We thank reviewer #2 for taking the time evaluating our manuscript. We provided a point-bypoint response to the reviewer's comments given in **bold** faced letters below.

The experimental results are interesting however the interpretation of the results and model analysis can be improved as pointed out below. Overall the authors reuse already established approaches and to a large extend confirm previous results. The progress in understanding of immersion freezing in solution droplets is therefore only incremental and the need for the performed analysis should be motivated better.

We thank the referee for the evaluating our manuscript. It is correct that we use previously established analyses of ice nucleation data, however, these i) have been applied the first time to humic acid as immersion IN and ii) for a wide range of water activity. Here, for each investigated system we conduct these analyses for 8 different aw to provide a yet not achieved comprehensive investigation of immersion freezing covering the typical range of atmospheric RH and T. We respectfully disagree with the conclusions that our results confirm previous results. As a matter of fact the opposite is more likely. We show that commonly applied immersion freezing paremeterisations cannot capture the effect of water activity. Furthermore, we show that when using statistically significant amounts of data acquired with little uncertainty, many of these parameterisations produce indistinguishable results hampering interpretation of the underlying ice nucleating sites claimed by using those parameterisations. Lastly, it is one of the very few studies showing that also for this organic IN, the heterogeneous ice nucleation rate coefficients are constant along the immersion freezing curve, a remarkable and not yet fundamentally understood finding in line with the water activity based homogeneous ice nucleation theory by Koop et al. (2000).

Specific comments:

4922, Line 20: Could it be that the initial particles consist of aggregates which break apart during sonication? Is this what is called "dissolution"?

We did not associate the brownish hue with very tiny, not visible particles. Once the particles are settled, the liquid appears visually clear but brownish, no particles are observed. However, it cannot be entirely ruled out that the brownish hue is a cause of non-visible tiny aggregates breaking up during sonication.

We change the sentence:

"PP exhibited a brownish hue within minutes of being sonicated indicating potential partial dissolution in water and aqueous $(NH_4)_2SO_4$ solutions."

to

"PP exhibited a brownish hue within minutes of being sonicated indicating potential partial dissolution in water and aqueous $(NH_4)_2SO_4$ solutions that may include break up of particulate aggregates."

4925, Line 21: Does the nucleation rate given here represent median hom. freezing temperatures of this specific experiment?

The homogeneous ice nucleation rate coefficient given here, J_{hom} , is derived from the water activity based homogeneous ice nucleation theory (Koop et al., 2000) for droplets volumes employed in our experiments. In this study we did not measure J_{hom} but have done so in a previous study employing aqueous (NH₄)₂SO₄ droplets confirming the water activity based homogeneous ice nucleation theory (Knopf and Lopez, 2009).

The homogeneous ice nucleation rate coefficient given here would be the necessary rate for half of the aqueous solution droplet population, without any immersed particles, to nucleate ice with droplet volumes like those in our experiments. The temperature at which an aqueous solution nucleates ice depends on the amount of solute but is always colder than for heterogeneous ice nucleation for similar aqueous solution. Droplets in presented experiments always contain immersed HULIS particles and nucleate ice at warmer temperatures than homogeneous ice nucleation. In the temperature range for heterogeneous ice nucleation experiments investigated here, J_{hom} is negligible for all our experiments (see also response to reviewer #3). Typically, J_{hom} decreases about 5 orders of magnitude for every 3 K increase at a constant a_w . At 3 K warmer than the given median homogeneous freezing temperature, $J_{hom} \sim 10^1$ cm⁻³ s⁻¹, and for droplet volumes of ~10⁻⁷ cm³, nucleation rates are around 10⁻⁶ s⁻¹. Again, at about 3 K warmer than the median homogeneous freezing temperature, the heterogeneous ice nucleation rate sare 1 s⁻¹. Thus, heterogeneous ice nucleation dominates homogeneous ice nucleation by about 6 orders of magnitude, thus occurrence of homogeneous ice nucleation is considered a negligible effect.

4925, Line 24: In your experimental data no obvious change for aw<1 can be seen in comparison to aw=1. I would expect the conversion to a glassy state to influence ice nucleation on HULIS. Can you provide an explanation for the absence of a change in the ice nucleation efficiency?

