Response to Anonymous Referees #1-3

We thank the referees for the critical reviews of the paper. We address the questions and comments point by point and made changes in the revised manuscript accordingly. We believe that the manuscript has been substantially improved by following the reviews. Responses are shown in blue. Figure and Table numbers refer to the revised manuscript.

Anonymous Referee #1

General comments:

The authors introduce a new method to study the collision efficiencies between aerosols and cooling water droplets at low temperatures, of interest for ice nucleation in contact mode. They derive the collision rate from experimental contact freezing data obtained with the ETH Collision Ice Nucleation Chamber CLINCH. They note that phoretic forces are possible factors affecting the scavenging of aerosol. The experimental collision efficiency is slightly higher than estimations given by theoretical expressions reported in literature. The paper brings new elements to the experimental determination of collision efficiency at low temperatures and is of interest for ACP readers. In general, the manuscript is well written, and the authors did a good job in showing its importance for contact freezing and for atmospheric aerosol scavenging. However, in the current form, the paper is missing some important details and clarifications related to measurements, uncertainties involved, role of phoretic effects, and comparison with theoretical estimations. For these reasons, I recommend publication in ACP after major revisions, as suggested below.

Major revisions

1) The principal concern is related to the way the paper addresses its main goal, expressed in Introduction, last paragraph "This study therefore provides experimental data to validate theoretical formulations exactly in this least explored parameter space". The key experimental finding is summarized in Fig 6. It describes a single data point of efficiency collision (E) for water droplet of 80 microns diameter (D) with an aerosol of 0.2 microns diameter (d) and compares it with estimations for theoretical formulations. The paper will benefit if authors show experimental data for a range of aerosol diameters of interest and water droplet of different diameters.

The size range will be constrained by the available instrumentation, and details should be described in the revised version. The scavenging of aerosol by water droplet and particularly the phoretic effects depend strongly of aerosol and droplet sizes. For details, see Wang and Pruppacher, 1977, Fig 2, page 1667; Wang et al., 1978 (W78) , Figs 1-5, with focus on Fig 5. For instance, Wang and Pruppacher (1977) used water radius in the range 150 – 2500 microns, and aerosol radius of 0.25 microns. See also their Table 1 (page 1665) with a summary of what other researchers used as size ranges for water droplets and aerosol in their experiments until 1974. Recently, Ladino et al (2011), operating the same nucleation chamber CLINCH, used water droplets having radii between 12.8 and 20.0 microns and aerosol particles having radii between 0.05 and 0.33 microns. In their Fig. 1, Page 1854, they give the range of aerosol and droplet size used by many investigators in previous work. Thus, it seems possible and important to have more measurements for aerosol diameters in the accumulation mode and compare them with theoretical estimations.

In this paper, we determine collision efficiencies at low temperatures from contact freezing data. This is very different from the approach presented in Ladino et al. (2011a). Ladino et al. (2011a) determined collision efficiencies at room temperature for $LiBO_2$ aerosols with concentrations of 100, 300, and 1000 cm^{-3}. The particles that were captured by the droplets dissolved in the droplets and droplets were collected at the bottom of the CLINCH chamber. Then, the solution concentration of the collected droplets was quantified with inductively coupled plasma mass spectrometry (ICPMS). In Ladino et al. (2011a), droplet size was varied in the range from 25.6 to 40 µm. Droplet evaporation was not an issue for these experiments because they were performed at water saturation at room temperature. The situation is different for contact freezing experiments because they are performed at ice saturation. Ladino et al. (2011b) state in their paper on contact freezing of kaolinite (Fluka) particles that: "However, as the RHW within CLINCH is below 100%, the droplets shrink because of evaporation. Thus, as the particle size changes with time, it may influence the terminal velocity, residence time, CE, N_{coll} and FE. Also thermophoresis becomes more dominant for evaporating droplets. A sensitivity study (not shown) to investigate the impact of the droplet size in both N_{coll} and

FE indicates that decreasing the droplet diameter by a factor of two, causes an increase in N_{coll} and a decrease in FE by 1 order of magnitude. This means that the droplet size is a key variable in these calculations. Unfortunately, we do not have the means to measure the droplet size neither along the chamber nor at the chamber exit. Further experiments on collision efficiency at temperatures below 0°C are needed to determine the correct number of collisions. Therefore, the above calculated freezing efficiencies are not useful for a quantitative interpretation of our results."

