Dear Editor,

We thank reviewer 2 for the review and detailed comments. The evaluation has helped us to improve the quality of the manuscript, and our reply to the respective comments is as follows. Also accordingly we have revised the manuscript and the modifications are highlighted.

Thanks once again,

-Authors

Anonymous Referee #2

The submitted manuscript describes measurements of the ice nucleation abilities of Arizona Test Dust (ATD) and Kaolinite particles in the deposition freezing mode. The resulting dataset was used to derive functions describing the surface heterogeneity of the used samples by fitting distributions functions for the contact angle based on classical nucleation theory (CNT). The resulting distribution functions were then used in model studies to test their applicability in cloud resolving model simulations. The approach to parameterize the surface heterogeneity of the dust samples is derived from previous studies but for immersion freezing. However, only recently, a paper by Wheeler & Betram (ACP, 2012) has been published that uses a similar approach for deposition freezing. In contrast to the submitted article, Wheeler & Bertram used four different models to test which model fits the data best. This publication is not **cited here but it should** and **I recommend** an extensive comparison with the data and derived distribution functions published there. It surprises me that the authors argue, that the step-wise appearance of their results with the distribution function in Figure 2 are the result of the non-linearity of CNT. CNT does not have functions that produce a periodicity like observed in Figure 2. This is also not the case for previous studies for immersion freezing and the already mentioned paper by Wheeler & Bertram, where the simulated functions are monotonous. The two data sets for ATD and Kaolinite in the present study seem to be very comparable (Figure 5), it is therefore surprising that the fit parameters for the PDF differ so much for both particle types. It would also help to **provide root mean square error (sums) for the results from the fits.** These observations together let me conclude that there might be a flaw in the data analysis routine. The current state of the paper does not provide enough information to draw a real conclusion about the data quality. I therefore recommend to reject the paper in its current state and **encourage the authors to re-submit it after major revisions of the paper.** In a new version the authors should take care to **describe experiment and data analysis more precisely and carefully.**

Some specific remarks for corrections will follow below.

General readability: **The text should be carefully sub-edited** for better readability. Especially the proper use of indefinite and definite articles like "the" according to english grammar should be checked. Often they are missing, the wrong type is used or an article is used where it is inappropriate. Some examples are given below. Secondly, **I recommend not to use symbols** (e.g.like T as a placeholder for the word temperature) in the text. Please **use the written words instead**. Also, **please refer to equations** like ... in equation (1) . . . and not just . . . in (1) ...

Reply: We thank the reviewer for pointing out the new published work: Wheeler and Bertram (2012), which is now cited in the revised section 1.
Root mean square error (RMSE) calculations are described in the revised manuscript. See section 2.2. The PDF parameters are iterated such that for each combination of mean and standard deviation one RMSE value is calculated. Then the parameters that are associated with the least RMSE are defined as the best fit PDF parameters. Using these PDF parameters modeled F_{ice} as a function of RH_{ice} is calculated. These modeled data points are fitted. Initially we discretized the integral (equation 3-revised manuscript) into 100 bins, sensitivity tests till 500 bins were also performed. We recently found that these numbers of bins are insufficient and increased to 2000. This yielded smooth curve and the step-wise appearance of PDF curve disappears. These details are described in section 2.2 and Fig. 2 is updated.
Following the reviewer's comment, experimental section 2.1 is revised (see below under reply to the respective comments). Manuscript is edited in grammer, and symbols for "temperature" are replaced with the word "temperature". Equations are referred as equation (1), (2) etc.

Abstract
Line 4: What is an onset single angle?

Reply: Sentence is revised. The word "contact" was missing.
New sentence reads as follows.
"Results show that onset single <u>contact</u> angles vary from ~18 to 24 degrees, while the PDF parameters are sensitive to those environmental conditions (i.e., temperature and dust size)".

Introduction
Page 2485, line 14: ...barrier for ICE nucleation.