The glass transition temperatures on previously studied humic acids suggest that for $a_w < 1$ the humic acid may be in a glassy state (Wang et al, 2012, Young and Leboeuf 2000, Koop et al., 2009). However, it should be kept in mind that in this system the humic acid is always immersed in an aqueous phase (when cooling from room temperature to freezing temperatures) which may affect the glass transition point. For this reason we stated this comment as "most likely" since we cannot be entirely sure. In the revision we exchange the "are most likely" with "may be". Lastly, we do not know how the morphology and other physico-chemical surface properties of the humic acid change when undergoing a glass transition and its effects on ice nucleation. Since the humic acid particles are solid to begin with, one would not expect significant changes in particle properties. In contrast to, e.g. a liquid to glass transition (Wang et al, 2012, Young and Leboeuf 2000, Koop et al., 2011).

4926, Line 2-7: Does the constant supercooling from the melting point (Tm-Tf ~const.) indicate that the change in Tf as function of aw is only due to a change in the bulk water structure and there is no change in the lowering of the nucleation energy due to the IN? Additional discussion could be of interest also in regard to the next comment.

We assume there is a misunderstanding of the concept of a shifted ice melting curve. The ice melting curve is not shifted vertically to derive the immersion freezing curve but horizontally. There is no constant supercooling in a a_w based description. As shown in Fig. 1 at lower a_w Tm-Tf is much larger than for higher a_w values. In response to the reviewer, we point out that for the same solute employed $(NH_4)_2SO_4$, Pahokee Peat and Leonardite do not nucleate ice with the same efficiency (i.e. they show different Tm-Tf at same a_w). Therefore, we expect that ice nucleation temperatures are affected not only by the freezing point depression, but also by the IN surface.

4926, Line 17-19: Contradicting to the suggestion that only aw is needed to describe immersion freezing in solution droplets, Reischel and Vali (1975) reported experimental results where they observed varying interactions of solute and IN in dependence of their nature.

Reischel and Vali (1975) observe that the quantity (Tm-Tf) can both increase and decrease with increasing solute concentration for various investigated IN. It should be noted that these experiments did not consider that water activity could change with

temperature. This is in part due to the lack of Pitzer ion interaction models for derivation of activity coefficients at the time of that study. Furthermore, in these experiments ambient relative humidity above the droplets was not controlled, implying condensation of water occurred from the humidified room air onto the frozen droplets (as low as -40° C), thereby altering droplet composition. Thus, one should be careful to compare those results with experiments that account for changes in a_w and control ambient conditions. Those more recent experiments all corroborate that for increasing solute concentration, heterogeneous freezing temperatures decrease for same IN and that immersion freezing temperatures can be described by a shift in a_w , derived from the freezing temperature and a_w (Zuberi et al., 2002; Zobrist et al., 2008a,b, Koop and Zobrist, 2009, Archuleta et al., 2005, Cantrell and Robinson, 2006, Knopf and Rigg, 2011, Knopf and Forrester, 2011, Alpert et al., 2011a,b).

4930, Line 2: There is a more recent publication by Smith and Kay (2012), including an updated fit curve of the diffusivity based on additional data. Accordingly the surface tension given in Zobrist et al., 2007 should be revisited.

Thank you for this important information. Indeed, we missed this publication and the new parameterisation for the diffusion coefficient of water needed in our analyses. This led us to reanalyze all data sets. As a consequence we have redone Figures 2-5, S2-3, and tables 3-4. This affected the resulting fitting parameters but does not change any of the previous conclusions of this paper. Visually, the differences in the figures are hardly noticeable. We change the original citation to the previous work by Smith and Kay on p. 4930, I. 7 to "(Smith and Kay, 2012)".

4930, Line 24 ff: Can you provide a physical explanation why a temperature dependence of the contact angle could be expect? The calculated temperature dependence of the contact angle is highly dependent (to the power of 3) on the chosen temperature dependence of the surface tension. Therefore it can be suspected that the derived change in contact angle is an artefact due to the uncertainty in the surface tension. As a sensitivity test: How would the temperature dependence of the surface tension change if the contact angle would be held constant. Would this lead to an unphysical temperature dependence of the surface tension? Depending on the author's response, the alphaT approach might have to be declared a parameterisation with limited physical meaning.