Therefore we switched on purpose to larger droplets (80 µm diameter) for the present study. For 80 µm particles, shrinkage within the chamber due to evaporation is negligible as predicted by our model calculations. It does not make sense to perform experiments with smaller droplets because they would shrink significantly and cannot be evaluated properly.

In this study, we determined collision efficiency at low temperatures directly from contact freezing experiments. However, not all freezing data from contact freezing experiments performed with CLINCH can be used to derive collision efficiencies. Two conditions need to be fulfilled:

- There has to be a temperature range where the freezing efficiency of an INP equals one.

- Freezing data with different particle concentrations with frozen fractions in the range between 0.1 – 0.9 are needed, which then can be fitted simultaneously to derive collision efficiencies.

This paper is one of three papers that we prepare to compare freezing efficiencies of contact and immersion freezing for the same aerosol types and sizes. For this, we collected data for AgI particles, kaolinite (Fluka) and ATD particles. Out of these datasets, only contact freezing data of AgI particles fulfilled the conditions that a temperature range exists for which a freezing efficiency of one can be assumed. We showed in the ACPD version of the paper the data point with AgI particles of 200 nm, for which frozen fractions for two residence times and four different particle concentrations could be obtained. In the revised paper, we now present a second data point for 400 nm AgI particles derived from three different particle concentrations. Experiments performed with 800 nm AgI particles yielded no useful data, because their abundance in the AgI suspension was too low to obtain stable particle flows at high enough concentrations to give frozen fractions well above the detection threshold of the IODE detector. For kaolinite (Fluka) and ATD particles no temperature range is present for which a freezing efficiency of one can be assumed. Moreover, it was not possible to vary particle concentrations in a large enough range. Therefore no value of collision efficiency can be derived. In one of the companion papers that we are preparing, we estimate an upper and a lower limit of collision efficiencies for 800 nm kaolinite (Fluka) particles. We now show these estimates as a range in Fig. 8.

2) The experimental data point shown with a E of 0.13 in Fig. 6, should be presented with an error bar, which can be represented similar to Ladino et al (2011) in their Fig. 7, page 1859, where "solid error bars represent the average uncertainty and the dashed error bars are the maximum and minimum range for E at a specific a and r" (in their work a is droplet radius and r is aerosol radius).

We cannot apply the same method to derive experimental errors as was done by Ladino et al. (2011a) because we performed a totally different type of experiment with a totally different evaluation procedure as explained above. We now show error bars in Fig. 8 and add an explanation how they were derived.

Also note, in their conclusions, page 1860: "The collection efficiencies for our experimental data agree within one order of magnitude with the theoretical calculations." Since the current study uses the same nucleation chamber and similar instrumentation as Ladino et al, the E value will probably compare with theory estimations in a similar fashion, after both the experimental errors and the uncertainties in the theoretical estimations are shown and discussed.

Ladino et al. (2011b) state in their paper on contact freezing of kaolinite (Fluka) particles that: "The freezing efficiencies can be calculated using experimental values of the collision efficiency (CE). Unfortunately, we cannot use the experimental collision efficiency data obtained with CLINCH [Ladino et al., 2011] because these experiments were conducted at much higher temperatures and different relative humidities with respect to water (RHW) that do not correspond to the conditions at which the freezing experiments mentioned above were conducted."

Our agreement with theory is also within one order of magnitude. Unfortunately, this is not good enough and a limiting factor for a comparison of immersion with contact freezing.

The E values estimated from the theoretical work have their own uncertainties and differences between different schemes. Such differences are at least one order of magnitude in the accumulation mode, as noted by previous work (see Wang et al., 2010; 2011 for comparisons and discussion of various formulations and comparisons with experiment). In the comparison from Fig 6, authors can display the uncertainty ranges from both experimental and theoretical estimations. In assessing the uncertainty of E from a theoretical expression, one can consider the possible variations of parameters in the experiment due to uncertainties of aerosol and water droplet sizes, electric charge, temperature, relative humidity (RH), etc. Then, use these variations to calculate a range of values for each aerosol size, and plot E versus particle diameter. This method will give some good idea about the uncertainties in the theoretical estimation of E.

We did such an analysis and found that most parameters showed a low sensitivity. We now show the sensitivity calculations that we have performed to make this more transparent. The most sensitive parameters were the charge for electrophoresis (shown in Fig. 7) and the temperature for thermophoresis and diffusiophoresis (shown in Fig. 6). In the revised manuscript we add a Table 2 that shows the dependency of some parameters when they are varied according to assumed realistic uncertainties.

3)The description of the experiment (Section 3) needs to be more detailed such that others can reproduce the results. A list of instruments and references can be included for this specific setup.