Reply: Added

Page 2486, line 7: THE contact angle.... The following sentence:
There are different definitions of the contact angle for different nucleation modes. The surface energies listed here define the contact angle for immersion freezing, for deposition nucleation, no liquid water is involved, hence no surfaces between liquid water and other phases play a role here. Since the paper focuses on deposition nucleation, the definition for deposition nucleation would be more appropriate here and it should be explicitly mentioned for which nucleation mode the definition is given.

Reply: Sentence is revised. New sentence reads as follows, "In deposition ice nucleation the contact angle of an ice embryo on an IN represents a relationship between the surface energies defined at the water vapor – ice, water vapor – catalyzing substrate and ice – catalyzing substrate interfaces (Fletcher, 1962)".

Line 12: . . . contact angleS derived from....

Reply: Added "s".

Line 14: ...even was applied to A global climate model.....

Reply: Replaced "the" with "a".

Lines 16/17: Elastic strain, aerosol surface irregularities, and active sites are NOT parameters of the standard CNT, so how should they be constrained then in CNT?

Reply: We agree with the referee. The sentence is revised. The new sentence reads as follows, "It should be noted that parameters such as the magnitudes of elastic strain, aerosol surface irregularities, and active sites might affect CNT calculations, but are not accounted in the CNT approach and are ignored in this study as uncertainties of these parameters are very large".

Line 22: Is there a reason why the authors did not consider these approaches here?

Reply: This paper focuses on two representations of contact angle in the CNT approach and their impacts on simulated cloud properties. Other approaches such as deterministic or a combination of deterministic and stochastic approaches described by Connolly et al. (2009) and Niedermeier et al. (2011), respectively, will be implemented in our next modeling study. We should also acknowledge the recent work: Ervens and Feingold (2012), who compared five different nucleation schemes, including above deterministic and soccer ball schemes, using a box model.

Line 29: . . . ice nucleation in climate models (delete THE).
This sentence the previous and the following two sentences on the next page do not make a lot of sense to me. It seems that the authors mix up parameters in parameterizations for climate models with CNT. It is not clear what kind of parameters they suggest are missing and if they are missing in CNT or the climate models. These sentences should be re-written to clarify what the authors intend to say. In addition, there is already a paper on deposition nucleation using the approaches from Lüönd et al. (2010): Wheeler and Bertram ACP (2012). This study should be also discussed here and the differences between the present study and the study of Wheeler and Bertram.

Reply: Completed. Deleted "the".
We meant the incorporation of PDF in CNT for deposition ice nucleation is missing. We did not mean parameterizations for climate models. Following the reviewer comment, we revised these sentences.
Wheeler and Bertram (2012) study is cited and discussed. In the revised paragraph, for completeness, we also discussed Niedermeier et al. (2011), Connolly et al. (2009), and Ervens and Feingold (2012) studies. The new paragraph reads as follows.

"The original framework of CNT can be generalized to incorporate the variability in surface properties of IN by assuming a PDF distribution of contact angles over the entire dust sample instead of single contact angle values (e.g. Marcolli et al., 2007). This modified approach using a log-normal PDF was employed by Lüönd et al. (2010) to constrain the laboratory immersion ice nucleation data. CNT was further modified by Niedermeier et al. (2011), where instead of a distribution of contact angles over the entire dust sample, they described a conceptual model that treats each particle consisting of a distribution of surface sites or properties of IN. They concluded that ice nucleation treatment models that are based on the stochastic theory might be influenced by the heterogeneity of surface properties depending upon the time and freezing temperatures. More recently Wheeler and Bertram (2012) used onset RH_{ice} and surface area distribution to test the PDF approach against other approaches for deposition ice nucleation. They showed that onset single contact angles based on the onset RH_{ice} do not fit the data well, while the PDF distributed contact angle model fits the data within experimental uncertainties.Connolly et al. (2009) developed a new parameterization based on their laboratory heterogeneous ice nucleation data. Unlike the CNT approach, their model is based on the singular theory, or deterministic approach. In this approach it is assumed that particles have multiple nucleation sites where ice could form and the ice formation rate is determined by the most efficient nucleation site. Such that in deposition ice nucleation experiments, as soon as any of those nucleation sites reach the characteristics RH_{ice}, the ice will form immediately and if this characteristic RH_{ice} is held constant, then no further ice nucleation events should occur, suggesting there is no time dependence. Recently, Ervens and Feingold (2012) explored the sensitivity of time-dependent CNT parameterizations against singular freezing theories in a box model that simulated immersion and condensation freezing nucleation mechanisms. They showed that predicted ice number concentrations from different ice nucleation schemes are sensitive to the parameters such as time, size of IN, temperature and supersaturation, and suggested that these parameters should be better constrained to simulate realistic cloud properties".