The contact angle is a parameter which characterises the energy balance to establish an interface between the water or aqueous solution, solid IN surface, and the ice embryo. Young's equation describes this physical interaction (Pruppacher and Klett, 1997). This study and previous work (Zobrist et al., 2007; Alpert et al., 2011a,b; Knopf and Forrester, 2011) observe a temperature dependent contact angle for a constant a_w. A recent study by Welti et al. (2012) found a similar relationship that the contact angle increases as temperature decreases. Furthermore, these authors use physical parameterizations of the interfacial energies, taken from Helmy et al. (2004) and Pruppacher and Klett (1997) and obtain a reasonable temperature dependent interfacial energy between the IN surface and the ice embryo corroborating the observed temperature dependency of the contact angle.

The reviewer is correct that the contact angle is highly dependent on the choice of interfacial energy between the aqueous and ice phase. The interfacial energy calculations used here were constrained by measurements of homogeneous ice nucleation (Koop et al., 2000, Zobrist et al., 2007, Koop and Zobrist, 2009, Alpert et al., 2011) and therefore represent the currently best available values. We performed the suggested sensitivity test, keeping the contact angle constant and determine the

temperature dependency of the interfacial energy between the ice embryo and solution. We find that in contrast to previous literature (Pruppacher and Klett, 1997; Zobrist et al., 2007, Alpert et al., 2011b, Welti et al., 2012) this would lead to an increase of the interfacial energy with decreasing temperature. Measurements and physically based parameterizations of interfacial energy by Zobrist et al., (2007) and Pruppacher and Klett (1997) predict that the interfacial energy will decrease with decreasing temperature, opposite of the result of the sensitivity test. Thus we conclude, keeping the contact angle fixed results in an unphysical temperature dependence of the surface tension and thus the temperature dependency of the contact angle is a real effect and the $\alpha(T)$ -model is a physically sound model of immersion freezing.

We will add a brief discussion on this issue on p. 4931, l. 9:

"The contact angle is defined by Young's equation which relates α to the three interfacial surface energies between the ice nucleus and ice, ice nucleus and aqueous solution (water), and ice and aqueous solution (Pruppacher and Klett, 1997; Alpert et al., 2011). These interfacial surface energies are temperature dependent and will be affected by the presence of solutes. A recent study by Welti et al. (2012) also found that the contact angle increases as temperature decreases. Using physical parameterizations of the interfacial energies taken from Helmy et al. (2004) and Pruppacher and Klett (1997), these authors derive a reasonable temperature dependent interfacial energy between the IN surface and the ice embryo and thus corroborate the observed temperature dependence of the contact angle being a physical phenomenon. Zobrist et al. (2007) have shown, that keeping the contact angle constant for all temperatures and varying the pre-exponential factor in Eq. 5, does not improve the representation of J_{het} with temperature compared to the implementation of a contact angle that varies with temperature. Here, we have determined that when keeping the contact angle constant, σ_{sl} increases with decreasing T in contrast to the expected behavior (Pruppacher and Klett, 1997; Zobrist et al., 2007; Alpert et al., 2011b, Welti et al., 2012) further supporting a temperature dependent contact angle where decreasing temperatures yield increasing contact angles."

4931, Line 13: Is there experimental evidence that the temperature dependence of contact angle is size independent for a large range of particle sizes (or at least the atmospherically relevant cases)?

Applying CNT, the contact angle is a result of J_{het} which is independent of IN surface area but dependent on temperature. J_{het} increases as temperature decreases. If a freezing event occurs at high temperatures, indicating a large J_{het} and thus an efficient IN, the corresponding contact angle is small. Using this contact angle, J_{het} for that temperature can be calculated which then by multiplication with IN surface area gives the nucleation rate. This is corroborated for a wide range of IN surface areas by the study of Zobrist et al., 2007 and by our recent study when looking at J_{het} for a variety of IN types investigated for atmospherically relevant particle surface areas immersed in various aqueous solutions (Knopf and Alpert, 2013). In summary, since J_{het} is only temperature dependent, the contact angle is also only temperature dependent.

4933, Line1-9: Does the fact that the nucleation rate is constant with changing aw indicate that there is no effect on the IN by the solute (see previous comments)?