We are using the same instrument as was described in detail in Ladino et al. (2011a) with some important modifications and refer to this paper for the basic setup. We describe in the experimental section of the present paper the parts of the setup that are important for the evaluation of collision efficiencies and components that have been changed compared with Ladino et al. (2011a).

In addition, the parameters of interest and their uncertainties need to be described quantitatively. For example, give the time evolution of temperature (T), relative humidity (RH), droplet diameter (D), size distribution of aerosol, charge on aerosol and droplet, estimations of loss of aerosol on walls. Is any significant variability of these parameters during individual experiments?

We added a Fig. 1 that shows the simulated time evolution of temperature and droplet size.

We also added Fig. 2 that shows the results of all the performed charge measurements. We describe the charge measurements in more detail in the revised text.

How many experiments were done to produce the data point from Fig. 6, and what is the variability of chamber parameters during those experiments?

Data points were measured 3 times and the average is shown in Figure 4. Some measurements were repeated some months later to examine the reproducibility. No significant difference was observed.

The experiment starts with water droplet of diameter 80 microns. Give the histogram of diameters of generated droplets (not all droplets have exactly 80 microns, there is a range of variation, and most likely, a narrow normal distribution with the maximum at 80 microns).

We now state the variation in droplet size in the revised manuscript. It is 80 ± 3 µm in diameter.

Once a droplet starts falling, it can evaporate in time since the chamber is subsaturated with respect to water. What is the droplet diameter versus time in chamber and what values do you use in the theoretical estimations of E?

For our 80 ± 3 µm droplets evaporation in the chamber is negligible from (80 µm to 79 µm). Droplet shrinkage due to evaporation is now shown in panel (c) of the new Figure 1. Ladino et al. (2011a and 2011b) used smaller droplets and had significant evaporation.

For comparisons of experimental E with theoretical E, it may be useful to calculate E for the observed/estimated range of diameter of the water droplets.

In the revised manuscript we calculate E also for 77 µm and 83 µm diameter droplets and show the results in the new Table 2.

Aerosol size is taken to have the average diameter of 0.2 microns, but how about standard deviation (STD)?

An example of a size distribution after size selection with a DMA is given e.g. in Fig. 5 of Lüönd et al. (2010). In a very recent paper (K. Ardon-Dryer, S. Garimella, Y.-W. Huang, C. Christopoulos, and D. J.

Cziczo: Evaluation of DMA Size Selection of Dry Dispersed Mineral Dust Particles, Aerosol Science and Technology, 49:828–841, 2015) mineral dust particles were measured again after size selection in a DMA, showing that for 500 – 1000 nm diameter particles, sizes were smaller than the DMA-selected diameter. This effect depended on particle morphology and was larger for less spherical particles. The AgI particles used in this study are not spherical, but deviation from spherical shape is smaller than for mineral dust.

How long do aerosol particles stay in the chamber? Is the aerosol size increased due to water condensation, coagulation or electrical interaction?

Aerosol particles travel through the chamber with the flow velocity of 0.017 m/s. They stay therefore 47 s in the chamber of 80 cm length. Water condensation below water saturation is not significant for AgI particles. The concentration of particles reduces by 10 cm^{-3} in about 100 s for concentrations of 5000 cm^{-3}. Hence no observable change in size is expected in 47 s.

The electric charge on water droplet is measured at beginning, but some statistics will be helpful, such as a distribution of charge, average, STD, min and max values. These values will be useful to estimate the maximum possible effects of electric charge on E. Does the charge on droplet stay the same during experiment? Can it change during experiment? Any assumption should be explained in more detail.

We added Fig. 2 to the manuscript that shows the outcome of all charge measurements. There are quite large variations of charge. Our conclusion of the sensitivity analysis is that droplet charge is a crucial parameter that is not well constraint in the present setup. We therefore intend to improve this for future measurements.

The charge on the droplets can only change by spontaneous discharge. This is highly unlikely for the charges that the droplets bear.

The electric charge on aerosol is assumed “only one elementary charge” (page 12189). There is no indication that these charges are measured in this study. Are they based on some references about the instrument. Please clarify and provide specific references. If some particles have more than one charge (even a few elementary charges), it can increase the variation of the estimated E from electrophoretic forces (Fig 5).