In section 3.4 we compared our results with Wheeler and Bertram (2012). The following sentences are added to the revised manuscript.

"Based on the onset RH_{ice} and dust surface area available for the deposition nucleation, Wheeler and Bertram (2012) calculated the PDF parameters for kaolinite and illite dust samples. Direct comparison with their PDF parameters for kaolinite data at -34 degC (~ -35 degC; assuming within temperature uncertainty) showed disagreements. They reported μ and σ as 0 and 54.14 degrees while we calculated 56.0 degree and 0.49, respectively".

"Comparing our results with Wheeler and Bertram (2012), the factors such as ice detection threshold and experimental technique could have contributed to the observed disagreements. Other factors, such as dust surface area and residence time, could also have played a role".

Page 2487, lines 7 and 13: delete "THE" after ...using

Reply: Corrected.

Page 2488, line 14: Did you mean vertical instead of horizontal? Or did you mean the parallel arrangement of the two plates instead of the orientation of the plates themselves. Please re-write this sentence to make this clearer.

Reply: Corrected. The new sentence reads as follows, "The chamber consists of two vertical parallel plates with an evaporation section attached at the bottom of the chamber to remove water droplets (Stetzer et al., 2008)".

Line 16: The principle of A continuous . . ..

Reply: Corrected.

Line 17: ...ensures THAT aerosol particles WHICH are placed . . ..

Reply: Corrected.

Lines 23 to beginning of next page: The description of what is controlled in the experimental setup is very vague and imprecise. e.g. the linear T gradient establishes by the process of heat transfer but cannot actively be controlled. The only parameters which are actively controlled are the two temperatures of the two walls. This should be clearly stated. The physical process by which the relative humidity profile is established and which controls the RH at the sample position is not correctly explained here. Also, it is not clear which flow setting is used: Is 10 lpm the total flow through the chamber, the total of both sheath flows, or the flow of one of the two sheath flows? Please be precise and clear here.

Reply: Following the reviewer comment, we revised the description of experimental setup. It now reads as follows.

"The chamber plates are independently temperature-controlled to develop a linear temperature gradient across them which, according to the principle of thermal gradient diffusion theory, produces a RH_{ice} profile between the plates (e.g. Rogers et al., 1988). At the beginning of the experiment, the chamber walls are coated with an ice layer (~ 0.5 mm thick) and the temperature gradient is set at zero, which creates ice saturation conditions (RH_{ice} = 100%) inside the chamber, and then the refrigeration system cools one plate and warms the other to increase the RH_{ice}. The total flow used is 11 Lpm; sheath and sample flows used are 10 and 1 Lpm, respectively, which limits the aerosol residence time to ~12 seconds within the ice chamber".

Page 2489, first paragraph: Precisely, ice nucleates on the surface of an aerosol particle, then the newly formed ice crystal grows but NOT the aerosol particle!

Reply: Revised. The sentence now reads as follows.