For clarification, the nucleation rate is constant along freezing curves for a constant value of Δa_w . It is important to note that along the freezing curve, T and a_w decreases, not only a_w as implied by the reviewer. Thus, the solute effect in terms of a freezing point

depression impacts heterogeneous ice nucleation. However, since immersion freezing temperatures are above homogeneous ice nucleation temperatures, the IN still initiates the freezing. Ammonium sulfate does not render the IN surface area. In other words the IN does not undergo any chemical or physical alterations due to the presence of this solute. Other components like the presence of sulfuric acid or strong oxidizing agents may alter surface properties and can affect IN activity.

4933, Line10-16: The close fit of the alpha(T) approach to the data is not surprising. Especially by using a different parameterisation for each aw – dependent *f* curve. It only indicates that it is possible to compensate deviations of CNT assuming a constant alpha (probably due to uncertainties in the temperature dependence of the surface tension and diffusion energy) by introducing a new parameter in the form of a temperature dependence of the contact angle.

As in our response above, we have shown that this is not the case. A constant contact angle will result in unphysical temperature behavior of the surface tension. Additionally, the very weak dependency of the diffusion energy on the diffusion coefficient (dln(D)/dT) and thus its uncertainties as discussed in this manuscript and previous studies (Alpert et al., 2011a, 2011b, Knopf and Forrester, 2011), cannot account for the statement given by the referee. Lastly, the α (T)-model represents a physical model based on CNT and not a parameterisation. We only fitted measured contact angle to obtain a continuous function of contact angle with T for purpose of depiction and application.

4933, Line17-30 ff.: This discussion is not elaborative enough. Of course the nucleation rate is independent of the frozen fraction as it describes the nucleation probability on the IN surface area immersed in one droplet at a certain temperature. The "commonly applied nucleation descriptions" were made to investigate the distribution of properties on the IN surfaces, in an ensemble of droplets. Their primary application is to investigate the underlying physics of ice nucleation and not to parameterise. The different approaches (single-alpha, alpha-pdf, active sites and deterministic) must be applied to the entire dataset (for one IN-species) simultaneously to judge how well one or the other model is able to describe the nucleation process in a physical way. The interesting questions the authors could address using their dataset are:

1. How well can aw be implemented in CNT based models (using their parameterisations).

2. How well do the different physical model approaches perform in comparison to the two data sets.

For that the different models need to be applied once to all the LEO data and once to all the PP data to obtain two sets of parameters for each model.

First a comment on "Their primary application is to investigate the underlying physics of ice nucleation and not to parameterise." We respectfully disagree with this statement. To investigate the underlying physics of any data set, a model has to be applied that is based on falsified physical parameters, physical axioms, or commonly accepted laws of nature. For example, since we know the fundamental properties of an electron and positron, we can invoke a physical model of the weak interaction force, design an accelerator, and test our physical model with the experimental data. Another example is: a functional GPS system relies on the fundamental law of relativity theory. Any test/interpretation of the GPS system using Newton's law may provide a high correlation, i.e. a very good fit (the relativity effect may only be a small percentage), but will not make the system work. Here, the α -PDF, active-site, and deterministic parameterizations are not founded on any fundamental (theoretical) falsified physical concepts, parameters, or laws. For example, we do not know the size of an active site that initiates ice nucleation (we do not even know if this concept/idea is correct), we do not know in detail what surface characteristics trigger ice nucleation, we do not know if the contact angle should

be log-normally distributed or not, we do not know the type of distributions that may describe active sites, we do not know why a deterministic approach may be valid when being in contradiction with quantum mechanics and statistical thermodynamics. None of the parameters and assumptions going into these fit-based parameterizations are fundamentally falsified but are arbitrarily chosen for a sake of applying different concepts. It is clear that such an approach will not result in falsification of a physical or chemical mechanism and for this reason it is called a parameterisation. Even for a good or well-fit parameterisation, one must be careful in interpreting any causation between the fitting functions/parameters and the physical processes which are described. One could find a log-normal distribution describing other processes not related to immersion freezing to fit the ice nucleation observations. Therefore, claims about the investigation or testing of underlying physics must be made with great care and understanding when applying parameteristions to laboratory data.

On the other hand classical nucleation theory, despite its weaknesses, is the most physically based model of nucleation and avoids inclusion of these non-fundamental concepts of active sites, α -PDF, etc. CNT considers that J_{het} scales with available IN surface area which is physically sound since we assume that nucleation is triggered by this surface, and which is a proven fact.