In our experiments, the dry AgI aerosols are passed to a differential mobility analyzer (DMA, TSI Model 3081) for size selection. Before the particles enter the DMA they pass through a neutralizer. The neutralizer does not neutralize charges, but rather brings the particles into a well-known charge distribution with a radioactive polonium source. The result is a Boltzmann distribution of negative and positive charged particles. In the DMA, particles with a specified electrostatic mobility diameter are selected assuming that particles carry only one elemental charge. However, multiple-charged particles with the same electrical mobility will also be selected. Figure 3 of Welti et al. (Welti, A., F. Lüönd, O. Stetzer, and U. Lohmann, 2009: Influence of particle size on the ice nucleating ability of mineral dusts. Atmos. Chem. Phys., 9, 6705–6715) shows that the contribution of such multiple-charged particles to the total amount of particles is large for particle sizes located in the upslope part of the sample size distribution. Therefore, to obtain a monodisperse sample, particle sizes that are downslope of the size distribution have to be sampled. This is also shown in Figure 5 of Lüönd et al. (2010). The size distribution of our AgI particles peaks at ca. 80 nm. 200 nm and 400 nm AgI particles are both downslope of the size distribution.

If some particles have opposite charges they can coagulate more efficient. Is this effect large enough to make a difference in E?

Only particles with negative charges were selected. We state this now in the revised manuscript.

4)Phoretic effects. One concern is that using one data point makes it difficult to assess the role of phoretic effects. Measurements done at various aerosol sizes can give a better idea about behavior of E in the accumulation mode. Moreover, measurements are done with all factors acting in the same time (from Brownian diffusion, impaction,and phoretic forces) and this makes it difficult to separate experimentally the role of various forces.

We now show an additional data point for AgI particles with diameter of 400 nm. Experiments performed with 800 nm AgI particles yielded no useful data, because their abundance in the AgI suspension was too low to obtain stable particle flows at high enough concentrations to give frozen fractions well above the detection threshold of the IODE detector.

In addition, we give an upper and a lower limit for collision efficiencies derived from kaolinite (Fluka) particles with diameters of 800 nm.

Prodi et al (2014) show that one way to isolate the phoretic forces is to do experiments in microgravity conditions. In their study they find that diffusionphoresis predominates, contrary to the statement from this paper that "The combined description of thermophoretic and diffusiophoretic forces indicate that for our experimental conditions of evaporating droplets in the presence of rather small aerosol particles, thermophoresis should exceed diffusiophoresis" (page 12188). This needs more analysis and clarification, to provide experimental evidence of strength of each phoretic factor.

Our calculations indicate that thermophoreis is 10^9 and 10^4 times higher for A06 for W78 formulations, respectively and opposite in signs.

For example, in the case of electric effects, the effects of image charges are not included and can be discussed in detail.

We discuss the influence of charges in detail in section 5.2 (Charge dependence of electrophoresis).

Specific comments

In abstract, "Freely falling 80, microns water droplets. . ." should indicate that 80 microns is the diameter of the water droplet.

We corrected this.

In the statement "The chamber is kept at ice saturation in the temperature range from 236–261K leading to slow evaporation of water droplets giving rise to thermophoresis and diffusiophoresis." must say something about the values and evolution of relative humidity (RH) during experiment.

The temperature can be set to a constant value within the chamber in the range of 236 – 261 K. Ice saturation is provided by ice covered walls. This defines the value of relative humidity in the chamber. There is no evolution of RH during the experiment.

The statement "Droplets and particles bear charges inducing electrophoresis" can contain more quantitative information about the charge on aerosol and water droplet.

We discuss the influence of charges in more detail in the revised manuscript.

The reported collision efficiency of 0.13 can be given with plus/minus standard deviation or the range observed values (min – max). This can be done after revisiting issues as mentioned at point (1) above.

We now give an upper and a lower limit together with the average value and show the data points in Figure 8 together with error bars.

The statement "This discrepancy is most probably due to uncertainties and inaccuracies in the description of thermophoretic and diffusiophoretic processes acting together." does not have much support with the available data from this experiment, but it can be improved by adding data, and presenting it with error analysis when com- pared with model estimation with their uncertainties, as mentioned in (1) above. The discrepancy you mention can be due at least in part to the experimental uncertainty or variability (please see the major comments above).

We take some of the weight off from this sentence by replacing the "most probably" by "probably".

Introduction

In the last paragraph (page 12172), "The present study investigates collision efficiency of 200nm diameter silver iodide (AgI) particles with 80 microns droplets at low temperatures" need to specify that 80 microns is the diameter of water droplet.

We do this in the revised version.

