 (right panel) of Wex et al. (2014)). The brown line represents the $\alpha$-pdf parameterization from Welti et al. (2012). The gray horizontal line indicates the maximum freezing efficiency. Note that the y-scale for panel (a) is different from the ones in panels (b) and (c).