Regarding to "How well can aw be implemented in CNT based models (using their parameterisations).":

Here, the effect of a_w on J_{het} is considered via determined $\alpha(T)$. If the three interfacial surface energies would be known for respective IN surface and a_w , then CNT could be applied as is and thus would cover the a_w dependence. Since this is not the case, the only solution would be to fit experimentally derived α for T and a_w in parallel which we found is not trivial. With these limitations in mind and as outlined in the manuscript where we clearly state that J_{het} currently cannot be derived outside determined ranges of $\alpha(T)$ and a_w . However, the laboratory investigated T and a_w ranges usually cover typical tropospheric conditions.

Regarding to "2. How well do the different physical model approaches perform in comparison to the two data sets.

For that the different models need to be applied once to all the LEO data and once to all the PP data to obtain two sets of parameters for each model."

We were intrigued by this suggestion and fitted the entire data set applying the α -PDF and active sites parameterisations. Obviously the performance of the single- α model is already insufficient for the individual cases, thus we did not fit all data sets using this method. The deterministic parameterization cannot be used to fit all data sets at once since it is a function of temperature only and cannot account for changes in aqueous solution. We added new Figs. 6 and 7 showing experimentally determined f and α -PDF and active sites parameterisation fits for LEO and PP, respectively, using one parameter set for all data as given in new table 5. New Fig. 8 presents corresponding PDF $p(\alpha)$ and active sites surface density for LEO and PP. As it could have been anticipated from Tables 3 and 4 the overall performance of these fits is very poor. The RMSE is up to one order of magnitude larger than for the individual a_w fitted frozen fractions. In some instances where the average (over all a_w derived) fit parameter set is similar to the individually analyzed f fitting parameters, the fits come closer to the experimental data set but then deviate significantly from f for other a_w. This clearly shows that these types of parameterisations do not yield parameter sets that describe particle properties, cannot capture immersion freezing when aqueous solutions are present, and thus, cannot capture immersion freezing occurring at subsaturated conditions in the atmosphere. An elegant solution to this problem uses a water activity based approach that has been recently published (Knopf and Alpert, 2013).



New Figures 6 and 7 showing experimentally determined f and α -PDF and active sites parameterisation fits for LEO and PP, respectively, using one fit parameter set for all data.



New Fig. 8 presents the PDF $p(\alpha)$ and active sites surface density for LEO(a) and PP(b) when fitting all available data sets at once.

We added a new paragraph on p. 4939, I. 9 to discuss these new results:

"To further test the applicability of the α -PDF, and active sites parameterizations, we fit our entire frozen fraction data set spanning all investigated a_w yielding one parameter set for each model. This is to test the common notion, that the resulting fit parameters potentially represent particle properties that should not depend on varying temperature, IN surface area, and a_w . Figures 6 and 7 show α -PDF and active sites fit parameterisations in comparison with experimentally determined f for LEO and PP, respectively. Corresponding fit parameters are given in Table 5. Overall, the fit performance is significantly poorer compared to the case of fitting f for individual a_w immersion freezing data sets as indicated by the RMSE values being larger by up to about one order of magnitude. This could have been anticipated from Tables 3 and 4 and Figs. S4-5, indicating a large variation of the fit parameters with respect to a_w to achieve an overall good fit. In some instances where the fit parameters for all data sets are somehow similar to the fit parameters derived from f at a given single a_w , the fits come closer to the experimental data sets. In most instances the fits deviate significantly from experimentally derived f as shown in Figs. 6 and 7. Figure 8 presents the PDF $p(\alpha)$ and active sites surface density for LEO and PP when fitting all available data sets at once. These distributions may reflect a sort of average distribution from those derived from fitting f determined at a single a_w . Clearly, these results corroborate our findings discussed above that current fit based parameterisations cannot capture immersion freezing occurring from aqueous solutions and thus at subsaturated conditions. Furthermore, this also strongly suggests that derived fit parameters do not represent fundamental particle properties. An elegant solution to this problem is provided by a water activity based model of immersion freezing (Knopf and Alpert, 2013)."