Experimental setup

In section 3.2, the authors must explain and justify why "The particles have a charge of 1e after the size selection by the DMA which was operated at 1 liter outflow and 10 liter sheath flow air." Can aerosols charge change after they are generated, and how much?. Is charge affecting the aerosol coagulation and how much? These details can be important for the electrophoretic effects (see comments at points 2 and 3 above).

The charge on the particle has been explained above. To gain or lose charge particles need to collide with each other. Collisions between equally sized particles are infrequent.

In section 3.3, "The mean charge on the droplets was about 65 fC (39 000e±20 000 e)". Does the charge on droplets remain constant after generation?

Spontaneous discharge for these charges is very unlikely. Therefore, collisions would be needed. However, with a distance of 2 mm between the droplets in the droplet stream such collisions can be excluded.

Please see comments at point 3 above and include a more detailed characterization of the charge distribution on water droplets.

We added Fig. 2 to the manuscript that shows the charge that we measured in our offline charge measurements. You can see from this figure that the charge was always positive and in one case zero but showed large variations when the droplet injector was turned on and off again.

4 Experimental results.

Is any change in the size of water droplet during experiment, and how this impacts the estimation of E? How is the droplet diameter changing in time due to evaporation?

There is no significant shrinkage in the size of water droplet during the residence time in the chamber. We show now the modelled shrinkage in panel (c) of Fig. 1 and it is about 1 µm when the temperature of the chamber was kept at 235 K.

The method to estimate E from the frozen fraction (eq 19) should be described in more detail. Does Kgeo change in time? What are the errors in this calculation? Discuss the number of experiments conducted to get the reported E value? The possible errors associated with this procedure need to be analyzed and presented in more details.

We do this in the revised manuscript.

8 Summary and conclusions

The range of values of the main parameters in chamber should be described. Instead of the statement "More importantly, comparisons of different theoretical formulations show considerable differences." I suggest, ". . .comparisons of different theoretical formulations show differences within one order of magnitude in the accumulation mode" which seems to be seen in many reported comparisons. The statements "There are large differences between the formulations for thermophoresis from A06 and W78 regarding size and temperature dependence. Calculated collision efficiencies for impaction in the size range from 0.5–2 microns strongly depend on whether a critical Stokes number is assumed. The temperature dependence of W78 is much larger than the one of A06." do not appear as significant conclusions since they refer to comparison of two schemes, which can be done in sections 5 and 7, in connection with Figs 3- 5. Also, it seems that A06 and W78 agree within one order of magnitude for the range of parameters used in this experiment. Instead of ". . .W78 is much larger than the one of A06", I suggest to compare them in a more quantitative manner, otherwise it could be misleading for someone reading only the conclusions. Reasons for such differences are given on page 12187, related to different regimes assumed, specific assumptions, and the comparison statements should be in that section. In the conclusion section, I think is more important to compare the experimental E with theoretical evaluations. A statement like "Our measurements agree with theoretical evaluations within one order of magnitude. . ." might be accurate (after you add the error bars in the experimental data and the estimated E). One short paragraph at the end can give more details and specifics about what measurements are needed in the future to improve the experimental data for characterization of phoretic effects and/or useful for ice contact nucleation studies. Such paragraph will put this work in perspective and show its potential, which is otherwise well illustrated in the main sections.

We revised the conclusions according to the reviewer suggestions.

Technical recommendations Page 12204. Table 2 can be eliminated. Its content can be added in Table 1 at the end.

We have done this.

Anonymous Referee #2

"Estimating collision efficiencies from contact freezing experiments" describes an experiment on 80 micrometer water droplets and 200 nm AgI aerosol where collision efficiency was inferred from the formation of ice. In brief, aerosol and droplet were allowed to interact in an ice saturated chamber so that ice formation could then be detected with a custom optical counter called IODE. The paper seems to therefore indicate what is measured is an ice nucleation rate, not a collision efficiency.

What is measured is a frozen fraction in the IODE detector. From the frozen fraction and the known aerosol concentration the collision efficiency was derived.

The authors assume that all contacts lead to freezing (which may or may not be valid, but proof of the equality is lacking in the paper).

The majority of the paper is not experimental, as the title seems to imply, instead being centered on theory of collision. As an example, section 2 is 'Theory' – 11 pages – while Experimental is section 3 – 3 pages. This is in no way a negative although a change in title seems warranted (see below). The theoretical calculations are more than an order of magnitude lower than the collision efficiency that is experimentally determined. The authors suggest that this is due to uncertainty in thermophoretic and diffusiophoretic theory – and this point is argued in the discussion section. This seems a theory that isn't supported with much evidence since it is based on only a single data point (one aerosol and one droplet size).