"Ice nucleates on the aerosol particles and the newly formed ice crystal grows to a size greater than the original aerosol size, and ice crystals greater than 1 micrometer exiting the chamber are counted with an optical particle counter (OPC; CLiMET, model CI-3100)".

Line 7: Delete THE at beginning of sentence.

Reply: Deleted.

Line 10: Please specify what type of aerosol generator was used (e.g. fluidized bed...) and explain the abbreviation DMA.

Reply: Revised. The sentence reads as follows.

"The dust particles are dry-dispersed (dry powder dispersion; TSI, 3433) and size-selected by a differential mobility analyzer (DMA; TSI, 3080)".

Line 13: It is not clear if the authors observed the contribution of multiple charges (if yes, how was it done?) or if this is a reference to literature (if so, please cite correctly).

Reply: We did observe the multiple charged particles. The contribution of doublet and triplet charged particles are described. The text is revised and added to the manuscript.

"For 100 nm diameter size particles, the DMA produced 152 nm (the size of double charged particles) and 197 nm (the size of triple charged particles) size particles, and their contribution was 36% and 16%, respectively. For 300, 400, and 500 nm diameter size particles, the contribution of these multiple charged particles was less than 10%. For sizes 100 and 300 nm particles, the multiple charge calculations were based on the routine experimental measurements, whereas for 400 and 500 nm particles the calculations are based on the Baron and Willeke (2001) calculations".

Our routine experimental methodology to calculate the multiple charged particles for 100 and 300 nm diameter particles is as follows. In our lab we operate DMA and CPC (or SMPS system) instruments and use commercially available monodisperse size particles (PSL spheres) to understand the resulting size distribution. From the resulting size distribution we calculate the percentage of multiple charged particles. For 100 nm PSL spheres we observe peaks of double and triple charged particles at ~ 152 and 197 nm, respectively. Their percentages were ~36 and 16%, respectively.
For 300, 400, and 500 nm size particles, the contribution from multiple charged particles (double and triple charged particles) was less than 10%. The following table describes the size of multiple charged particles. Only 100 nm has significant contribution and these numbers are described in the paper. Multiple charged particles for sizes 400 and 500 nm were based on the Baron and Willeke (2001) calculations.

Size (nm)	Double charged particles		Triple charged particles	
	Size (nm)	Contribution (%)	Size (nm)	Contribution (%)
100	152	36	197	16
300	506	10	705	10
400	696	10	982	10
500	880	10	1250	10

Line 14: ...size particles THE DMA produced.....

Reply: Corrected.

Line 15: Where do the percentages for 152 nm and 197 nm particles come from?

Reply: This is described above. See reply for the comment 'page 2489, Line 13'.

Line 16: 500 nm sizeD particles....

Reply: Corrected.

Line 19: How were the RHi corrections been done?

Reply: We meant calculating RH_{ice} and temperature corresponding to the location of aerosol lamina as described in Rogers (1988), but these calculations are already incorporated into the ice chamber control software. This sentence is not required and is thus deleted.

Lines 22-26: The term "modified" does not seem correct to me here. CNT does not make any assumptions about the nature and heterogeneity of a surface that catalyzes ice nucleation. To me the following aspects should be carefully separated: CNT provides a formula based on physical laws to describe a nucleation rate for a certain contact angle of a certain surface area. In contrast, different models exist to describe the surface heterogeneity of a sample of particles. For each surface (fraction) of these models, CNT can be applied in its pure form. This should be made clear in the text. I also recommend to reverse the order of equations 1 – 3 to better represent the relation between CNT and the surface model (parameterization).

Reply: Following the reviewer comment, we changed the title of sub-section 2.2. It now reads as "PDF- *contact angle* model".

The paragraph is revised. This now reads as, "The framework can be modified to incorporate the surface properties of IN (Lüönd et al. 2010; Wheeler and Bertram, 2012) by distributing the contact angles among the IN. In this study we adopt the PDF approach for contact angle from Lüönd et al. (2010) and calculate the PDF parameters using the deposition ice nucleation data from our laboratory".