In our conclusions, p. 4943, l. 1 we add the following "When using a single parameterization of a probability density distribution of contact angles or active sites distribution to fit all individual a_w immersion freezing data simultaneously, frozen fraction curves are not reproduced. This implies that these formulations cannot be applied to immersion freezing of aqueous solutions and suggests that derived fit parameters do not represent independent particle properties."

We add this important finding to the abstract, p. 4918, l. 24:

"Furthermore, when using a single parameterization of α -PDF or active sites distribution to fit all individual a_w immersion freezing data simultaneously, frozen fraction curves are not reproduced. This implies that these fitting formulations cannot be applied to immersion freezing of aqueous solutions and suggests that derived fit parameters do not represent independent particle properties."

4934, Line14-19: As the authors point out in the discussion of the single-alpha model the lognormal distribution of contact angles can converge to a delta function at its extreme. In consideration of this fact, additional explanation is needed to clarify the statement of a bias due to the extension of the function from 0 to 180°. Also looking at the contact angle distributions provided in the supplementary Fig. 2 and 3 the probability of contact angles of 0 or 180° seem to be too small to be of any importance.

We have not performed a detailed sensitivity analysis of this effect. Although, mathematically this statement is correct, it may, indeed, be not as important. We suggest to leave out this discussion since it has no effect on the remainder of the findings and discussion. In the revised version we will omit lines. 14-19.

4935, Line12-18: The performance of the single-alpha model (the steepness of slope) is strongly related to the temperature dependence of the used surface tension. This could be discussed.

Please see comments above.

4938, Line 8-27: Based on the comparison of the models which were applied to each aw experiment separately and yields the result that, the more free fit parameters a model contains, the better the fit to the data, the authors express doubt of the usefulness of such descriptions. As pointed out above the comparison of the five models could be improved by applying them to the whole range of the experimental data and thereby testing their performance taking into account aw. The discussion should be changed depending on these results. To highlight the

applicability of the alphaT approach, a physical explanation for the change of contact angle with temperature is necessary. It could be mentioned what other studies (Lüönd et al., 2010; Welti et al., 2012) using the same models to investigate the size and time dependence of immersion freezing concluded on the applicability of the different approaches to describe these features. **Please see comments above which address these points.**

4939, Line 3-5: The fact that the necessary super cooling with respect to the melting point Tm-Tf remains nearly constant seems to contradict the hypothesis of an interaction of the solute with the IN surface (Reischel and Vali, 1975).

Please see discussion above.

4940, Line 5: Lüönd et al., 2010 could be cited as additional reference for the size dependence of immersion freezing temperatures.

We include Lüönd et al., 2010 as suggested.

4940, Line 10: Welti et al., 2012 could be cited for the time dependence of immersion freezing. **We include Welti et al., 2012 as suggested.**

4940, Line 15: It would be interesting for the reader to which differences you are referring. Aging effects, coatings?

We did not refer to a potential difference between laboratory and atmospheric IN in regard to the chemical or physical surface properties. We meant, as stated, different applied particle surface areas. Particles applied in laboratory experiments may possess surface areas which are by orders of magnitude different compared to the particle surface areas present in the atmosphere.

4940, Line 16-23: Fitting a contact angle distribution or active site density assumes that these are particle properties which do not depend on ambient parameters. Therefore it is generally not true that such results are only valid for the experimental dataset from which they are obtained. Also from the alpha-pdf, single-alpha and active site model it is possible to calculate (apparent) nucleation rates at a given temperature (cf. Welti et al., 2012). The line of argumentation in this section should be adapted accordingly. As mentioned above the authors should explain in more depth how the \Box (*T*) approach is usable to gain "physical explanation" and for "exploiting the underlying physics".

Please see also comments/response above which address these points. We further add: The formulation of a contact angle or active distribution does assume that these fit parameters represent particle properties as the reviewer states. However, there are two caveats in this regard: 1. As discussed above the formulations of the contact angle distribution and active site density are not founded on fundamental physical principles and thus we do not even know if these concepts and fit parameters relate to particle properties. 2. When fitting these approaches to laboratory data, the resulting fit parameters are constrained by applied laboratory nucleation time scales and IN surface areas since those are implicitly included within the fit function and, one can even argue that, the ambient thermodynamic variables temperatures and RH also constrain the fit (which for obvious reasons should be avoided). This is because resulting parameters are derived for frozen fraction at a given temperature range only. A parameterization just establishes a correlation between f measured over given T interval, and e.g. the α -PDF. Although α -PDF or active site is assumed to be T independent, those are derived by means of separation of variables from the frozen fraction fitting function, the latter being a function of temperature, surface area and cooling rate. Outside any temperature, surface area, cooling rate, or water activity interval the α-PDF or active site distribution could look vastly different – we do not know this since we have no physical model of this applied concept. Applying a linear fit to any data set is an analogous example. One can assume that the slope is independent of the dependent variable (x). However, if outside the fitted range of x the slope changes, the slope becomes dependent on x. To infer or to avoid these issues a physical model has to be applied.