Up to now, the theoretical formulations have not been tested experimentally for low temperatures. We present here for the first time collision efficiencies well below 0°C. It is likely that the theoretical formulations of thermophoresis and diffusiophoresis are responsible for the low values at low temperatures because they show the strongest temperature dependence of all contributions to collision efficiency. Moreover in the revised manuscript we show now an additional data point for 400 nm diameter AgI particles and a collision efficiency range for 800 nm diameter kaolinite particles.

This topic is well suited for ACP and the work is of contemporary interest in the atmospheric sciences since ice nucleation in general, and the largely unexplored mechanism of contact ice nucleation specifically, are in need of constraint. There are, however, some serious issues with this paper that need to be addressed before publication. The major issue is the presence of only a single data point (one aerosol and one droplet size) in the concluding Figure 6 and, realistically, there should be several points across the aerosol range to help determine where the discrepancy between experimentation and theory lies. I stress that this is not a minor change and significant experimentation is required to make this paper suitable for publication. Such a paper would be of great importance in the field. The authors appear to be in a good position to do this and I therefore recommend 'major revisions'.

In the revised version we give an additional data point for 400 nm diameter AgI particles and a collision efficiency range for 800 nm kaolinite (Fluka) particles, which support that the theoretical formulations yield too low collision efficiencies at low temperature. The reasons why we cannot present more data points are explained in the response to Referee #1.

Alternatives seem to be (a) simply publishing the single size aerosol and droplet data shown here but not trying to draw conclusions by comparison to theory which isn't warranted with the lack of constraint offered by a single data point or (b) publishing a theoretical review paper without data. I find these alternatives not preferable and highly recommend more experimentation and a revised paper with enough data to allow proper interpretation.

Suggestions for improvement:

1. Since the theory and experimental results differ by an order of magnitude more experimental points are warranted. This is further highlighted by the amount of text spent on theory versus experiment (roughly 4 times as much). Specifically, Figure 1 is data for 80 micrometer droplets and 200 nm aerosol. A great deal would be learned from variation of droplet and aerosol size and this would seem the best way to constrain the reason for the difference between theory and experiment. Just looking at Figure 6, and the plots of theory leading to this, several more points with varied aerosol size seem

required to draw any reasonable conclusion. Thus I suggest that several more figures of the Figure 1 type be prepared at different aerosol and drop size. 2 or 3 more points, at variable aerosol size, would greatly help in understanding the difference here. As the adage goes, an infinite number of lines can be fit to a single data point. At this time, all the authors show is that the single data point is high by more than an order of magnitude but this does not make a satisfactory conclusion for the paper. Furthermore, experiments could be devised to test if the authors' suggestion that thermophoretic and diffusiophoretic effects might be the cause based on the variation of these forces with size.

We explain in the response to Referee #1 that datasets need to fulfill several requirements to be suitable for the type of evaluation performed for 200 nm aerosol particles and now in addition for 400 nm aerosol particles. We have acquired considerable more data which all cannot be used. This includes contact freezing experiments with 800 nm AgI particles.

There is also a significant uncertainty in charge, stated as 39k elemental charges +/- 20k, that could contribute. Currently the authors point to a 'worst case scenario' of charge but the means of measuring charges seems unconstrained (see below).

The charge is indeed not well constrained in our measurements as we discussed in response to Referee #1. We intend to improve this in future experiments.

2. Change the title. This paper is truly a comparison of theory to contact freezing experiments, not just experiments on collisions at low temperature.

We changed the title to: Comparison of measured and calculated collision efficiencies at low temperatures.

The authors have not demonstrated that every collision leads to an ice nucleation event and if they can not do this they can not decouple collisions per contact ice nucleation event. I agree that in this regime it is extremely likely that every collision leads to an ice nucleation event but the authors need to more explicitly state this assumption (starting in the abstract –around sentence 4) but unless the authors prove it the implied assumption they are the same is not acceptable.

A temperature range where all contacts lead to freezing is a prerequisite for the evaluation that we apply. We are confident that this condition is fulfilled for AgI particles of 200 and 400 nm diameter for T < 247 K. If AgI particles were not active in contact mode, they nevertheless should lead to nucleation in immersion mode after colliding with the droplet. With the same AgI aerosols we performed also immersion freezing experiments in our IMCA/ZINC setup (the setup is described in Welti, A., Lüönd, F., Kanji, Z. A., Stetzer, O., and Lohmann, U.: Time dependence of immersion freezing: an experimental study on size selected kaolinite particles, Atmos. Chem. Phys. 12, 9893–9907, doi:10.5194/acp-12-9893-2012, 2012). These measurements showed frozen fractions of 1 for T < 250 K and particle diameters of 200 and 400 nm. This data will be presented in a companion paper that is in preparation. We will mention this in the revised manuscript.