Order of equations is reversed to better represent the relation between the original and PDF based CNT. The original equation 3 now becomes equation 1.

Page 2490, line 6: ...residence TIME . . ..

Reply: Corrected.

Line 11: Sv,i is the saturation ration not the supersaturation (the following formula is also not correct).

Reply: We are sorry for the typo. Now it reads as follows, "$S_{v,i}$ is the saturation ratio (RH_{ice})"

Line 15: Why is this formula given here, when a fixed (non-temperature-dependent) constant from literature is used?

Reply: Agree, formula is removed.

Line 21: I assume this refers to equ. 2 not 1?

Reply: Corrected. It is indeed equation 2 (where PDF parameters are defined).

Page 2491, lines 6 – 9: As already mentioned earlier, it is not entirely clear to me how the "continuous" fit curve is produced. The mathematical procedure should be better described, also how and which parameter was discretized. Does "further, we did not find any sensitivity" mean, that with increasing number of bins, the fit curve did not change anymore? Please provide RMSE or a similar parameters to describe the quality of the fit.

Reply: Mathematical procedure is described in the section 2.2. The new paragraph reads as follows.

"The methodology to obtain the PDF parameters that best describes the experimental data is as follows. The integral from equation (3) was discretized into 2000 bins. Next, for the given measurement conditions (temperature, r, t, $S_{v,i}$), the PDF distribution parameters, σ and μ, are iterated to find the best fit between F_{ice}^{mod} and F_{ice} values by minimizing the root mean square error (RMSE) between them. The RMSE was calculated as in equation (4):

$$\text{RMSE} = \sqrt{\frac{1}{N}\sum_{1}^{N}[F_{ice} - F_{ice}^{mod}]^2} \quad (4)$$

Where N is total number of data points. The best fit PDF parameters, which are associated with the least RMSE are tabulated in table 1 and 2 as a function of measurement conditions. For measurement conditions at -35 degC and 400 nm size ATD particles, Fig. 2 shows F_{ice}^{mod} curve and F_{ice} values and, the inset shows the associated PDF distribution".

Initially with further increasing in number of bins from 100 to 500, the shape of fit curve did not changed. However, we now increased the number of bins to 2000, which changed the shape of the fit curve. The RMSE values are added to the table 1 and 2.

Line 12: How can equ. 1 be modified? Please provide details.

Reply: We wanted to say using CNT (single contact angle) one can calculate onset single contact angles based on the onset RH_{ice}. This is revised for clarity. See new added equation (5) and related text.

Lines 6 – 9, 16: You are discussing results (Fig 2) here already, but the results section only comes later!

Reply: Section is revised. The results are moved to section 3.1.

Page 2492, lines 17 – 19: Why mention the value of N0 two times here?

Reply: Corrected. We deleted the second N_0.

Line 23: THE CRM was also....

Reply: “The” added.

Page 2493, line 9: ...size OF ATD particles....

Reply: “of” added.

Line 10: Wouldn’t it make more sense to
plot Fice against RHi instead of RHw? The nucleation rate is a function of Si not Sw!!!

Reply: It is correct that heterogeneous nucleation rate is a function RH_{ice}. The new figures are plotted against RH_{ice} instead of RHw. See revised Fig. 4 and 5.

Lines 20 – 24 (and next page): **How should** the existence of active sites be the reason
for a scatter in the PDF parameters? Marcolli et al. (ACP, 2007) described a surface model that assumes active sites, but the PDF does not. It is also not argued well, why different PDF’s are derived for different temperatures and particle sizes. In a first guess I would assume that the contact angle distribution should be the same for different experiment temperatures as it describes a particle property. It might be different for different sizes if one assumes e.g. that the chemical composition may vary for different sizes but **this should be discussed.** In general, it appears to me that the authors do not connect their phenomenological observations to the physical concepts behind CNT and the PDF approach well enough. E.g. in lines 1 – 5 (page 2494) the authors argue that the particle to particle variability is the cause for a scatter in PDF parameters but the underlying assumption of the PDF is already a particle-to-particle variability in the contact angle.