Reiterating previous responses, the $\alpha(T)$ -model does not apply any fits. J_{het} is derived from experimental data directly without any fitting. From these values α is derived according to classical nucleation theory – no fit involved, just a physical model. It is because of this physical model that we claim a relationship exists between particle contact angle and thermodynamic conditions of temperature and a_w. Only for the purpose to obtain a continuous function of J_{het} we can fit $\alpha(T)$ using any function. J_{het} (and frozen fractions) derived in this manner are not constrained by applied IN surface areas or experimentally defined nucleation time scales (or temperature).

Lastly, our data clearly shows that the claim that resulting fit parameters are particle properties is not supported when looking at frozen fractions obtained at different a_w and when fitting the entire data set as described above. In Figs. 4-7 we have compared in detail frozen fraction calculations using the different descriptions. Metrics such as the root mean square error and the sum of the squared difference are sufficient to evaluate their reproducibility of the data set on which they were based. An analysis on nucleation rates from fitted frozen fractions will not give any additional insight into what the data presented already shows.

On p. 4940, I. 10-16, we refer the reader and reviewer to Westbrook and Illingworth, 2013 and Ervens and Feingold, 2013 for a detailed discussion regarding the constrain of the fit-based immersion freezing analysis by IN surface areas and nucleation time. Here we extend this result by claiming that these fit-based parameterizations also cannot account for a solute concentration continuum.

4941, Line 10-11: If the immersion freezing mechanism is independent of the nature of solute in combination with any IN is an unanswered question. Reischel and Vali (1975) reported that this is not so simple.

Please see comment above.

Supplement: The curves shown in Fig. 2 and 3 for the active site surface density look very different in comparison to the curves reported in Marcolli et al. 2007, Lüönd et al., 2010 or Welti et al., 2012 for this model.

The particles used here are very different in nature than mineral dust and we have no reason to suspect the resulting active site surface densities should be exactly the same. In fact, the frozen fraction curves for Lüönd et al., 2010 and Welti et al., 2012 on which the active site surface densities are based scatter significantly, in comparison with our data which has much less scatter. We therefore do not expect for the resulting active site surface densities to look exactly the same.

Technical corrections:

4919, Line 19, 20, 21: you could use the acronym "IN" for ice nucleus here. In addition it is the ice that nucleates on the IN and not the IN who nucleates ice. Consider to reformulate the definitions accordingly.

"IN" is an acronym for "ice nuclei" (plural). We wish the keep the term "ice nucleus (singular)" as it is. We follow the suggested reformulation of the definitions.

4921, Line 5: There are no "temperatures colder than heterogeneous ice nucleation" there are temperatures where homogeneous nucleation becomes more efficient than heterogeneous nucleation. Reformulate.

p. 4921, I.5, We will modify the sentence as follows: "If heterogeneous ice nucleation does not occur, ice formation can commence from concentrated aqueous solutions via homogeneous ice nucleation and can be described by a_w and T, independent of the type of solute (Koop et al., 2000; Knopf and Lopez, 2009; Knopf and Rigg, 2011).

4928, Line 4: "r" might not be the best choice for a variable for the cooling rate as it is usually used as variable for the particle radius. I propose to use " γ ". **Since y may be misread as surface tension, we change "r" to "cr".**

4928, Line 17: ...temperature decrease > 10K... Also, in response to reviewer #3, we change to "...temperature decrease of about 10K..."

Fig.1: Experimental data for hom. *T*~ could be of interest to compare.

As mentioned above experimentally derived homogeneous freezing for similar sized aqueous ammonium sulfate droplets were determined with same experimental setup in a previous study (Knopf and Lopez, 2009).

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