3. 19k – 59 k elemental charges seems extremely large and this value caught my attention. The authors include a few statements on the atmospheric range is in the paper but these are only found in the conclusions and seem to indicate some 100s to 1000s. The text in this regard is rather vague, including statements of attraction and repulsion but little on the atmospheric relevance. The atmospheric range should be moved higher, into the experimental part for comparison. Please explain why such a large charge was used? Please include more data on how charge was measured and if any calibration was used (such as particles of known charge). As it stands, this seems a large area of uncertainty and one that needs to be expanded upon.

We write in section 7.2 (Implications for contact freezing): "In addition electric forces act on the particles which may significantly contribute to the overall collision efficiency. Evaporating cloud droplets and aerosol particles released from evaporated droplets from the same region of the cloud are supposed to have like charges (Tinsley and Leddon, 2013). For particles of sizes that act as INP such as mineral dusts, the predominant effect of their charge, irrespective of sign, is an increase in the collision rate due to the short-range electrical image-charge attraction (Tinsley and Leddon, 2013). Layer clouds such as stratocumulus and altostratus are weakly electrified producing droplet charges in the consequent gradients of electric field of the order of 100 e on 20 µm diameter cloud droplets (Zhou et al., 2009). Thunderstorm clouds are strongly electrified (Tinsley and Leddon, 2013) with cloud droplets bearing elementary charges in the range of 10000 - 100000 e. Taking the effect of image charges into account will therefore increase the collision rate of particles with droplets even more.” This discussion includes references for readers that want to know more about this subject. Since the manuscript is long already, we prefer not to extend this discussion further. The droplets obtain their charge in the droplet injector. This charge is constant once the droplet injector is turned on but can change to a different value when the droplet injector is turned off and on again. We added Fig. 2 to the revised manuscript that shows the results of all the charge measurements that we performed offline to determine the charge of droplets acquired during injection and we describe the charge measurements in more detail in the revised manuscript. We agree that charge is not well controlled in our experiments and intend to improve this for future studies with the CLINCH setup.

4. Regarding the assumption that all freezing is caused by contact nucleation: it is understood these are pure water droplets and conditions, per Figure 1, are outside the homogeneous regime. However, the authors need to show they don’t have any freezing going on in the absence of aerosol. Please include some control experiments, e.g. in Figure 1.

We performed blank experiments to determine droplet freezing in the absence of aerosols as described in the Section 3.4 (experimental procedure). From these experiments we derived the range of homogeneous droplet freezing and the detection limit for heterogeneous freezing. We show now the detection limit of heterogeneous freezing as black horizontal line in the panels of Fig. 3.

5. The section “Comparison with previous experimental work” has some issues. First, as mentioned above, it needs to be clear that the authors are assuming freezing events = collisions.

We state this more explicitly in the revised manuscript.

6. Second, “Comparison with previous experimental work” includes a comparison to several room temperature experiments, including that of Ladino et al. (2011), which apparently comes from this same research group. This caught my attention because a comparison is made between the theory here and the old Ladino et al. (2011) experiments in the final figure, as if this was the summation figure of this manuscript. The purpose seems to be to show that the theory used here is solid and the statement is made, regarding Ladino et al., that “their experimental results are in general agreement with the theoretical predictions.” First, Figure 6 should really be the concluding figure of this paper since it combines the lab and theory performed here. Figure 7 should be moved up since its purpose seems to be to show agreement of theory with previous experiments. Note that Figure 7 calls “Ladino et al. experiment” but no year is included for reference. Also, I believe with multiple data points this should be the plural, ‘experiments’.

We keep the Figure with the experimental results from Ladino et al. as the last Figure so that the Figures follow the order of the text.

7. Finally, and most important, I think the reference here (if the text is correct) is Ladino et al. “Experimental Study of Collection Efficiencies between Submicron Aerosols and Cloud Droplets” (so the figure caption should be 2011b) and the copied data are Ladino et al. Figure 7.

This paper is now 2011a. The one about contact freezing of kaolinite particles is 2011b.