Reply: We define active sites as the favored sites for the ice to nucleate. In this section we are trying to explain the variability in the measurements, e.g. the activation spectra of dust particles (Fig. 4), using the active sites concept. Results show that ice nucleating properties of dust particles are a function of temperature, RH_{ice} and size. To explain the variation in the activation spectra, at any measurement condition, we think each dust particle has different surface property than the other or the distribution of active sites from particle-to-particle basis is different. The idea is based on the soccer ball approach by Niedermeier et al., 2011. However, we do not have any measurements of active sites to support this premise. Therefore, considering these limitations, we will remove the active site argument from the discussion section.

PDF parameters are used to parameterize the activation spectra of dust particles (also see Wheeler and Bertram, 2012). If the activation properties of dust particles vary (see Fig. 4) then the PDF parameters also vary. This is the reason why we see different PDF parameters for different temperature and particle sizes (Table 1 and 2). The following text is added in revised section 3.1.

“Described in the section 2.2, the PDF- θ parameterization assigns a single contact angle for each IN, and the best fit PDF parameters produce a probability of occurrences of these contact angles that is given by a PDF distribution. The PDF distribution represents the spectra of activated fraction. If the activation properties of dust particles vary with temperature and size (see Fig. 4), then the PDF parameters also vary and may explain the scattering of the PDF parameters shown in table 1 and 2".

Page 2494, line 10: I would be careful with this statement: If the PDF approach correctly describes a particle population, at low activated fractions, only the most efficient particles with the smallest contact angles are activated. So, a contact angle, derived from a low activated fraction does not describe the whole population but only the most active fraction!

Reply: Reviewer is correct in pointing out that in PDF distribution only particles that have the smallest contact angles are going to activate. Reviewer is also correct that the smallest contact angle does not describe the whole population of dust particles, but the most efficient particle among the population. This is acknowledged and rewritten in section 3.1. The revised text reads as follows.

"It should be also noted that the particles having the smallest contact angle will induce nucleation first and other particles will activate later, when favorable conditions exist. The sensitivity of such contact angle distribution towards cloud properties is described in section 3.3".

Page 2495, line 20: from 5_ to 30_ both, Ni and IWC, decrease....

Reply: Corrected

Page 2496, lines 5 – 7 and following paragraph and following page: Higher nucleation rates for smaller contact angles are a direct consequence of the CNT, so some of the results discussed here are somewhat trivial and do not require simulations to be drawn.

Reply: It is true that smaller contact angles leads to higher ice nucleation rates. Here we wanted to investigate the sensitivity of simulated cloud properties to the distribution of contact angles. Various cloud simulations were undertaken. We find that cloud microphysical properties are sensitive to the change in contact angles. See section 3.3 and Fig. 8.

Page 2498: Please add Wheeler & Betram and their results for the PDF model in the discussion here!

Reply: In section 3.4 (last paragraph) we have discussed the Wheeler and Betram (2012) results as follows.

"Based on the onset RH_{ice} and dust surface area available for the deposition nucleation, Wheeler and Bertram (2012) calculated the PDF parameters for kaolinite and illite dust samples. Direct comparison with their PDF parameters for kaolinite data at -34 degC (~ -35 degC; assuming within temperature uncertainty) showed disagreements. They reported μ and σ as 0 and 54.14 degrees while present study 56.0 degree and 0.49, respectively".

"Comparing our results with Wheeler and Bertram (2012), the factors such as ice detection threshold and experimental technique could have contributed to the observed disagreements. Other factors, such as dust surface area and residence time, could also have played a role".

Table 3: Some columns are named -3 (temperature) I guess these are -30?

Reply: Yes, corrected.

References:

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