If that is the case then Ladino et al. stated in their paper “We did not have equipment to measure the droplet and particle charges.” and yet here a charge of 10k is applied for the stated agreement. Please clarify in the text and the response : is this the correct reference? How was this charged arrived upon, as a best fit or was it measured? Is this a correction to an old paper? If so that should not be done in this manuscript but as an addendum to the original journal article.

Ladino et al. (2011a) write: “We did not have equipment to measure the droplet and particle charges. If the droplets have one or more charges, electroscavenging could play a role in our experiment, generating a source of uncertainty since electroscavenging was not included in the theoretical calculations.” We used a different droplet injector from the one used by Ladino et al. (2011a), however, with the same working principle (piezo element). We assumed a charge of 10000 e for our calculations of the collision efficiency experiments performed by Ladino et al. as a rather conservative estimate. In the revised version we show additional lines for an assumed charge of 50000 e.

In conclusion, this is a well-written paper that should make a fine addition to ACP if more experiments to help lead to conclusions, not assumptions, are made. This is highlighted by the single data point in Figure 6 that leaves the reader unable to interpret the experiments or the theory being used to interpret them. This is no small amount of work but it is required for a publishable paper. This review was made before reading the first Reviewer’s comments. It is worth noting that many points - on the need for more data, uncertainty, and charge quantification - were made independently and highlight the needs in these areas.

Anonymous Referee #3

The authors describe a novel experimental approach to measure the collection efficiency of aerosol particles by falling droplets. By using silver iodide particles, which are potent ice nuclei, it is assumed that at low enough temperatures, collection of a single aerosol particle leads to contact freezing with a probability of unity. From the observed frozen fraction of droplets, the authors deduce the collection efficiency under the given geometrical constraints. Under the geometrical constraints of their setup and for a given droplet and particle diameter, they find an collection efficency which is almost one order of magnitude above the various theoretical formulations that are used for comparison. From this finding the authors conclude that the collision efficiency between droplets and aerosols, which is crucial for contact freezing and aerosol scavenging may be underestimated in current models. I consider these skillful experiments to be a clever and novel approach to tackle the notoriously difficult problem of measuring collection efficiencies between droplets and aerosol particles. The presentation is very good and the work fits very well in the scope of ACP. The conclusions seem somewhat premature however, as the current theoretical descriptions of aerosol scavenging are proven and tested over many years.

Up to now, the theoretical formulations have not been tested experimentally for low temperatures. We present here for the first time collision efficiencies for conditions well below 0°C.

They should not be dismissed by a single experiment without assessing all possible experimental issues with care. In this respect, I feel the manuscript falls short and I like to ask the authors to improve it. The most manifest (list may not be exhaustive) issues that come to my mind are:

1. Are all particles silver iodide? What about potassium nitrate contaminations or coatings? If a fraction of the particles were poor ice nuclei the analysis would have to be modified considerably.

We looked in this issue in detail. Electron microscopy on particles has been performed. The particles were irregularly shaped and consisted mainly of AgI with minor fractions of KNO_3. Such a composition is in accordance with literature data of precipitated AgI particles. The electron microscopy data will be shown in a companion paper which is in preparation and focuses on contact freezing compared with immersion freezing of AgI aerosols. The presentation of all material in one publication would lead to a too long paper.

2. What is the geometry of the silver iodide particles (is their effective density lower than bulk density?) Electron microscopy of collected particle samples may answer both questions.

The particles are irregularly shaped. We do not have information on density. Impaction depends on the density of the particles. Our sensitivity analysis showed that the dependence on density is small as shown in the newTable 2 listing sensitivities.

3 Droplets. are falling in the wake of the previous droplets, which may have depleted the aerosols on their track.

The droplet size is 80 µm and the distance between droplets is 2 mm. Depletion of aerosols can therefore be excluded.

4. Droplet charge is crucial here. From the description of how it was measured, it might be that the voltage of the deflection plates induces charges on the droplets which might not have been there during the experiment. It would be very important to measure the charge on the droplets during the experiment. (This might be possible using an induction –tube)

With the current setup, it is not possible to measure charge during the experiment. For future studies we intend to do modifications to the setup to improve charge control.

Additional points that should be addressed:

It would be very desirable having measurements at more aerosol particle sizes. In my understanding this would mean only to set the DMA to a different voltage? Has this been done, what are the results?

The same point was raised by referees #1 and #2. It is addressed in detail in the response to referee #1.

Why is the discussion centered around a temperature of 261K if the experimental data are derived from measurements at T<245K?

We show now in the revised manuscript Fig. 8 calculated for T = 245 K.